

# Ultrasonic Investigations of Hydrogels Containing Barium Ferrite Particles

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We have attempted to establish a systematic and accurate method for evaluating the sound velocity of polymer gels containing magnetic particles using 2.25- and 10-MHz ultrasonic waves at 295.5 K. The sound velocity of the gels gradually decreased with the increasing volume fraction of particles. The experimental data were well fit by the Harker and Temple model that is known for the coupled-phase model of suspensions. The effect of the magnetization direction on the gel modulus has also been discussed by means of the elastic theory. The longitudinal modulus of magnetic gels after magnetization was higher than that before magnetization. Moreover, it was clear that the longitudinal modulus increased and decreased when the strain direction was perpendicular and parallel to the magnetization, respectively. The observed anisotropy in the modulus at these frequencies would be ascribed to the magnetic interaction between magnetic particles in the range of  $\sim 100\ \mu\text{m}$ .

## 1. Introduction

Magnetic gels have been widely investigated as stimuli responsive polymer gels such as the electric and magnetic fields, temperature, pH, salt, solvent concentration, and visible light.<sup>1–7</sup> The polymer gel containing the ferromagnetic fluid called ferrogel is a typical example of magnetic gels. Under a gradient magnetic field, it is well known that ferrogel shows abrupt elongation and contraction behavior.<sup>8,9</sup> Contrary to the gradient field, under a uniform magnetic field, it has been reported that the equilibrium compressive modulus of the ferrogel under the field was much higher than that without the field.<sup>10</sup> The mean change in modulus increased with increasing magnetic field, and it saturates above 0.2 T. In the ferrogel, the finely distributed ferromagnetic particles are attached to the flexible network chains by an adhesive force, resulting in direct coupling between the magnetic and mechanical properties. Detailed descriptions of the magnetic gel have been reviewed in the literature.<sup>11</sup>

The magnetism of magnetic gels can be classified as two types depending on the size of the magnetic particles dispersed in the polymer network. The ferrogel is a chemically cross-linked network swollen by a ferrofluid that is a colloidal dispersion of monodomain magnetic particles with a typical size of  $\sim 10\ \text{nm}$ . No magnetic hysteresis was seen in the magnetization curve for the ferrogel, suggesting that the magnetism of ferrogel is superparamagnetism, which is the same as that of ferromagnetic fluids. This means that the magnetic moment in ferrogel is not induced without a magnetic field. On the contrary, the magnetism of magnetic gels corresponds to ferromagnetism when the diameter of the particle is larger than  $\sim 100\ \text{nm}$ . The magnetic gel used in the present study is a chemically cross-linked network containing a magnetic substance with a typical diameter of  $\sim 10\ \mu\text{m}$ . The magnetic gel shows magnetic hysteresis on the magnetization curve, suggesting that the magnetism of the

gel corresponds to ferromagnetism. Although the magnetic field is not applied to the gel, the gel keeps remnant magnetization characterized by the ferromagnetic substance. This enables us to investigate the effect of magnetization on physical properties without applying the magnetic field simultaneously.

