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Polymer 45 (2004) 3811–3817
polymer
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Electrorheological response of swollen silicone gels containing barium titanate

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Received 5 January 2004; accepted 18 March 2004

Abstract

We have investigated storage moduli of silicone gels containing barium titanate in the presence of dc electric fields. The gels containing barium titanate swollen by silicone oil showed a storage modulus reduction, i.e. negative electrorheological effect. Contrary, no negative electrorheological effect was observed in the unswollen gels and silicon gels without barium titanate. Swollen silicone gels and most of silicone/$BaTiO_3$ gels obeyed empirical quadratic dependence in electric field strength. Although an apparent phase separation was not observed in the swollen gel, microscopic phase separation may occur due to the difference in electric conductivity between particles ($\sim 10^{-10}$ S/cm) and silicone oil (10^{-9} S/cm), as a result, the negative electrorheological effect appears. The effects of frequency, degree of swelling, and the field strength have been discussed.

Keywords: Silicone gel; Electrorheology; Negative electrorheological effect

1. Introduction

The physical properties of stimuli-responsive soft materials dramatically change corresponding to the external stimuli such as temperature, pH, electric and magnetic fields. These materials are called as intelligent materials and have been harnessed in novel systems, for example, sensors, actuators, and biomedical applications. We have been investigated the intelligent gels, consisting of inorganic compounds and polymer networks, in response to physical stimuli. Some gels respond to magnetic fields, others respond to electric fields depending on the dispersed particles.

Gels in response to magnetic fields are called as magnetic gels. The polymer gel containing magnetic fluid undergoes an abrupt elongation and contraction behavior under non-uniform magnetic fields [1]. The behaviors are due to the fact that the finely distributed ferromagnetic particles are attached to the flexible network by an adhesive force, as a result a direct coupling between magnetic and rheological properties. Besides this, elastic moduli of the magnetic gel can be controlled by magnetic field. Mean change in the modulus increased with increasing magnetic field and it saturated above 2 kOe, according to uniaxial compression measurements [2]. The mean and maximum change in modulus at 4 kOe was 31 and 71 Pa, which corresponds to 19 and 46%, respectively, compared to no field. Recently, we have investigated the relationship between the magnetization direction and longitudinal modulus of the magnetic gel using ultrasonic wave with 10 MHz [3,4]. The change in longitudinal modulus was cleared to be depending on the magnetization direction. The change in modulus $\Delta M'/M'_0$ was approximately 0.1–0.7%, which is much smaller than the modulus change obtained by the uniaxial compression measurement.

On the other, there are a lot of gels in response to electric fields. Bending motion of polyelectrolyte gels under electric field is very famous phenomenon, and it has been tried to apply actuators or artificial muscles [5]. In this report, however, we are focusing on the rheological properties of gels under electric fields. Gels or elastomers that the rheological properties change with applying electric fields are called as electrorheological (ER) gels. Silicone elastomers containing titania demonstrate bending phenomena under high ac electric fields [6]. Silicone elastomers containing semi-conducting polymer particles undergo the storage modulus change under dc electric fields [7].

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doi:10.1016/j.polymer.2004.03.056

According to the study, the electrorheological effect was observed in the rubbery state of the elastomers with many lines of adjacent particles spanning the space between electrodes. Electrorheological silicone elastomers containing particles based on silica and titania compounds have been reported [8].

The electrorheological phenomenon first found in fluid system such as colloids, suspensions, and emulsions, and has been well investigated in the system. The viscosity of the ER fluid can be controlled by switching of the electric field. This feature has been utilizing as dampers and actuators being worked by electric fields. Some ER fluids show the viscosity increases under electric fields, which is called by the positive ER effect, others demonstrate the viscosity decreases under electric fields, which is called by the negative ER effect. The negative ER effect has been found in, for example, solid particles suspending solution [9], magnesium hydroxide/silicone oil suspensions [10] and Teflon/silicone oil suspensions [11]. However, as far as we know, the negative ER effect has not ever been found in network polymers, i.e. gels or elastomers.

