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Electroviscoelastic effect of polymeric composites consisting of polyelectrolyte particles and polymer gel

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The dynamic viscoelasticity of polymeric composites consisting of silicone gel and polymethacrylic acid cobalt(II) salt (PMACo) particles was studied in d.c. electric fields. It was measured by applying sinusoidally varying shear strain or compressive strain to the composites. It was found that the electric fields enhanced the storage and loss moduli of the composites, and changed the loss tangent (electroviscoelastic effect). The amount of the electroviscoelastic effect was influenced by the content of absorbed water in the PMACo particle, the fraction of PMACo particles, and the intensity of the electric field. It also depended on the amplitude and frequency of the applied strain. The increments of the compressive moduli due to the electroviscoelastic effect were much larger than those of the shear moduli.

1. Introduction

It is well known that some kinds of suspensions of fine particles dispersed in non-conducting oil stiffen rapidly when subjected to an electric field. This phenomenon is called the electro-rheological (ER) effect and is caused by alignment of dispersed particles between the electrodes [1, 2]. The electroviscoelastic effect concerns the ER effect in polymeric materials such as polymer gel. In previous work [3] we have measured the dynamic viscoelasticity of silicone gels containing polymethacrylic acid cobalt(II) salt particles in d.c. electric fields and found that the silicone gels with high volume fractions of particle showed changes of the dynamic shear modulus and loss tangent by the application of d.c. electric fields (electroviscoelastic effect). Movement of the particles was not observed in the gels by our microscopic observation, while it has been done in an ER suspension to produce the ER effect. However, in gels showing the electroviscoelastic effect almost all of the particles have already contacted each other and have formed many winding paths between the electrodes before application of an electric field.

The ER effect in suspensions or in gels occurs through a microscopic bonding between the particles due to an induced dipole–induced dipole interaction. For an isolated dielectric spherical particle in a dielectric medium of different permittivity [4], the induced dipole moment for a particle is given by

$$\mu = 4\pi r^3 \varepsilon_v \varepsilon_1 \kappa E \qquad (1)$$

where

$$\kappa = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}$$

In Equation 1, r is the radius of particle, ε_v the permittivity in a vacuum, E the intensity of applied field, and ε_2 and ε_1 the permittivities of particle and medium, respectively. Equation 1 is an expression obtained formally for the volume polarizability of a particle.

In ER suspensions, straight chains or columns of dispersed particles, which remains parallel to the direction of the applied field, are formed between electrodes by the application of electric fields [5]. The bonding force F between adjacent particles in the column due to an induced dipole–induced dipole interaction is calculated from Equation 1:

$$F = \frac{3}{2}\pi r^2 \varepsilon_v \varepsilon_1 \kappa^2 E^2 \qquad (2)$$

We now consider the deformation of columns in a cubical composite (L = length, C = particle content) under a shear strain or a compressive one. Here, the number of the column n in the cube is given by

$$n = 3CL^2/2\pi r^2 \qquad (3)$$

If the bottom electrode is fixed and the upper one is moved, a column is deformed by a shear strain from the perpendicular direction or by a compressive strain from the parallel direction of electric field (Fig. 1).

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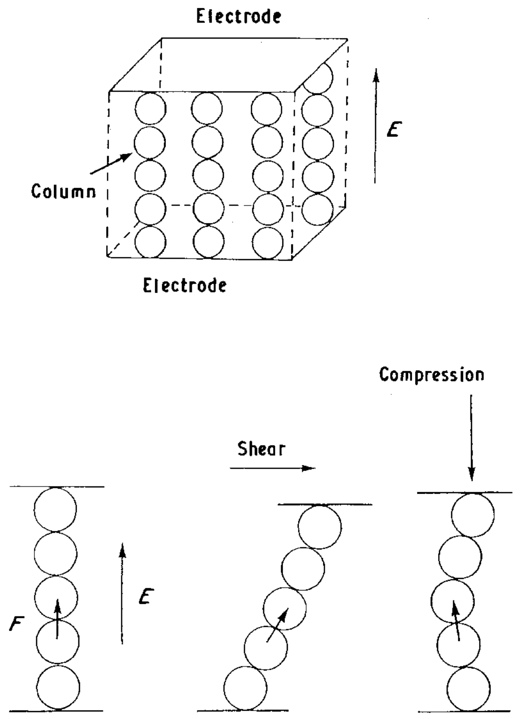

Figure 1 Deformation of a column of particles in particulate composite.

When the column is deformed by a constant strain, a larger shear force or compressive force is needed in the presence of electric field than in no field because a bonding force exists in the column. So the bonding force can make accessible the macroscopic mechanical properties of the composite such as the storage and loss moduli. As the macroscopic mechanical properties reflect the deformation of all columns in the cube, they may be related to C, ε_1, κ^2 and E^2 if the amount of the electroviscoelastic effect is expressed easily by multiplying F by n. This article will discuss how the electroviscoelastic effect affects the experimentally observed macroscopic mechanical behaviour of the particle-filled composites. We have prepared silicone gels with many columns of polyelectrolyte particles, and have measured the dynamic viscoelasticity of the composites by shear or by compression in d.c. electric fields.