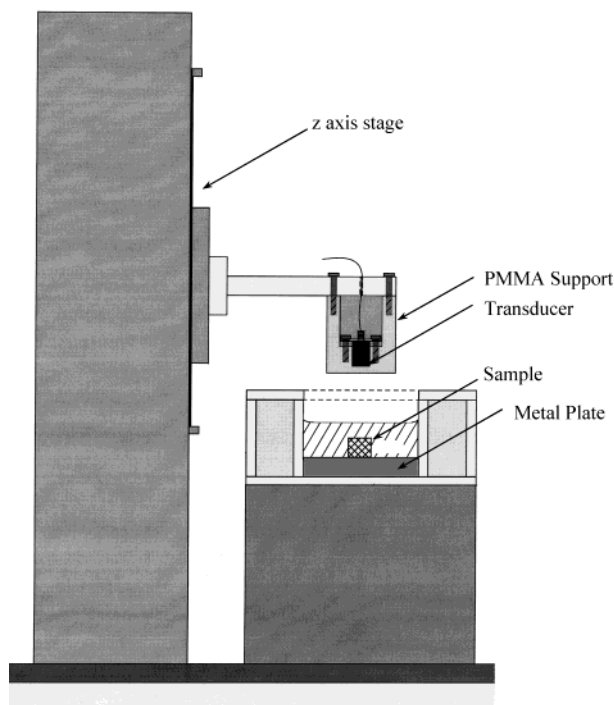
Ultrasonic testing has been used widely in the field of polymer thin films, suspensions, and dispersions. Urlick and Ament presented one of the first ultrasonic investigations of suspensions and dispersions and measured both absorption and velocity calculated on various aqueous solutions.<sup>12,13</sup> A few years ago, the theoretical ultrasonic treatment of a two-phase medium was improved and applied to different systems,<sup>14–17</sup> taking into account the thermal and hydrodynamic interactions between particles and the continuum. Some investigation systems have been developed to test and compare the different theories on colloidal suspensions and gels with an ultrasonic spectrometry technique.<sup>18–20</sup> Although the vitrification process is clearly pointed out by ultrasonic measurements,<sup>21</sup> the sol–gel transition passes without any particular incidence on the velocity and absorption. It has been shown on a single system that ultrasonic methods associated with rheology allow a complete and a better description of the  $\alpha$  relaxation. The dynamics of  $\alpha$  relaxation, a phenomenon related to the glass transition, involving polymer chain units and resulting in cooperative movements has been also reported.<sup>22</sup> Besides these, using the thermally responsive nature of an *N*-isopropylacrylamide (NIPA) gel, an attenuator for an ultrasonic wave has been reported.<sup>23</sup>

Recently, we have investigated the effect of the magnetization direction on the longitudinal modulus of magnetic gels and have revealed that the change in the modulus due to magnetization depends on the magnetization direction.<sup>24</sup> In the first half of the paper, we describe the gel synthesis and experimental setup that lead to the acoustical characterization of the poly(vinyl alcohol) gel and its compounded gel with barium ferrite particles. The velocity variations versus volume fraction of particles have been used to represent the Harker and Temple model showing a coupled-phase model of suspensions. The

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**Figure 1.** Experimental setup to measure the ultrasound velocity and attenuation in polymer gels. The ultrasonic wave generation and treatment system is not represented.

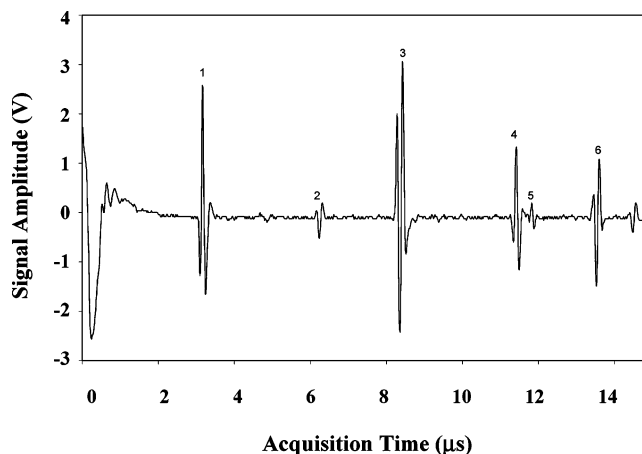
effect of magnetization on the gel modulus has been also discussed in the last half of the paper.

## 2. Experimental Section

**2.1. Samples Synthesis.** The magnetic gel was prepared by mixing a 10 wt % PVA aqueous solution with magnetic particles of barium ferrite BaFe<sub>12</sub>O<sub>19</sub> (Sigma-Aldrich Co.). A glutaraldehyde was used as a cross-linking agent in the presence of hydrochloric acid. The mean and maximum diameters of a magnetic particle were about 15 and 45  $\mu\text{m}$ , respectively. The weight concentrations of magnetic particles to that of PVA,  $c_p$ , were 10 and 15 wt %. The concentration of hydrochloric acid was constant at 15 wt % with respect to the PVA aqueous solution. The cross-linking density  $\nu$  was varied from 0.5 to 20 mol %, and the cross-linking reaction was carried out at room temperature. We obtained PVA gels with various cross-linking densities in a similar manner with magnetic gels without magnetic particles. The shape of the samples for the ultrasonic measurement is a disk with a diameter of 9–15 mm and a thickness of 4–5 mm depending on the degree of swelling. The magnetic gel was immersed in purified water for a few days until the gel had reached an equilibrium swelling.