We have briefly reported that silicone/$BaTiO_3$ gels swollen by silicone oil exhibited the negative electrorheological effect under electric fields [12]. This paper clarified that the effect only seen in the swollen gel strongly related to the swelling properties. It was found that the swollen silicone/$BaTiO_3$ gels exhibited the negative electrorheological effect under dc electric field. The change in modulus obeyed the quadratic dependence on electric fields and the maximum change in modulus was approximately −41% at 2 kV/mm observed in CAT 0.2. Unswollen silicone/$BaTiO_3$ gels showed slightly positive change in the storage modulus. Swollen silicone gels showed a large positive change in modulus in the presence of electric fields. Similar to the silicone/$BaTiO_3$ gels, unswollen silicone gels did not show any change in modulus. Although a phase separation was not observed in the silicone/$BaTiO_3$ gels, the negative electrorheological effect might be originated from the electric conductivity of $BaTiO_3$ particles and silicone oil in which the gel swelled.

In this paper, we have made detailed investigations of the negative electrorheological effect of the swollen silicone/$BaTiO_3$ gels. The effects of degree of swelling and $BaTiO_3$ concentration on the negative electrorheological effect have been described.

2. Experimental part

2.1. Sample preparation

We prepared pre-gel solution by mixing of poly(dimetylsiloxane-*co*-methylvinylsiloxane) (KE-104 Shinetsu Chemical Co, Ltd) and poly(dimethylsiloxane-*co*-methylhydrogensiloxane) (CAT-104 Shinetsu Chemical Co, Ltd) as a crosslinker containing Pt catalysts. As listed in Table 1, the weight fraction of the crosslinking agent (CAT) to the polymer (KE) was varied from 0.1 to 0.3. The weight fraction of $BaTiO_3$ to KE was also varied from 0.1 to 0.5, corresponding to 1.6–6.4 vol% in feed. Finely $BaTiO_3$ particles (Aldrich chemical company, Inc.) with the maximum diameter of 3.0 μm were added to the pre-gel solution. The density of $BaTiO_3$ particles was 6.080 g/cm^3. The solution was in vacuum with stirring for 10 min, and was poured in a glass mold with silicone spacer to make a sheet-shaped gel with the size of $10 \times 10 \times 1.5$ mm^3. The mold filled with pre-gel solution was heated on a hot stage at approximately 150 °C. The curing time was varied from 30 to 90 min depending on the concentration of the crosslinking agent CAT. After curing, the gels were immersed in the silicone oil (KF-8010 Shinetsu Chemical Co, Ltd) for 7 d until equilibrium swelling was reached, and they were provided for rheological measurements.

2.2. Rheological measurements

Dynamic viscoelastic measurements were carried out using a rheometer (MR-300V2, Rheology Co, Ltd) in which allowed to measure the complex modulus under electric fields. Frequency range of the dynamic viscoelastic measurements was varied from 0.1 to 10 Hz, and the strain amplitude γ was around 0.05. The gap in which the gel was sandwiched by two parallel plates was changed between 1.40 and 1.70 mm. This corresponds to the strain with 0.8 to the sample thickness. To keep the gap distance for viscoelastic measurements of swollen $BaTiO_3$ gels is difficult because the sample thickness was changed depending on the crosslinking density. We started the viscoelastic measurement when the stress relaxation of the gel had finished. The dc electric field up to 2 kV/mm was applied to the gel to find out the electric field dependence of storage modulus. The rheological measurement was carried out at the room temperature (22 ± 2 °C). Each storage modulus was determined from at least an average of four measurements.