2. Experimental procedure

2.1. Preparation of specimens

Polymethacrylic acid cobalt(II) salt (PMACo) particles with a small amount of absorbed water up to 16.7 wt % were used as polyelectrolyte particles. The PMACo particles were obtained as follows; first, sodium polymethacrylic acid hydrogel was prepared by a radical polymerization of 0.1 mol of methacrylic acid, 0.1 mol of sodium hydroxide and 0.005 mol of N, N′-methylenebisacrylamide in 100 ml of distilled water using tetramethyldiaminomethane as a reaction initiator. Next the obtained sodium polymethacrylic acid hydrogel was immersed in a cobalt(II) chloride aqueous solution to exchange sodium ions for cobalt(II) ions. Then the hydrogel of polymethacrylic acid cobalt(II) salt was dried at 130 °C and broken to pieces by a mill to give the PMACo particles. After heating the particles at 130 °C for 5 h again, the particles were set in the air to absorb moisture up to 16.7 wt %. The obtained PMACo particles had a cobalt content of 22.7%, and 75 μm average diameter.

The silicone gels with columns of PMACo particles was prepared as follows: 0–15 g of the PMACo particle were mixed with 20 g of prereaction solution of silicone gel (Toray Silicone Dow Corning Co., SE1886). The prereaction solution mixed with the particles was sandwiched between two Au-deposited polyester films as electrodes. Then a d.c. electric field with an intensity of 1 kV mm^{-1} was applied between the electrodes across the prereaction solution to form columns of particles, and finally it was heated at 70 °C for 10 h under the d.c. field to give the specimens.

2.2. Measurement of dynamic viscoelasticity

The dynamic viscoelasticity of the specimen in d.c. electric fields was measured using a viscoelastic spectrometer (Iwamoto Seisakuzyo Ltd, VES-F). The test apparatus for a shear viscoelastic test as shown in Fig. 2a was used. The specimen was sandwiched between an inner plate (size 8 mm × 8 mm) and two outer plates, and then the inner plate was connected to a servo motor and the outer plates to a torque transducer in the viscoelastic spectrometer. The gap between the inner and the outer plates was 1 mm. In setting the specimen, the column of PMACo particles in the gel was set parallel to the direction of applied field. A voltage up to 5 kV d.c. was applied between the inner and outer plates, and then the inner plate was vibrated by sinusoidally varying the shear strains, $\gamma = \gamma_0 \sin 2\pi f t (\gamma_0$ = amplitude of shear strain, f = frequency of strain). Torque acting on the outer plates was measured by the torque transducer to give the storage and the loss moduli G', G'' and the loss tangent $\tan\delta$.

The dynamic viscoelasticity for the compressive mode was measured by a test apparatus as shown in Fig. 2b. The specimen (thickness, L_0 = 2 mm) was sandwiched by two platinum plates (size 20 mm × 27 mm), and then a voltage up to 5 kV d.c. was applied between the plates. After an initial compressive strain of 0.1 ($\Delta L/L_0 = 0.1$ where ΔL = deflection) was applied and one plate connected with the servo motor was vibrated by sinusoidally varying compressive strains, $\varepsilon = \varepsilon_0 \sin 2\pi f t$ (ε_0 = amplitude of strain). The torque on the other plate was measured to give the moduli E', E'', and the loss tangent.

3. Results and discussion

3.1. Influence of absorbed water in particle

It is well known that the ER effect in suspensions depends strongly on the amount of absorbed water in the particle. The amount of absorbed water influences the permittivity of the particle, and so the electroviscoelastic effect caused by the bonding force between particles may also be determined by the permittivity of the particles, that is, the amount of absorbed water. To investigate the influence of absorbed water on the