**2.2. Ultrasonic Measurements.** We used the ultrasonic pulse–echo method, which is a simple and reliable way to measure the ultrasonic properties of hydrogels; it consists of using a pulsed wave emitted and received by only one transducer. This method has been widely developed in the field of dispersions, suspensions, alloys and blends, and gel-forming systems.<sup>12,13,22</sup> These ultrasonic measurements are extremely sensitive to the quality of interfaces in the system, the change in the thickness of the sample, the temperature, and also to the sensor orientation in relation to the reflection surface.

The experimental setup we built for our experiments is shown in Figure 1. The gel sample was sandwiched between the steel plate and the PMMA support in which a transducer was settled. To compress the gel sample, we used a z-axis stage (SP26-



**Figure 2.** Typical ultrasonic waveform and amplitude of the received signal versus time after reflection on different interfaces.

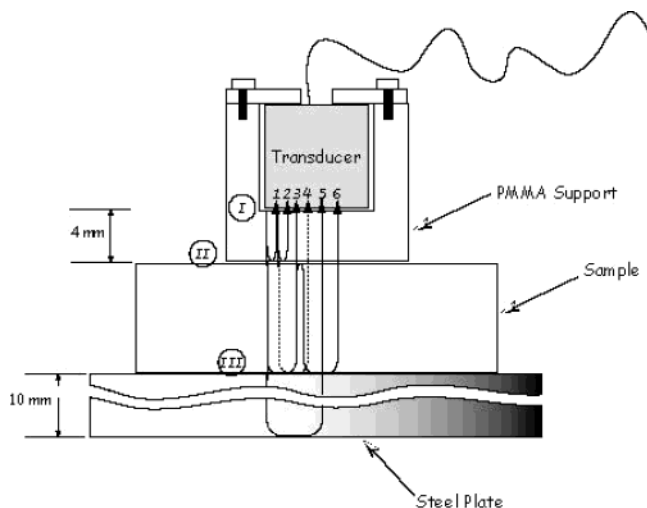
100, Sigma Koki), which allowed a displacement of the transducer around  $\pm 150$  mm starting from the center position. The resolution of the apparatus can be set between 0.025 and 2  $\mu\text{m}$  for one step of the rotation of the controlling stepping motor, and we decided to use 0.1  $\mu\text{m}$  in the present study. The ultrasonic wave proceeds through the gel sample and comes back to the transducer after reflecting off of a steel support.

The transducer is fixed into a poly(methylmetacrylate) (PMMA) support and attached to the moving arm of the z-axis stage. The PMMA was one suitable supporting material because of its good capability in transmitting ultrasonic waves (absorption coefficients around 100 Np/m and longitudinal velocity above 2600 m/s). Moreover, because PMMA is a transparent material, we can easily see and define the position of the first contact between PMMA and the gel sample.

The transducers generated a 2.25-MHz central frequency (V133 SM,  $\phi$  9 mm Panametrics, Inc.) and 10-MHz (V112 SM,  $\phi$  6 mm Panametrics, Inc.) longitudinal waves and also functioned as a receiver. The bandwidths at  $-6$  dB for 2.25- and 10-MHz transducers were 2.42 and 9.7 MHz, respectively. Only the experiment for the influence of particles on sound velocity was performed at 2.25 MHz. The signal-generation system (model 5077 PR, Panametrics, Inc.) was used as a pulse emitter–receiver; it initially sent a 300-V rectangular pulse to the transducer and treated the response before sending it to the digital oscilloscope (TDS 744A, Tektronix Co.). The measurements were performed at 295.5 K using a thermostatic bath with an accuracy of  $\pm 0.2$  K.

