

Electrorheological Behaviors of Barium Titanate/Gelatin Composite Hydrogel Elastomers

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ABSTRACT: Electrorheological (ER) elastomers, based on a gelatin hydrogel as matrix in which barium titanate ER particles are dispersed, were investigated. The behavior of particles was observed by a microscopic method. The ER effects of the elastomers are described with the compression modulus as a function of both particle concentration and intensity of the externally applied electric field. The result demonstrates that the particles were aligned in the matrix under an externally applied dc electric field. Furthermore, it was found that alignment of the particles increases the elastomer's modulus. In addition, both the chain effect and filler effect of the particles can dominate the modulus. The peak of

modulus appears when using the elastomer with a particle weight fraction of 1.5% because of the complex dominations of the two effects. In like manner, the largest incremental modulus appears. Based on the results, we found that the modulus of the elastomer cured under an electric field is greater than that without an electric field, and increases with the increasing field. Thus ER behavior of the elastomer can be controlled by the electric field intensity. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2517–2521, 2004

Key words: hydrogels; elastomers; aligned particles; modulus; electrorheological behavior

INTRODUCTION

Electrorheological (ER) materials act as intelligent soft substances. Their rheological properties change substantially with the application of external electrical fields. These materials have many possible applications, such as actuators, dampers, clutches, hydraulic valves, high power vibrators, chucks, torque transducers, and artificial muscle.^{1–6} ER materials thus constitute one of the important research subjects in soft-matter science.^{7–9} One of these materials, ER fluids, is a complex system that is normally composed of polarizable particles, possessing high dielectric constant and low conductivity, and a low dielectric constant insulating oil in which the particles are dispersed. They also display excellent performance in applications that include reversible, fast responses to an application of an electrical field and changes in apparent viscoelasticity, as well as yield stress, controlled by an applied electric field.^{10,11} Despite their large and rapid ER effects, ER fluids have several impediments in practical application, one of which is the sedimenta-

tion and aggregation of suspended particles, when left undisturbed for long periods of time, leading to a sluggish initial response and the possible formation of a solid cakelike layer of aggregated particles at the bottom of the vessel. This obstacle of ER fluids has hindered their ability to keep up with the demands of industrialization and widespread application and also hinders the development of ER fluids.^{1,12} Possible solutions to this problem, in previous works, include doping TiO₂ and montmorillonite clay,¹³ coating polyaniline onto barium titanate,¹⁴ organic/inorganic hybrid,¹⁵ and self-assembly.¹⁶ However, all these methods have thus far not been able to solve the problem perfectly.

ER elastomers, which represent another kind of ER material, have recently attracted considerable attention in the research communities.^{6,17–20} This material consists of polarizable particles and chemically crosslinked polymers. The particles in the elastomer are locked into the matrix network, which can eliminate the particle's coagulation. At the same time the viscoelastic properties of the matrix are changed by the interaction between polarized particles induced by the electric field, so the ER effect of elastomers has been demonstrated. For appropriate applications, the advantages of ER elastomers over fluids include no leakage, no attrition, and sedimentation of particles. In addition, there is a possibility of producing custom-made ER objects of exactly the right shape and size for each application. ER elastomers will have further widespread applications in potential technologies.^{17–20}

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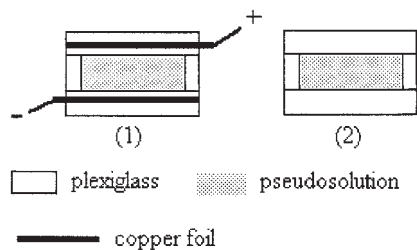


Figure 1 Side view of container for curing the two elastomers (1) cured under the applied dc electric field, (2) cured without applying the field.

The matrices of previously studied ER elastomers are mostly nonaqueous organic polymers, similar to ER fluids, such as silicone gel.^{6,17,18} Their synthesis is highly complex, they are expensive, and they are environmentally unfriendly. These problems limit the practical development of ER elastomers. Herein, we select gelatin/water composite systems as matrices of the ER elastomers. Because gelatin is a crude water-soluble organic macromolecule, it is easily synthesized, inexpensive, and friendly to the environment. This article reports on the preparation of the aqueous ER elastomer, which is a gelatin with dispersed barium titanate, and the investigation of its response to an applied dc electric field.