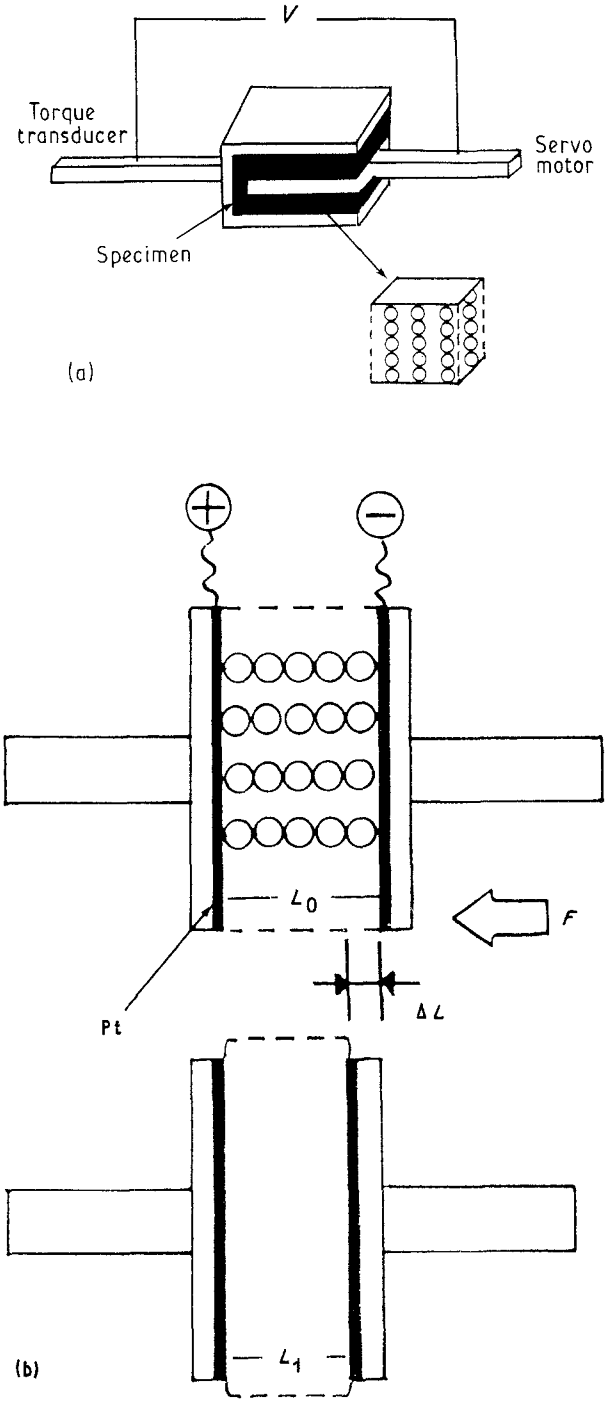

Figure 2 Test apparatus for dynamic viscoelasticity in (a) shear and (b) compression.

electroviscoelastic effect, we prepared specimens using the PMACo particles with the concentration up to 16.7 wt %. Fig. 3 indicates the effect of the content of absorbed water on dielectric constant of the PMACo particles. The dielectric constant was measured as follows. The PMACo particles were compressed in a disc with 10 mm diameter and 1 mm thickness. Upper and lower faces of the disc were coated with Ag paste (Fuzikura Kasei Ltd, Dotite D-550S). Then a sinusoidally varying voltage with 1 V amplitude was applied between the two faces by an impedance analyser (Hewlett Packard 4192A), and dielectric constants in the range from 10 Hz to 5 MHz were measured. In Fig. 3, the dielectric constant at 100 Hz was used.

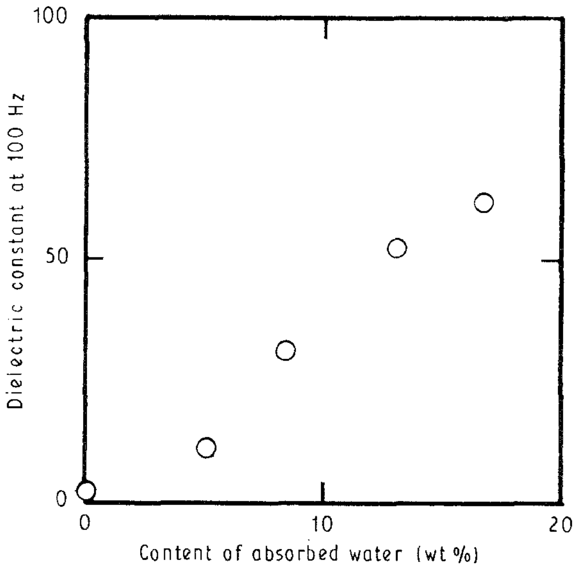

Figure 3 Dielectric constant of polymethacrylic acid cobalt(II) (PMACo) particles versus the content of absorbed water in the PMACo particles. The dielectric constant was measured using a disc (thickness 1 mm, diameter 10 mm) prepared by compressing the PMACo particles.

Fig. 3 shows that the dielectric constant increases with the content of absorbed water.

Next we studied the relationship between the dielectric constant and the amount of the electroviscoelastic effect. According to Equation 2, it is expected that the amount of the electroviscoelastic effect is related to κ^2. Fig. 4a shows the increments of G' and G'' ($\Delta G'$ and $\Delta G''$) induced by electric fields versus the dielectric constant of the particles. The electroviscoelastic effect has been observed in all specimens except the gel free of absorbed water. The electroviscoelastic effect makes G' and G'' increase. $\Delta G'$ and $\Delta G''$ increase with the dielectric constant of the particle, and after a while reach constant values. In Fig. 4a, the solid line and the dotted one represent $\Delta G' = 100\kappa^2$ and $\Delta G'' = 50\kappa^2$, respectively. On calculating κ, the value $\varepsilon_1 = 2.7$ as the dielectric constant of silicone gel and the dielectric constants at 100 Hz of the particles were used. The experimental results are qualitatively related to κ^2.

The increments of the compressive moduli, $\Delta E'$ and $\Delta E''$, due to the electroviscoelastic effect are given in Fig. 4b. They also increase with the dielectric constant, and become constant. The solid line and the dotted one represent $\Delta E' = 20\kappa^2$ and $\Delta E'' = 5\kappa^2$, respectively. Both lines explain the experimental results roughly. As shown in Fig. 4a and b, it has been found that the amount of the electroviscoelastic effect depends strongly on the dielectric constant, that is, the content of absorbed water in the PMACo particles.