**2.3. Calculation of Ultrasonic Parameters.** A typical waveform measured on a PVA gel with a sample thickness of 2.054 mm is shown in Figure 2. The ultrasonic wave traveled first into the PMMA plate before crossing through the gel and impinging on the gel–steel interface. Because of the construction of this “three-layer system”, the number of echoes is important; that allowed us to determine both the velocity and attenuation by means of comparisons between different echoes. Therefore, it was not necessarily to know the ultrasonic features of PMMA because the first echo was used as a reference to measure the ultrasonic properties of the gel.

We represent in Figure 3 the paths of the ultrasonic wave after reflecting and transmitting at different interfaces. This picture shows how we interpreted the acoustical response of the system in terms of ultrasonic wave paths. Indices I, II, and III represent the interfaces of transducer/PMMA, PMMA/gel, and gel/steel, respectively. The nature of each wave (1 to 6) was found by varying the distance PMMA–steel and analyzing



**Figure 3.** Schematic illustration representing ultrasonic wave paths in the gel sample. The numbers (1 to 6) correspond to the order of the different echoes in the time range seen in Figure 2.

the different moving (or nonmoving) echoes: Echoes 1 and 2, being the only two nonmoving echoes, are related to the PMMA/gel interface. Echo 3 comes from the reflection at interface III; its phase opposition according to echo 1 is due to the impedance of the steel plate, which is higher than the impedance of the gel ( $Z_{\text{steel}} \gg Z_{\text{gel}}$ ). Conversely, at interface II, the impedance of the emitting medium ( $Z_{\text{PMMA}}$ ) is higher than that of the transmitting medium ( $Z_{\text{gel}}$ ). Echo 4 is received after two round trips in the PMMA layer and one round trip in the gel. The echo has the same phase shift as echo 1 because a phase opposition occurs not at interfaces I and III but at interface II. The amplitude of echo 5 is extremely small because the wave traveled into 20-mm-thick steel. The phase opposition is caused by the reflection at the bottom face of the steel plate. The last echo (echo 6) that we considered was received after two round trips into the gel medium. It is obvious that echo 6 moves faster than the echo 3 by twice the flight time.

Because the echoes have been characterized, we can estimate the sound velocity  $V$  in the gel medium by using the following equation,

$$V = \frac{d_g}{\tau_g} \quad (1)$$

Here,  $d_g$  stands for twice the thickness of the gel sample.  $\tau_g$  is equal to two times the propagation time, which is equal to the difference between the propagation times of echos 4 and 3.

The sound velocity strongly depends on the  $z$  position in the lower region of displacement; on the contrary, it is almost constant from 8 to 10 mm. It was clear that the deviation in velocity was caused by the accuracy of the position on the  $z$ -axis stage, and it became large when the position was far from the center of the stage. Accordingly, we decided to measure the sound velocity for gels only around the center position of the stage, where a constant value of sound velocity was obtained for pure water.

For the measurement of polymer gels, the sound velocity was determined by the time difference between two echoes after the mechanical relaxation. When a small strain is applied to the gel, the signal passing through the gel as seen in Figure 2 immediately shifts to a different time region. For each step in strain of less than 10  $\mu\text{m}$ , stress relaxation was finished within a few seconds, and the sound velocity was almost independent

**TABLE 1: Density and Impedance of Water, PMMA, and Steel**

	density ( $\text{kg/m}^3$ )	impedance ( $\text{kg/m}^2\text{s}$ )
water	1000	$1.47 \times 10^6$
PMMA	1170	$3.11 \times 10^6$
steel	7800	$4.50 \times 10^7$

of the strain in the region of  $\gamma < 10\%$ . We have analyzed this equilibrated sound velocity after mechanical relaxation not only for PVA gels but also for magnetic gels. The sound velocity of PVA gels increased with increasing cross-linking density, satisfying the power law described as a function of the degree of swelling.