3. Results and discussion

Both silicone gel and silicone/$BaTiO_3$ gels showed swelling behaviors in silicone oil. The gels reached an equilibrium swelling approximately 4 d after the gel had immersed in the oil. The degree of swelling at the equilibrium Q_{eq} was summarized in Table 1. As seen in the table, the degree of swelling largely depends on CAT and $BaTiO_3$ concentrations. In the samples for CAT series, the degree of swelling of CAT0.1 was highest than those of the others. As increasing the CAT concentration, i.e. as increasing the cross-linking density, the degree of swelling decreased. In the samples for BTO series, the degree of swelling took a maximum at BTO = 0.1 and decreased with

Table 1
Degree of swelling, initial storage modulus, and electrorheological parameters of swollen silicone gel and swollen silicone/$BaTiO_3$ gels

	Samples[a]	W_C/W_K (wt%)[b]	W_{BTO}/W_K (wt%)[c]	Q_{eq}[d]	G'_0 (Pa)[e]	E_0 (kV/mm)[f]
Silicone/$BaTiO_3$ gel	CAT0.1	10	50	2.3	4.86×10^3	−0.49
	CAT0.2	20	50	1.9	1.11×10^4	−0.49
	CAT0.3	30	50	2.0	1.17×10^4	−0.38
	BTO0.1	20	10	2.6	2.23×10^4	0.40
	BTO0.2	20	20	2.4	8.17×10^4	−0.56
	BTO0.3	20	30	2.3	7.40×10^4	−0.48
	BTO0.4	20	40	2.2	7.09×10^4	−0.83
Silicone gel	SG 0.2	20	0	2.2	4.90×10^3	0.17

[a] Abbreviations of the samples.
[b] Weight ratio of CAT to polymer.
[c] Weight ratio of $BaTiO_3$ to polymer.
[d] Degree of swelling in silicone oil.
[e] Storage modulus at 0.1 Hz without electric field.
[f] Electric field strength parameter in Eq. (6).

increasing the BTO concentration. This strongly suggested that the CAT systematically worked as a cross-linker.

Fig. 1 shows the frequency dependence of the storage modulus of swollen silicone/$BaTiO_3$ gels under various electric field strengths. The storage modulus strongly depended on both the frequency and the field strength. It was obvious the storage modulus of the swollen silicone/$BaTiO_3$ gel decreased as increasing the field strength, i.e. the negative electrorheological effect. A significant change in modulus was found at the lowest frequency $f = 0.1$ Hz. The effect of electric fields on storage modulus tended to be smaller in a higher frequency region. Generally, storage moduli of cross-linked polymers are nearly independent of the frequency. It is well known that an entangled polymer solution or melt flow as a high-viscosity liquid with $G' \propto \omega^2$ at very low frequencies. Frequency dependence of storage modulus without and with ($E = 2.0$ kV/mm) electric field can be evaluated as $\propto\omega^{0.4}$and $\propto\omega^{0.5}$, respectively. Consequently, swollen silicone/$BaTiO_3$ gels behave as a high-viscosity liquid in low frequencies. At 0.1 Hz the loss modulus G'' of the swollen silicone/$BaTiO_3$ gels was nearly comparable to G', however in a high frequencies, G'' was 1 order of magnitude lower than G', indicating the gels are more elastic than viscous.

Fig. 2 shows the frequency dependence of the storage modulus of unswollen silicone/$BaTiO_3$ gels without and with electric fields. The data under the electric field strength with 1.5 kV/mm have been eliminated because there was no

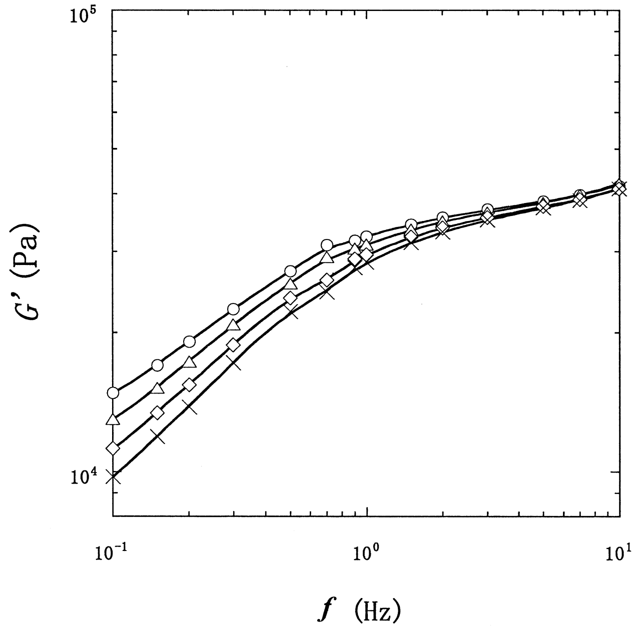

Fig. 1. Frequency dependence of storage modulus of swollen silicone/$BaTiO_3$ gels as a function of electric fields; (○): 0 kV/mm, (△): 1.0 kV/mm, (◇): 1.5 kV/mm, (×): 2.0 kV/mm.