3.2. Effect of particle content

The effect of PMACo particle content on the increments of the moduli due to the electroviscoelastic effect are given in Fig. 5a and b. Changes of the storage and loss moduli by the application of an electric field are observed in specimens with the particle content over 15 wt % on the shear mode, and

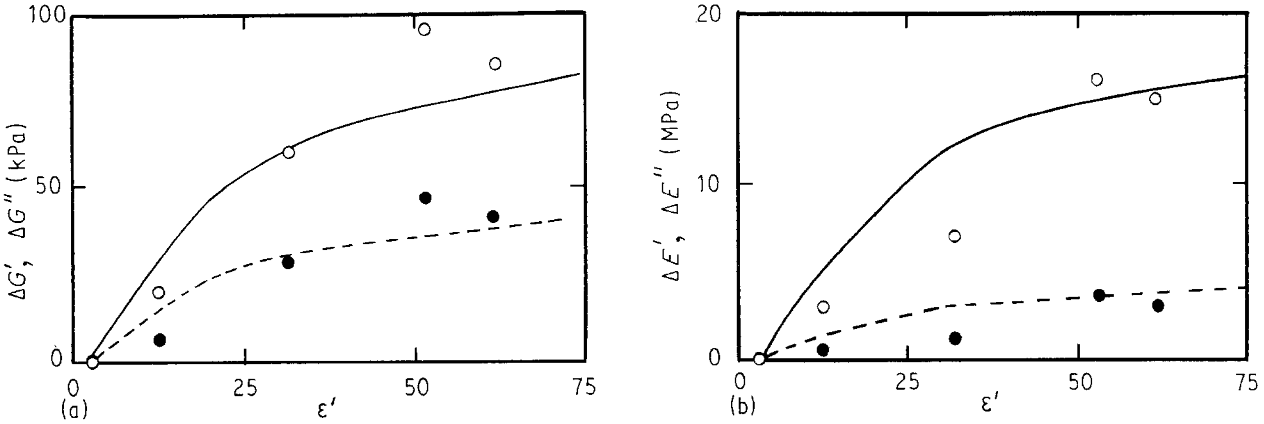

Figure 4 Effect of the dielectric constant of the particles on the electroviscoelastic effect: (a) increments of the shear storage and loss moduli, (o) $\Delta G'$ and (●) $\Delta G''$ by the application of an electric field of 5 kV mm^{-1}, and (b) increments of compressive storage and loss moduli (o) $\Delta E'$ and (●) $\Delta E''$, induced by 2 kV mm^{-1}. The specimens have a constant content of PMACo particles of 46 wt %. In (a) the solid line and the dotted one represent $\Delta G' = 100\kappa^2$ and $\Delta G'' = 50\kappa^2$, respectively. Here κ is $(\varepsilon' - \varepsilon_1)/(\varepsilon' + 2\varepsilon_1)$ where ε' and ε_1 are respectively the dielectric constants of PMACo particles at 100 Hz and of silicone gel (equal to 2.7). In (b) the solid line and the dotted one represent $\Delta E' = 20\kappa^2$ and $\Delta E'' = 5\kappa^2$, respectively. In Figs 4 to 6, the tests of the dynamic viscoelasticity were made by applying a sinusoidally varying shear strain $\gamma = \gamma_0 \sin 2\pi ft$ (at $f = 10$ Hz and $\gamma_0 = 0.025$) or by a sinusoidally compressive strain $\varepsilon = \varepsilon_0 \sin 2\pi ft$ (at $f = 10$ Hz and $\varepsilon_0 = 0.025$).

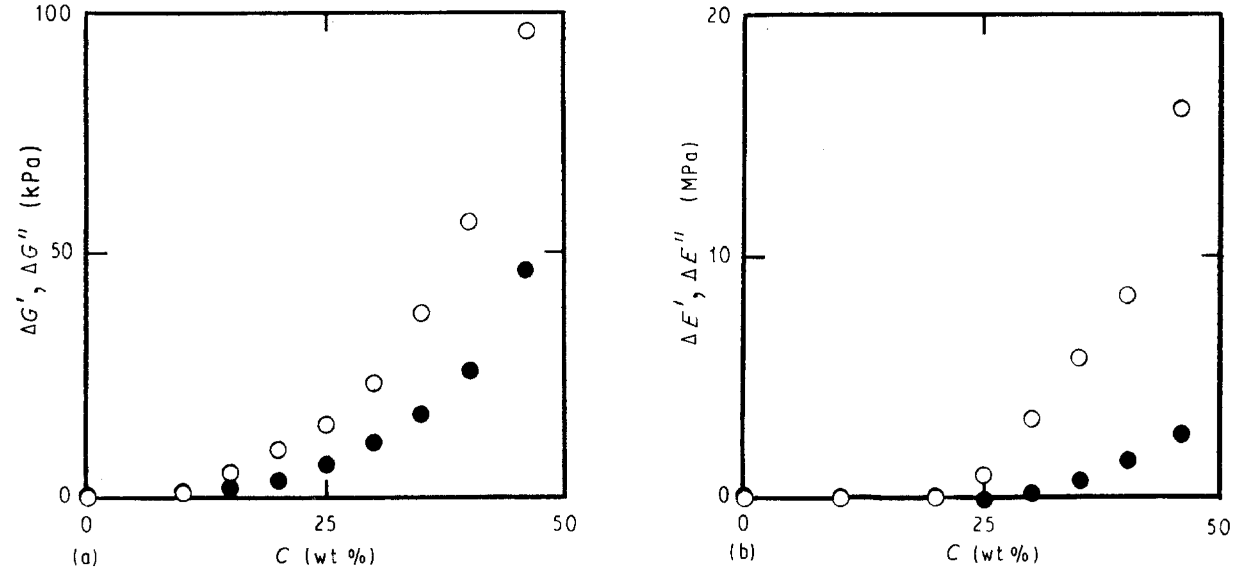

Figure 5 Relationships between the particle content C and (a) the increments of shear moduli (o) $\Delta G'$ and (●) $\Delta G''$ by the application of 5 kV mm^{-1}, and (b) the increments of compressive moduli (o) $\Delta E'$ and (●) $\Delta E''$ induced by 2 kV mm^{-1}. Specimens with a constant content of absorbed water of 13 wt % were used.