### 3. Results and Discussion

**3.1. Influence of Particles on Sound Velocity in Magnetic Gels.** We studied the influence of the volume fraction of particles on the compression phase velocity in magnetic gels. To understand the behavior of the two-phase medium well, we tried to describe it by means of Harker and Temple theory for ultrasound wave propagation in suspensions.<sup>16</sup> Several models dealing with the propagation of ultrasound through suspensions or dispersions exist, and recently Tebbut and Challis<sup>19</sup> pointed out that mainly four models are relevant and useful for describing such kinds of systems.

The earliest models were developed by Urick<sup>12</sup> and Urick and Ament.<sup>13</sup> The models are based on a phenomenological approach and work well for spherical and mobile particles and with particular system for which the phase velocity is independent of frequency, particle concentration, and particle size. We did not use these models because of the following reasons. First, because the diameter of the magnetic particles is much larger than that of the distance between two cross-linking points, the particles are completely fixed by the network and can neither move nor rotate in the gel matrix. Second, the magnetic particle is just a powder state; it does not have an exact spherical shape.

Allegra and Hawley<sup>15</sup> developed a model that takes into account the thermal transport process between particles and the continuum.<sup>17,19</sup> The thermal effects are important in the cases of liquid–liquid systems or when considering liquid–solid systems having different thermal properties; however, the densities and acoustical properties are very close to themselves. When the continuous phase is a gel, the densities and acoustical impedance values of particles and the continuous phase are quite different, as shown in Table 1. Therefore, we can assume that the thermal transport mechanisms (and consequently the thermal wave intensity) at the interface between the gel matrix and the particle could be negligible, particularly in the low solid volume fraction domain. Furthermore, Allegra and Hawley also assumed that the shape of dispersed particles is spherical.

The Harker and Temple model is based on the construction of four differential equations that are continuity equations at the interface of particle and the continuum, that is, the conservation of momentum. Equation 2 describes the viscous drag of the dispersed phase in the gel matrix and yields the complex wavenumber  $k^*$  of the particle-dispersed gel media as follows:

$$k^{*2} = \omega^2[(1 - \varphi)\chi_c + \varphi\chi_p] \times \frac{\rho_c[\rho_p(1 - \varphi + \varphi S) + \rho_c S(1 - \varphi)]}{\rho_p(1 - \varphi)^2 + \rho_c[S + \varphi(1 - \varphi)]} \quad (2)$$

Here,  $\omega$  is the angular frequency of an ultrasonic wave.  $\rho_c$ ,  $\rho_p$ ,

$\chi_c$ , and  $\chi_p$  represent the densities and compressibilities of a continuum consisting of a polymer network and water and magnetic particles, respectively. When the polymer concentration was constant at 10 wt %, the volume fraction of magnetic particles  $\varphi$  was determined by the following equation:

$$\varphi = \frac{10\rho_c c_p}{q\rho_p(100 + 9c_p)} \quad (3)$$

$\rho_c$  and  $\rho_p$  (5.296 g/cm<sup>3</sup>) are the densities of a continuum and a magnetic particle, respectively.  $q$  is the degree of swelling, and  $c_p$  is the weight concentration of magnetic particles. In eq 2,  $S$  has been defined by using  $Q$  and  $R$ :

$$S = Q + iR \quad (4)$$

$Q$  and  $R$  were also defined as follows:

$$\begin{aligned} Q &= \frac{1}{2} \left( \frac{1 + 2\varphi}{1 - \varphi} \right) + \frac{9\delta}{4a} \\ R &= \frac{9}{4} \left( \frac{\delta}{a} + \frac{\delta^2}{a^2} \right) \\ \delta &= \left( \frac{2\eta_{\text{eff}}}{\omega\rho_c} \right)^{1/2} \end{aligned} \quad (5)$$