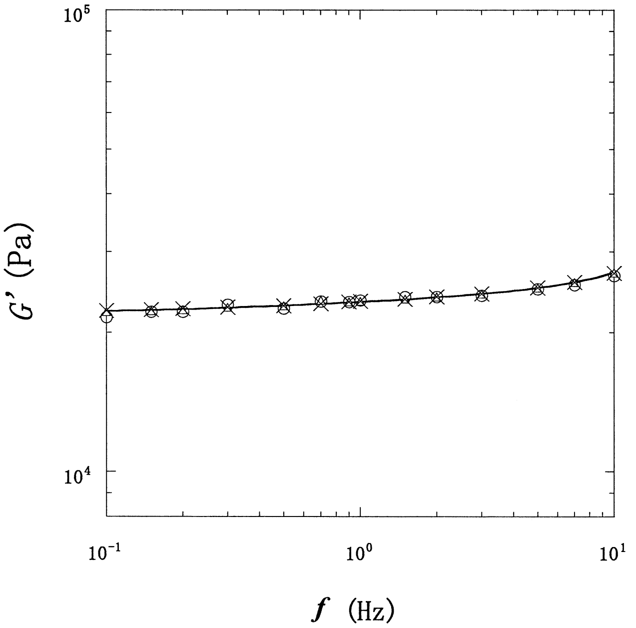

Fig. 2. Frequency dependence of storage modulus of unswollen silicone/$BaTiO_3$ gels as a function of electric fields; (○): 0 kV/mm, (△): 1.0 kV/mm, (×): 2.0 kV/mm.

electric field dependency on the storage modulus. Oppositely to the swollen gels, the storage modulus was almost insensitive to the frequency $G' \propto \omega^0$ that is a typical frequency dependence of the storage modulus of crosslinked polymers. The storage modulus was also independent of the electric field strength. This strongly suggested that the silicone oil in which the gel swelled played an important role of the negative electrorheological effect.

Fig. 3 shows the frequency dependence of the storage modulus for swollen silicone gels under various electric field strengths. Similar frequency dependence as swollen silicone/BaTiO$_3$ gels was found, however, the modulus of the swollen silicone gel increased under electric fields, i.e. the positive electrorheological effect. A clear change in modulus was found in a lower frequency region and the change was diminished with frequency, as well as the swollen silicone/BaTiO$_3$ gels. In low frequencies, fitting the experimental storage moduli without and with ($E = 2.0$ kV/mm) electric fields to a power law in ω give exponent values of 0.5 and 0.6, respectively. The exponent value increased with increasing the electric field strength as well as swollen silicone/BaTiO$_3$ gels.

Fig. 4 shows the frequency dependence of the storage modulus for unswollen silicone gels under various electric field strengths. Similar to Fig. 2, the data under the electric field strength with 1.5 kV/mm have been eliminated because there was no electric field dependency on the storage modulus. It was evident that the storage modulus was independent of the electric field strength. This strongly suggests that the negative electrorheological effect only seen in the swollen silicone/BaTiO$_3$ gels is not simply due to the electric response of the silicone oil.