with the content over 25 wt % on the compressive mode. Fig. 5a and b show that the electroviscoelastic effect reflects more strongly on the storage modulus than on the loss modulus. If the electroviscoelastic effect is expressed simply by multiplying F by n, it is predicted from Equations 2 and 3 that the increments of the moduli are proportional to the content of the PMACo particle, but the results obtained are not in agreement with this prediction.

3.3. Effect of field intensity

The electroviscoelastic effect is induced by the application of electric fields, and so we have studied a field intensity dependence on the electroviscoelastic effect. The prediction mentioned above suggests that the increments of the moduli are proportional to E^2. The relationships between G', G'' and tan δ, and E are plotted in Fig. 6a. $G'(E)$ and $G''(E)$ in the presence of an electric field are expressed by

$$\begin{aligned} G'(E) &= G'(0) + 4E^2 \\ G''(E) &= G''(0) + 2E^2 \end{aligned} \qquad (4)$$

where $G'(0)$ and $G''(0)$ are the moduli in the absence of an electric field and E the intensity of applied field. The values of $\Delta G'$ and $\Delta G''$ exhibit a quadratic dependence on the field intensity. This is in agreement with the simple prediction. As $\Delta G'$ shows a larger change than $\Delta G''$ does, the value of tan δ decreases with increase of the field intensity. By calculating the change of tan δ induced by 5 kV mm^{-1} in terms of δ, it is equal to a change of 8°.

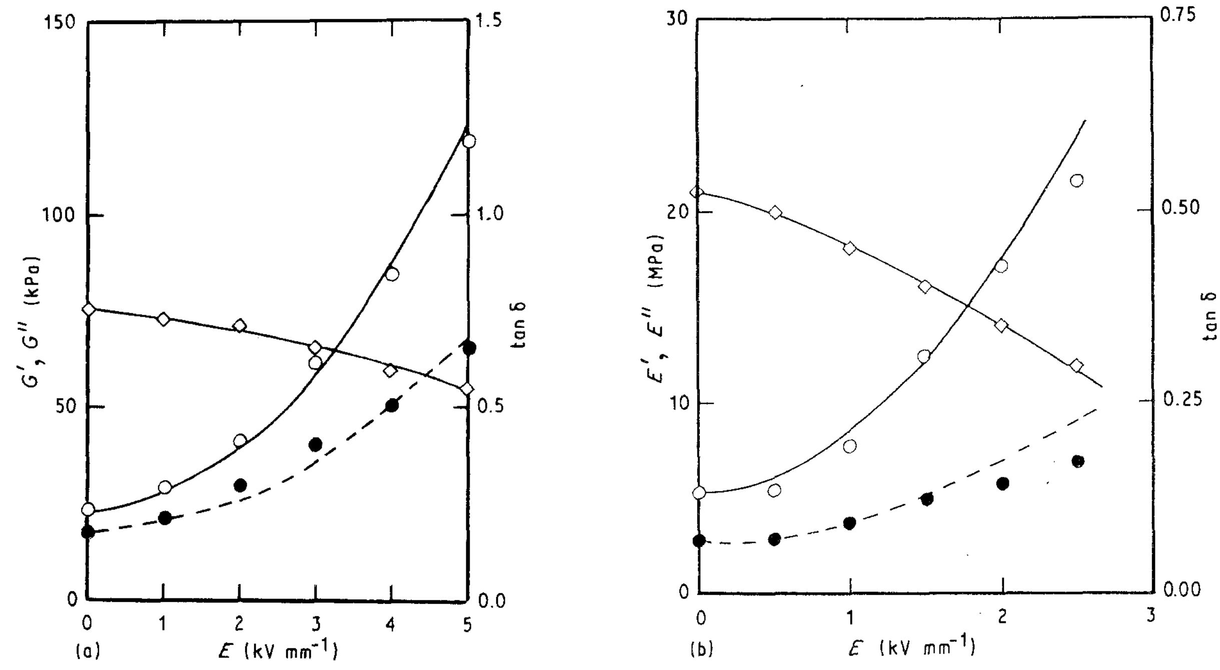

Figure 6 Effect of applied field intensity on the moduli and the loss tangent: (a) shear moduli (○) G', (●) G'' and (◇) tan δ; (b) compressive moduli (○) E', (●) E'' and (◇) tan δ. In Figs 6 to 10, a specimen with a particle content of 46 wt % and a content of absorbed water of 13 wt % was used.