$a$  is the average radius of a magnetic particle, which equals 15  $\mu\text{m}$ , and  $\eta_{\text{eff}}$  is the effective viscosity of the continuum. The effective viscosity for spheres was explained by the following equation considering hydrodynamic interactions:<sup>16</sup>

$$\eta_{\text{eff}} = \eta(1 + 2.5\varphi + 10\varphi^2) \quad (6)$$

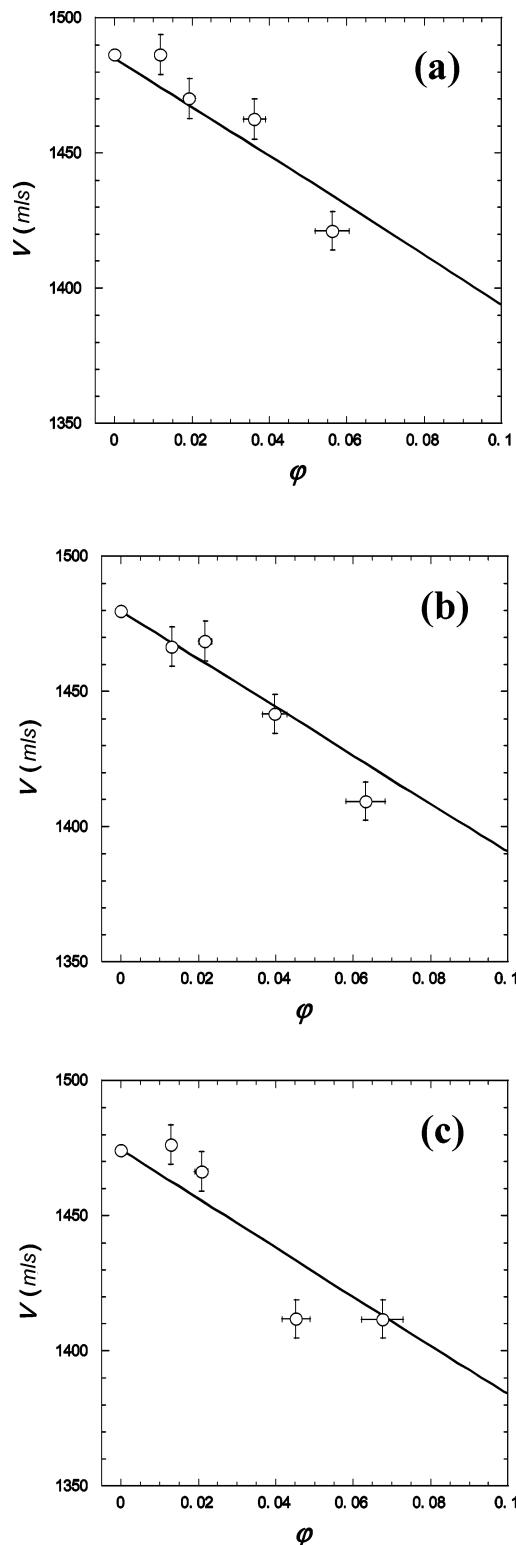
Here,  $\eta$  is the viscosity of the continuum phase, which equals 1 Pa·s. The compressibility  $\chi$  in eq 2 is explained as a basic relation in terms of the density  $\rho$  and velocity  $V$ :

$$\chi_{c,p} = \frac{1}{\rho_{c,p} V_{c,p}^2} \quad (7)$$

Here, subscripts c and p also represents the continuum and the magnetic particle, respectively. We obtained the wave velocity  $V$  of the whole system from the above expressions:

$$V = \frac{\omega}{\text{Re}(k^*)} \quad (8)$$

The relation between the wave velocity and volume fraction of magnetic particles is shown in Figure 4. Each sound velocity and density value for the magnetic gel was determined from two measurements using different samples, and the experimental errors of sound velocity and density are marked by error bars in the Figure. Large errors in sound velocity for magnetic gels ( $\sim 1.0\%$ ) originated not from inaccuracies in the sample-thickness determination, echo-position determination, and z-axis position but from the modulus variation of magnetic gels. The modulus variation is mainly caused by variations in the particle density and network density. The sound velocity was dominated by the ferrite concentration, and influences of cross-linking density on the sound velocity were not observed. The sound velocity gradually decreased with the increasing volume fraction of magnetic particle for all gels. The continuous lines in the Figures represent the theoretical values obtained by using eq 2. Even though the gels show high viscosity compared to the viscosity of the suspensions, the experimental values were in



**Figure 4.** Experimental sound velocity at 10 MHz (○) and theoretical dotted lines calculated by the Harker and Temple model for magnetic gels with different cross-linking densities: (a) 10 mol %, (b) 15 mol %, and (c) 20 mol %.

good agreement with the theoretical values over the whole range of volume fraction. The reason for the deviations between experimental and theoretical data can be explained by viscosity variations because the model does not take into account the viscosity variations when the viscosity is higher than 10 Pa·s.