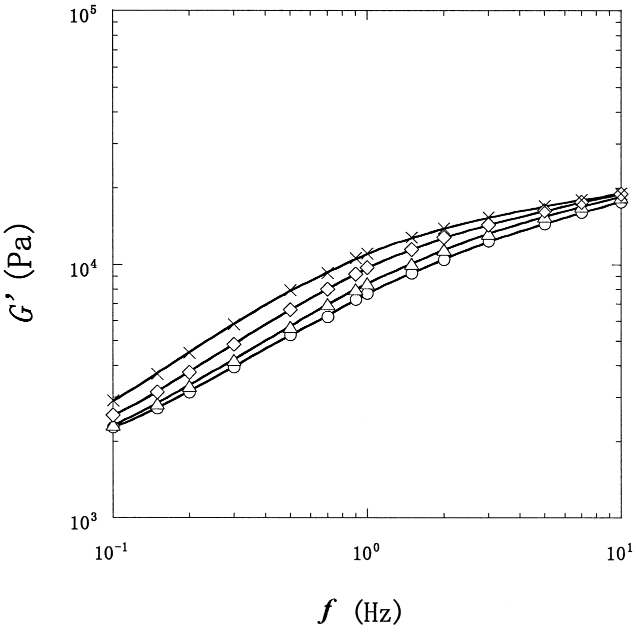

Fig. 3. Frequency dependence of storage modulus of swollen silicone gels as a function of electric fields; (○): 0 kV/mm, (△): 1.0 kV/mm, (◇): 1.5 kV/mm, (×): 2.0 kV/mm.

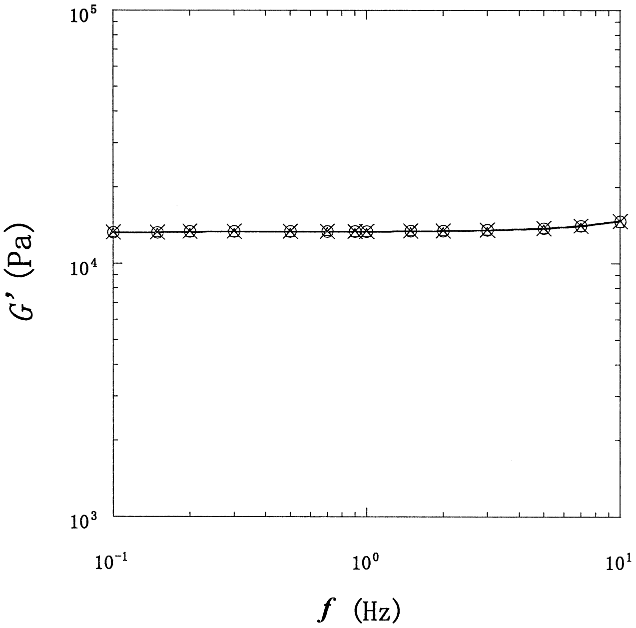

Fig. 4. Frequency dependence of storage modulus of unswollen silicone gels as a function of electric fields; (○): 0 kV/mm, (△): 1.0 kV/mm, (×): 2.0 kV/mm.

According to the literature [11], the negative electrorheological effect seen in suspensions was interpreted using a complex dielectric mismatch parameter β^*. We tried to understand the negative electrorheological properties in swollen silicone/BaTiO$_3$ gels in terms of β^*. The electric field-induced dipole p in a sphere can be written as follows,

$$p = 4\pi\varepsilon_0\varepsilon_f a E_0 \beta^* \tag{1}$$

Here, ε_0 and ε_f is the dielectric constant in vacuum and the relative dielectric constant of fluid, respectively. a stands for the radius of a dispersed sphere. E_0 represents the applied field, and β^* is the complex dielectric mismatch parameter given by

$$\beta^* = \frac{\varepsilon_p^* - \varepsilon_f^*}{\varepsilon_p^* + 2\varepsilon_f^*} \tag{2}$$

where the subscripts p and f refer to the particle and host liquid, respectively. For dc and low frequency ac fields, direct currents should be dominant in comparison with dielectric response. Hence, β^* can be rewritten as follows,

$$\beta^* = \frac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f} \tag{3}$$

When the relation in electric conductivity satisfies with $\sigma_f \gg \sigma_p$, the dielectric mismatch parameter equals to $\beta^* = -1/2$. For this negative value of β^* the dipole moment is opposite to the applied field and particles cannot form chains between electrodes. For example, teflon particles migrated to the positive electrode resulting in a structure which consisted of two layers: a relatively pure liquid and a more concentrated suspension [11]. In the suspension, this leads to the decrease in shear stress with electric field; i.e.

this is the origin of the negative electrorheological effect. The electric conductivity of the $BaTiO_3$ particles and the silicone oil used in the present study were 10^{-10} S/cm and 1.6×10^{-9} S/cm, respectively. Although such apparent phase separation was not observed in swollen silicone/$BaTiO_3$ gels, more microscopic phase separation may occur in spite of each $BaTiO_3$ particles are completely embedded in the gel matrix; as a result, the negative electrorheological effect may be observed.