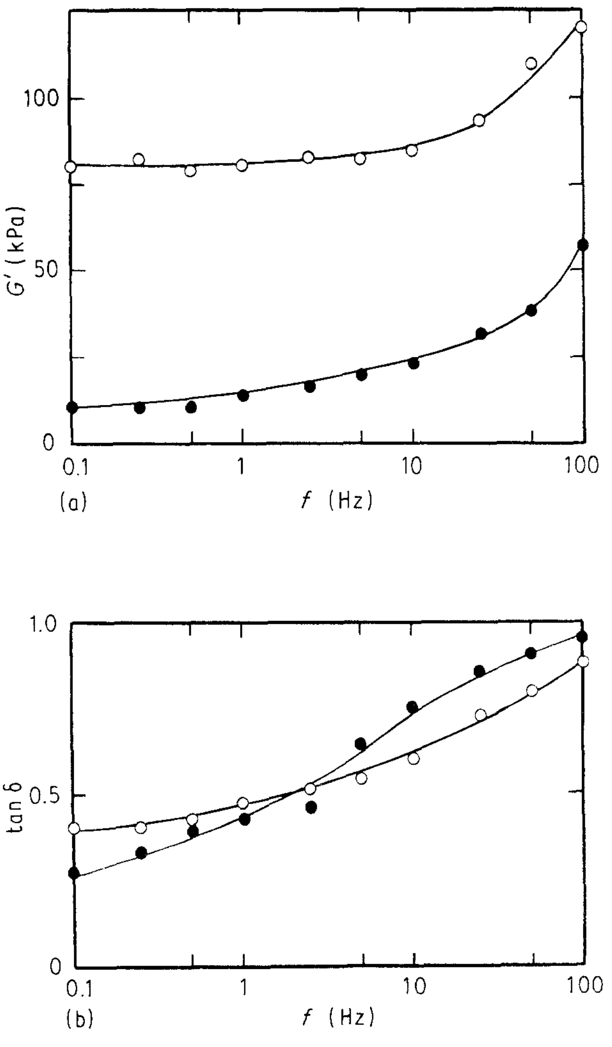

Figure 7 Relationships between the frequency of sinusoidally varying shear strain $\gamma = \gamma_0 \sin 2\pi ft$ and (a) the storage modulus, (b) the loss tangent. The experiment was made at a constant amplitude, $\gamma_0 = 0.08$; electric field (●) 0, (○) 4 kV mm^{-1}.

Fig. 6b shows the relationships between E', E'' and tanδ, and the field intensity. $E'(E)$ and $E''(E)$ are given by

$$E'(E) = E'(0) + 3.0E^2$$
$$E''(E) = E''(0) + 1.0E^2 \qquad (5)$$

The increments of E' and E'' due to the electroviscoelastic effect exhibit a quadratic dependence on the field intensity. These results agree with the predicted one qualitatively. The loss tangent varies with the field intensity. There has been a loss of 11.6° in δ under 5 kV mm^{-1}. In general, the values of the compressive moduli are three times those of the shear moduli in an isotropic material. However, as shown in Fig. 6a and b, $E'(0)$ and $E''(0)$ are much larger than $G'(0)$ and $G''(0)$, and the electroviscoelastic effect produces huge changes in the compressive mode. This is because the specimens are not isotropic materials, having a lot of columns of PMACo particles. Fig. 6a and b shows that the rigidity and the damping term of energy absorption of the composites can be controlled by the intensity of the applied electric field.

3.4. Effect of frequency of strain

As many researchers have reported that the ER effect depends on the strain rate [6], we have examined the effect of strain rate on the electroviscoelastic effect. In a test of the dynamic viscoelasticity a sinusoidally varying shear strain $\gamma = \gamma_0 \sin 2\pi ft$, or a compressive strain $\varepsilon = \varepsilon_0 \sin 2\pi ft$, is applied to the specimen. So the strain rate, $d\gamma/dt$ or $d\varepsilon/dt$, is expressed by

$$d\gamma/dt \text{ (or } d\varepsilon/dt) = 2\pi f\gamma_0 \cos 2\pi ft \quad \text{(or } 2\pi f\varepsilon_0 \cos 2\pi ft) \qquad (6)$$

Equation 6 suggests that the electroviscoelastic effect depends on the frequency and the amplitude of the strain.

To investigate the influence of strain frequency on the electroviscoelastic effect, the dynamic viscoelasticity was measured in the frequency range from 0.1 to 100 Hz at a fixed amplitude of small strain, $\gamma_0 = 0.08$ or $\varepsilon_0 = 0.025$. The influence of the frequency are shown in Fig. 7a and b. At a frequency up to 1 Hz, the specimen has a constant value at 0 kV mm^{-1} ($G' = 12$ kPa) or at 4 kV mm^{-1}($G' = 55$ kPa). Above 1 Hz, G' increases gradually with f, whether an electric field is applied or not. However, it has been noted that the increment of G' due to the electroviscoelastic effect remains constant in the measured range. The specimen shows characteristic behaviour of the loss tangent. In the low frequency range, the value of tan δ is increased by the application of an electric field, while it is decreased in the high frequency range. The slope of a tan δ–log f curve is gentle in an electric field. The specimen also tends to show similar behaviour in the compressive mode (Fig. 8a and b). The increment of the storage modulus, $\Delta E'$, is little influenced by the frequency of applied strain. There is interesting behaviour of tan δ as observed in the shear mode. The slope of a tan δ–log f curve becomes gentle under the influence of an electric field.