**3.2. Influence of Magnetization Direction on Gel Modulus.** When the magnetic gel is compressed, the mutual positions of



**TABLE 2: Effects of Magnetization on Sound Velocity for Magnetic Gels with Different Cross-Linking Densities and Magnetization Directions**

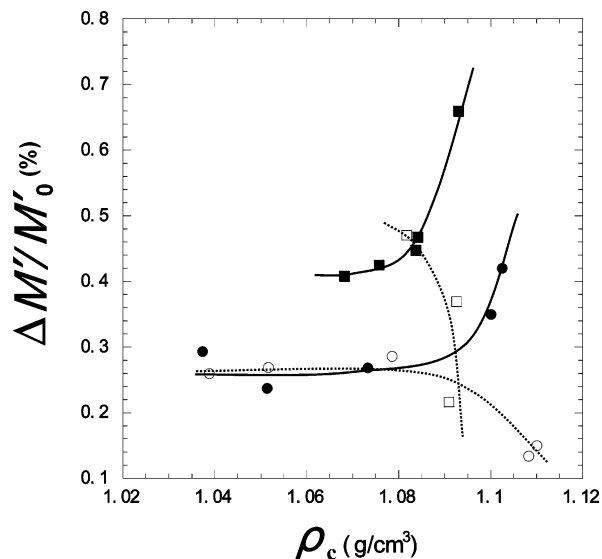
cross-linking density (mol %)	magnetization direction	sound velocity (m/s)	
		before magnetization	after magnetization
0.5	perpendicular	1515.9 ± 0.8	1518.1 ± 0.8
	parallel	1515.0 ± 0.8	1517.2 ± 0.8
2.0	perpendicular	1535.0 ± 0.8	1538.2 ± 0.8
	parallel	1533.0 ± 0.8	1533.8 ± 0.8

magnetic particle will be changed; as a result, the magnetic interactions between magnetic particles should be changed. The change in the magnetic interaction would be dependent on the magnetization direction. We prepared two kinds of gels with different magnetization directions; the magnetization directions were perpendicular and parallel to the strain, respectively. The ultrasonic wave propagates parallel to the strain. Owing to the experimental restriction that we cannot measure the sound velocity simultaneously with the application of the magnetic field, we have made the gel magnetized in advance of the ultrasonic measurement. The magnetization was carried out under a uniform magnetic field with 1 T to saturate the magnetic moment of barium ferrite particles. Generally, the field strength of 1 T is enough to saturate the magnetic moment in ferromagnetic substances such as barium ferrite particle with a diameter in the micrometer range. The magnetic gels after magnetization showed a remanent magnetization, and they were immediately provided for the ultrasonic measurement. Using gels with different magnetization directions, we have measured and compared the sound velocity to find out the influence of the magnetization direction on the gel modulus.

To find the effect of magnetization on sound velocity correctly, we have compared it using the same gel—10 wt % particle concentration and 0.5 mol % cross-linking density—because the modulus variation of the gel is much larger than the modulus change due to magnetization. As we measure the equilibrium sound velocity, the sound velocity is almost independent of the strain. Changes in sound velocity for magnetic gels with different cross-linking densities and geometries of magnetization directions are presented in Table 2. The experimental errors in the sound velocity were extremely small compared to the one in Figure 4 because the sound velocity did not include the errors due to the modulus variation of the magnetic gel. For both of the perpendicular and parallel geometries, the mean change in sound velocity was 2.2 m/s. It was evident that the sound velocity of the magnetic gel with magnetization was higher than that without magnetization, independent of the geometries. It was also clear that the change in sound velocity was nearly independent of the geometries.