Fig. 5 shows the electric field dependence of the change in storage modulus at $f = 0.1$ Hz of a swollen silicone gel and swollen silicone/$BaTiO_3$ gels. The change in storage modulus was defined by

$$\frac{\Delta G'}{G'_0} = \frac{G' - G'_0}{G_0} \tag{4}$$

where G' and G'_0 stand for the storage modulus with and without electric fields, respectively. It was clear that the change in modulus of swollen silicone/$BaTiO_3$ gels decreased with increasing the electric fields. Maximum change in modulus with -40.8% was observed in the swollen CAT 0.2 gel. On the contrary, the storage modulus of silicone gel without $BaTiO_3$ particles increased as the electric field was raised. The change in modulus of electrorheological elastomers can be fitted by the empirical equation

$$G' = G'_0\left[1 + \left(\frac{E}{E_0}\right)^2\right] \tag{5}$$

Here, E is the electric field strength and E_0 is the electric field strength at which the field induced effect equals the elastic. To evaluate E_0 both the cases of positive and negative electrorheological effect, the equation should be slightly modified as

$$\left|\frac{(G' - G')}{G'_0}\right| = (E/E_0)^2 \tag{6}$$

Solid lines in Fig. 5 represent the least mean squares fitting of the experimental data and the estimated E_0 for these gels were presented in Table 1. The experimental data of silicone gel and silicone/$BaTiO_3$ gels except for BTO 0.1 were considerably well fitted by Eq. (6). The obtained E_0 was one order of magnitude lower than that reported by the literature [8], indicating the gels used in the present study were easy to change its elasticity in spite of $BaTiO_3$ particles in the gel has a random distribution.

Fig. 6 shows $BaTiO_3$ concentration dependence of the change in storage modulus at $f = 0.1$ Hz for swollen silicone gel and silicone/$BaTiO_3$ gels. The change in the modulus of BTO 0.1 did not follow the quadratic dependence in electric fields, and it had a tendency to take a maximum around 1 kV/mm. It can be understood that the change in the modulus was divided for two contributions: one is the positive response, the storage modulus increases with electric fields as well as silicone gels; another is the negative response, the modulus decreases with the field similar to silicone/$BaTiO_3$ gels with high concentration of $BaTiO_3$ particles. For BTO 0.2 gel, the change in modulus monotonously decreased with electric fields, therefore the positive response was disappeared.

$BaTiO_3$ concentration dependence of the change in storage modulus is presented in Fig. 7. It was clear that the change in the modulus also strongly depended on $BaTiO_3$ concentrations. In a lower concentration $0 < c_{BTO} < 0.1$,