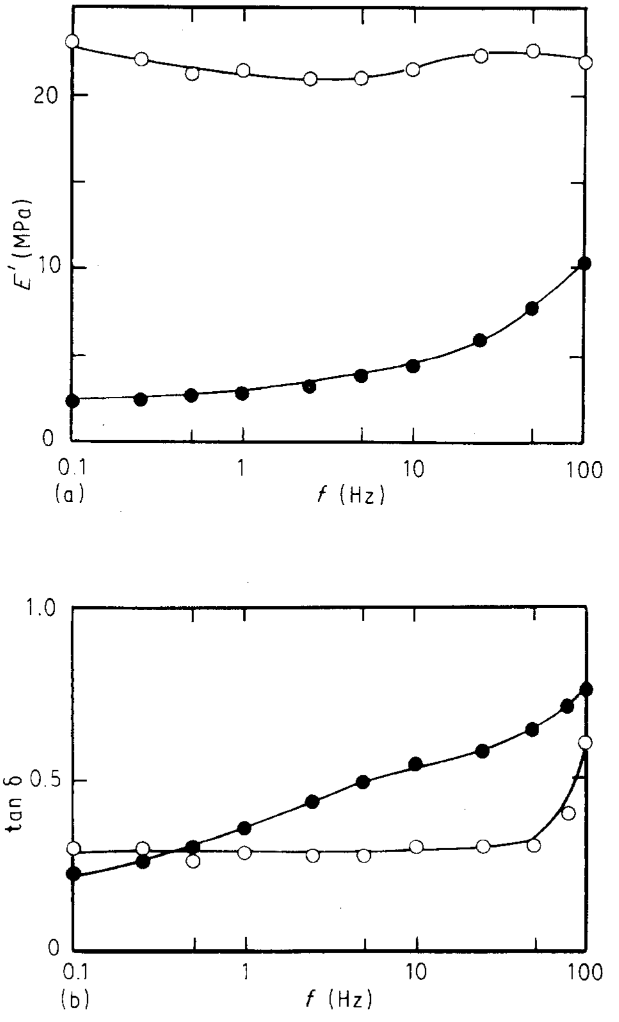

Figure 8 Relationships between the frequency of sinusoidally varying compressive strain $\varepsilon = \varepsilon_0 \sin 2\pi ft$ and (a) the storage modulus, (b) the loss tangent. The experiment was made at a constant amplitude, $\varepsilon_0 = 0.025$; electric field (●) 0, (○) 2.5 kV mm^{-1}.

3.5. Effect of amplitude of strain

The influence of the amplitude of the shear strain was measured in the range of γ_0 from 0 to 0.4 at a fixed Frequency f of 10 Hz. Fig. 9a and b shows the relation ships between G' or tan δ and γ_0, respectively. The value of G' under 0 kV mm^{-1} remains constant against γ_0. Tan δ also shows a constant value of 0.75 in the absence of an electric field. In the presence of an electric field of 4 kV mm^{-1}, G' decreases gradually with γ_0 while tan δ increases with γ_0 and approaches 0.75 of the value in no field. The results show that the electroviscoelastic effect depends on γ_0. This is because the columns of particles lean little by little with the increase of γ_0 and becomes unstable.

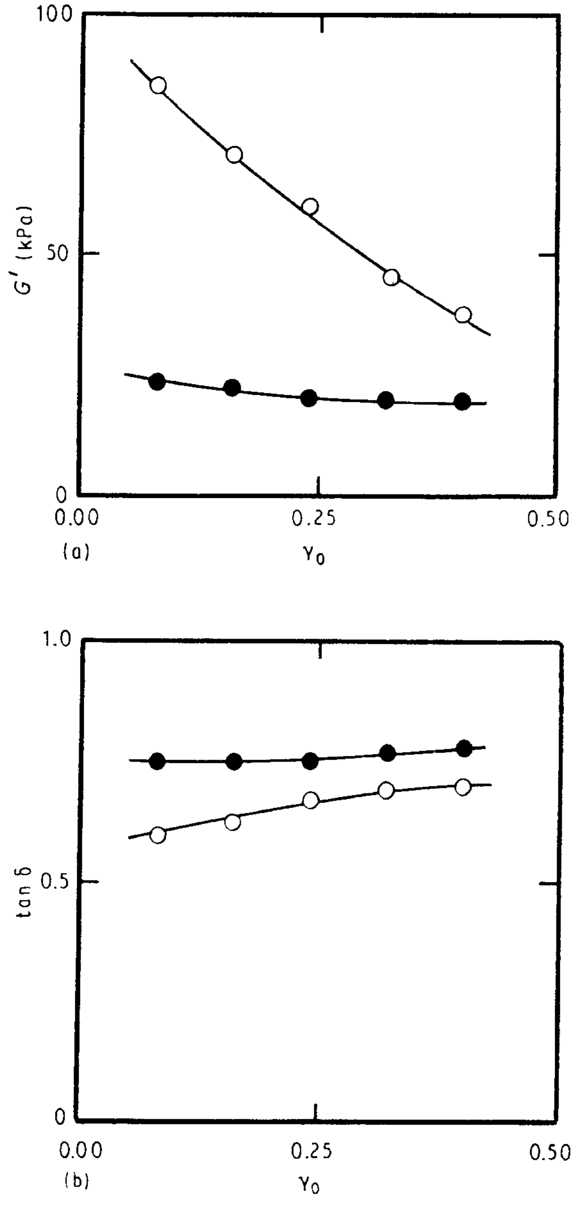

Figure 9 Effect of the amplitude of sinusoidally varying shear strain on (a) shear storage modulus and (b) loss tangent. Electric field (●) 0, (○) 4 kV mm^{-1}. In Figs 9 and 10 the experiments were made at a fixed frequency of 10 Hz.