We observed the large change in velocity for the gel—10 wt % particle concentration and 2.0 mol % cross-linking density—with perpendicular geometry; however, there was no apparent change in velocity for the parallel geometry. When the magnetization direction is perpendicular to the strain, the mean change in sound velocity was about 3.2 m/s. However, the velocity showed a small change ( $\sim 0.8$  m/s) when the magnetization direction was parallel to the strain direction. This strongly suggests that the change in sound velocity depends on the geometry of magnetization and strain directions.

Figure 5 shows the density ( $\rho_c$ ) dependence of the change in longitudinal modulus for magnetic gels with different magnetization directions. The longitudinal modulus  $M'$  was estimated by eq 7, and the change in modulus  $\Delta M'/M'_0$  was also evaluated by the following equation:



**Figure 5.** Density dependence of the change in the longitudinal modulus at 2.25 MHz for magnetic gels. (●, ○) 10 wt % and (■, □) 15 wt. % particle concentrations. Continuous lines and dotted lines show the perpendicular and parallel geometries with respect to the magnetization directions.

$$\frac{\Delta M'}{M'_0} = \frac{M' - M'_0}{M'_0} \quad (9)$$

$\Delta M'$  is the change in longitudinal modulus, and  $M'_0$  represents the modulus without magnetization. It was clear that the modulus of the magnetized gel was higher than that of the gel without magnetization for different particle concentrations and geometries. This result qualitatively coincides with the previous results in terms of mechanical measurement.<sup>10</sup> In a lower cross-linking density region, the change in velocity was almost independent of the geometry of magnetization and the strain directions. When the magnetization direction was perpendicular to the strain direction, the mean change in the modulus was about 9 MPa, corresponding to 0.35% of the initial modulus. However, the modulus showed a small change of 3.8 MPa corresponding to 0.15% of the initial modulus when the magnetization direction was parallel to the strain direction. This suggests that the change in the modulus depends on the magnetization direction. The changes in the modulus with respect to the initial modulus for  $c_p = 10$  and 15 wt % are about 0.28 and 0.4% in a lower-density region, respectively. Moreover, the change in the modulus was constant in a lower-density region; however, it strongly depended on the density in a higher-density region. When the stress direction was perpendicular to the magnetization, the change in the modulus increased. On the contrary, the change in the modulus decreased when the stress direction was parallel to the magnetization. With increasing density, the distance between magnetic particles becomes short; therefore, the anisotropy due to the magnetic interaction between particles might be enhanced. To compare with the previous study,<sup>10</sup> the observed modulus change by means of the ultrasonic method was much smaller than that estimated by the mechanical compression testing. The amplitude of the change in the modulus due to magnetization at 2.25 MHz was nearly equal to that measured at 10 MHz. This indicates that the large change in the modulus due to magnetization can be understood within a macroscopic range because the ultrasonic properties in the megahertz range reflect the viscoelastic properties in the range of approximately 100  $\mu\text{m}$  in the case of our system.

#### 4. Conclusions

We presented the measurement for evaluating the sound velocity of polymer gels using 2.25- and 10-MHz ultrasonic waves at 295.5 K. The sound velocity of poly(vinyl alcohol) gels containing barium ferrite particles gradually decreased with increasing volume fraction of magnetic particles. It was found that the experimental data was well fit by the coupled-phase model of suspensions; however, the viscosity of the gel was extremely high compared to that of the suspensions. The influence of magnetization on the gel modulus has also been discussed. The sound velocity of the magnetic gel after magnetization was higher than that before magnetization. Moreover, it was also shown that the change in sound velocity had a tendency to increase and decrease when the strain direction was perpendicular and parallel to magnetization, respectively. This can be explained by the fact that the magnetic gels are anisotropic in the longitudinal modulus depending on the magnetization direction according to the elastic theory. This mechanical anisotropy can be ascribed to the magnetic interactions between magnetic particles arising in the range of  $\sim 100$   $\mu\text{m}$ . Because the vibrational mode of materials is closely related to the mechanical characteristics, this feature might be useful for constructing and improving variable stiffness devices for tunable vibration absorbers and dampers.

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