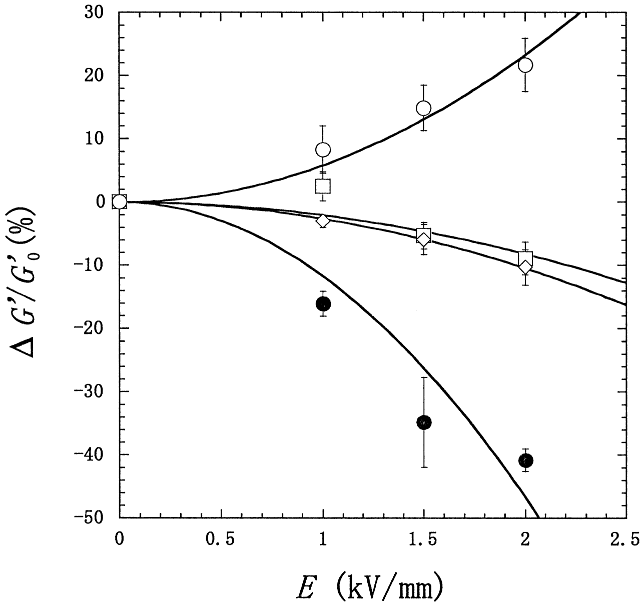

Fig. 5. Electric field dependence of the change in storage modulus at $f = 0.1$ Hz for swollen silicone/$BaTiO_3$ gels with various CAT content; (□): CAT 0.1, (●): CAT 0.2, (◇): CAT 0.3, (○): SG.

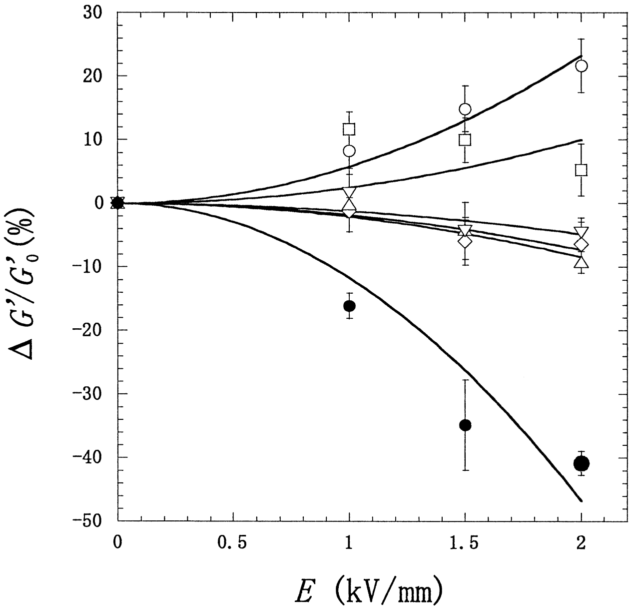

Fig. 6. Electric field dependence of the change in storage modulus at $f = 0.1$ Hz for swollen silicone/$BaTiO_3$ gels (CAT = 0.2) with various $BaTiO_3$ concentrations; (□): BTO 0.1, (◇): BTO 0.2, (△): BTO 0.3, (▽): BTO 0.4, (●): BTO 0.5, (○): SG.

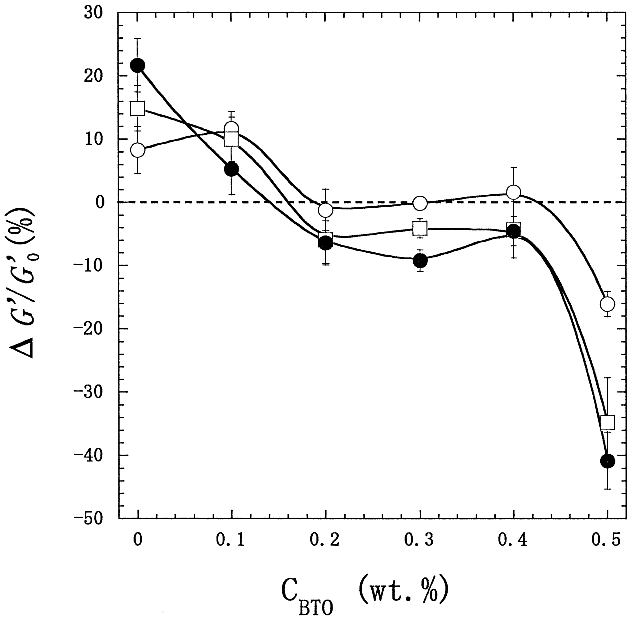

Fig. 7. Change in storage modulus at $f = 0.1$ Hz for swollen silicone/BaTiO$_3$ gels (CAT = 0.2) as a function of BaTiO$_3$ concentration; (○): 1.0 kV/mm, (□): 1.5 kV/mm, (●): 2.0 kV/mm.

the change in modulus tended to have a positive value for all fields. There was less change or slightly negative change in modulus in a middle concentration $0.2 < c_{BTO} < 0.4$. The change in modulus took a negative value in a higher concentration $c_{BTO} = 0.5$.