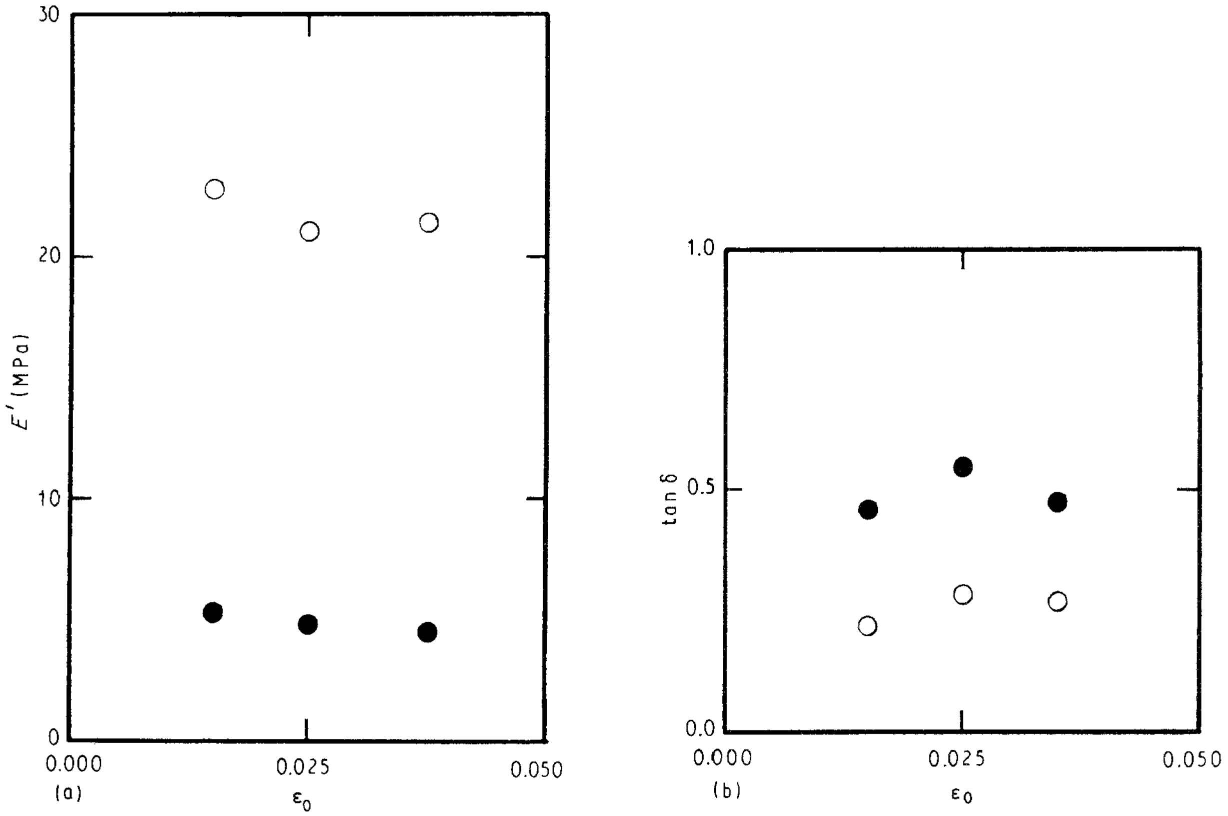

Figure 10 Effect of the amplitude of sinusoidally varying compressive strain on (a) storage modulus and (b) loss tangent. Electric field (●) 0, (o) 2.5 kV mm^{-1}.

Fig. 10a and b illustrate E' and tan δ versus ε_0, respectively. The experiments were carried out in the range of ε_0 from 0.015 to 0.035. Values of both E' and tanδ remain constant against ε_0 in no field as well as in the presence of an electric field of 2.5 kV mm^{-1}. The electroviscoelastic effect on compression is roughly independent of ε_0. This result suggests that the columns do not break down in the measured range even if they are buckling.

4. Conclusions

In this paper, the dynamic viscoelasticity of polymeric composites consisting of silicone gel and PMACo particles was measured not only in shear but in compression under the influence of electric fields. We have made interesting observations, i.e. changes of the storage and loss moduli and of the loss tangent in gels, by the application of electric fields. We have called these phenomena the electroviscoelastic effect. The present experiments have provided useful results to understand the electroviscoelastic effect. The electroviscoelastic effect occurs through a bonding between particles due to an induced dipole–induced dipole interaction. The electroviscoelastic behaviour of the composites has been explained roughly by a simple model based on this interaction.

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