Fig. 8 shows the initial storage modulus at $f = 0.1$ Hz of swollen silicone and swollen silicone/BaTiO$_3$ gels as a function of BaTiO$_3$ concentrations. The lowest initial storage modulus was observed in the silicone gel without BaTiO$_3$ particles. The initial storage modulus increased with BaTiO$_3$ concentrations and took a constant around $c_{BTO} = 0.3$ and decreased again at $c_{BTO} = 0.5$. There have been reported that the change in dynamic moduli of electrorheological elastomers related with initial moduli. However, no significant relation between the initial storage modulus and the change in modulus by electric fields was observed.

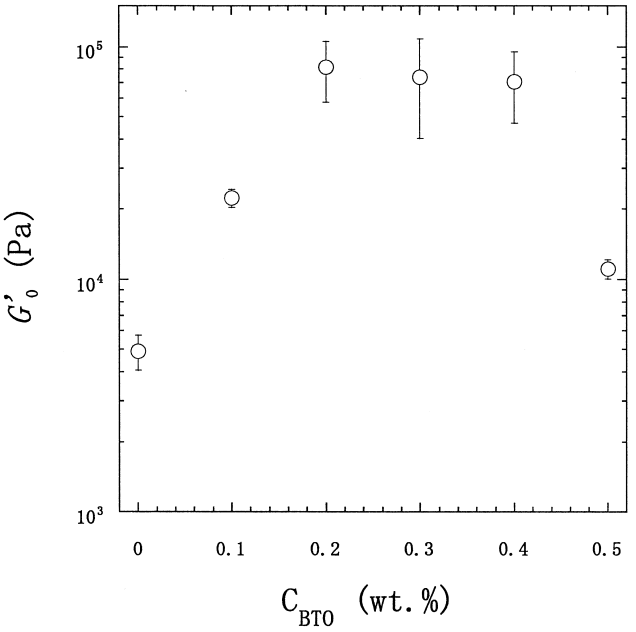

Fig. 8. BaTiO$_3$ dependence of initial storage modulus of swollen silicone/BaTiO$_3$ gels with CAT = 0.2.

4. Conclusion

We have investigated storage moduli of silicone gels containing barium titanate in the presence of dc electric fields. It was found that the silicone/BaTiO$_3$ gels swollen by silicone oil exhibited the negative electrorheological effect under electric fields. Compared to the swollen gels, no electrorheological effects were observed in unswollen silicone/BaTiO$_3$ gels, suggesting the electric coupling of particles and oil played an important role. Change in storage modulus of the swollen gels was strongly affected by both cross-linking density and BaTiO$_3$ concentration. Swollen silicone gels showed a large positive change in modulus, oppositely, the unswollen silicone gels did not show any change in modulus under electric fields. Swollen silicone gels and silicone/BaTiO$_3$ gels without $c_{BTO} = 0.1$ obeyed empirical quadratic dependence in electric field strength. The electric conductivity of the BaTiO$_3$ particles and the silicone oil used in the present study were 10^{-10} S/cm and 1.6×10^{-9} S/cm, respectively. Although an apparent phase separation was not observed in the swollen silicone/BaTiO$_3$ gel, microscopic phase separation may occur in spite of each BaTiO$_3$ particles are completely embedded in the gel matrix; as a result the negative electrorheological effect was realized. Besides this, non-linear response may affect the negative electrorheological behaviors since viscoelastic measurements were carried out in non-linear viscoelastic regime ($\gamma \sim 0.05$). The present results would be not only the elucidation for the origin of the negative electrorheological effect in crosslinked polymers but also contribute to the application as variable modulus materials driven by electric fields.

Acknowledgements

The authors would like to thank Mr R. Uchino for technical assistance of electrorheological measurements. This research is supported by a Grant-in-Aid for Scientific Research Encouragement of Young Scientists (B) from Japan Society for the Promotion of Science (Proposal No. 15750176).

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