EXPERIMENTAL

Materials

Gelatin (B.R.; $\bar{M}_w = 77.970$; $\bar{M}_w/\bar{M}_n = 1.16$) was obtained from the Third Chemical Factory of Tianjin, China. Barium titanate (BaTiO_3) particles were synthesized in our laboratory according to the literature,¹⁴ and observation of XRD patterns confirmed that the size of BaTiO_3 particles was about 6–14 μm . Formaldehyde solution (A.R. 40%), as crosslinking reagent, was diluted to 2%. Deionized water was used in all investigative procedures.

Preparation of the BaTiO_3 /gelatin–water composite hydrogel elastomer

The 15% water solution of gelatin was first prepared with gelatin and deionized water at 60–70°C. Specific amounts of BaTiO_3 particles were dispersed in various gelatin/water solutions ($\text{BaTiO}_3 = 0, 0.5, 1.0, 1.3, 1.5, 1.7, 2.0, 2.5, 3.5, 4.5, 5, 7.5, \text{ and } 10 \text{ wt } \%$), with agitation for about 30 min. Each mixture was transferred into two custom-made casting cells and cured with and without a parallel dc field (1 kV/mm), respectively (see Fig. 1). After 0.5 h, the composite physical gels were obtained and then infused into the chemical crosslinking agent (formaldehyde solution, 2%) for 0.5 h to obtain a chemically crosslinked elastic gel. The

temperature was maintained at 25–30°C during the curing process. ER elastomers, with aligned or randomly distributed particles, were prepared. In addition, various ER elastomers were prepared using a similar method under the applied fields of 0–2.7 kV/mm.

Microstructure observation

Direct observation of particle distribution was achieved using a microscopic technique. To ascertain that alignment of particles was obtained after sample preparation, a Nikang optical microscope (Japan), with a custom-built ER stage, was used to observe the dispersion of particles in the ER elastomer after microtoming the specimen to a thickness of less than 0.5 mm at ambient temperature.

Compression modulus measurement

The elastic modulus of elastomers is one of the main mechanical properties. It is measured, for example, with shear stress and compression stress. Here, we describe it with compression modulus. According to elastic theory, the compression modulus (Y_c) can be explained by the following formulas:

$$Y_c = \frac{F/A}{\Delta L/L_0} \quad (1)$$

$$A = A_0 \left(\frac{L_0}{L_0 - \Delta L} \right) \quad (2)$$

where F is the uniaxial force applied to a sample over its corresponding area A , A_0 is sample's original area, L_0 is the original width of the sample, and ΔL is the change in width of the sample after the force has been applied.¹⁹

The continuous static-state loading measurement was carried out using custom-made apparatus, described in Figure 2. The force was loaded onto the transmitter (millimeter) instrument, and then im-

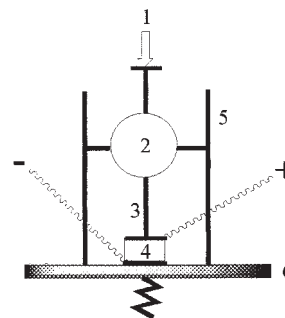


Figure 2 Scheme for the apparatus of measuring elastomer compression modulus.

pressed to the sample. A dc electric field was applied, with magnitudes ranging from 0 to 2.7 kV/mm, to the sample across the 3-mm gap. The sample ($20 \times 20 \times 3 \text{ mm}^3$) was compressed slightly to ensure adequate contact with the copper electrodes ($20 \times 20 \text{ mm}^2$) wrapped by insulating material. The direction of the applied force was identical to that of the applied field for curing and measurement. When the sample was compressed, the ΔL was obtained by use of the millimeter instrument. With continuously increasing force, a series of ΔL values were obtained, after which a stress-strain curve was obtained. Based on the results, the stress and strain in the elastic region were chosen and fitted linearly, following the formula $F/A = Y_c(\Delta L/L_0)$. The compression modulus (Y_c) of the elastomer was thus obtained. Measurements were taken while the temperature was maintained at 25–30°C.

RESULTS AND DISCUSSION

Distribution of particles in the BaTiO₃/gelatin–water composite elastomer

We used a gelatin/water solution (15% gelatin) as the continuous phase and BaTiO₃ particles as the dispersed phase (BaTiO₃ = 1.5 wt %), to prepare the composite elastomers in the presence or absence of an applied dc field and then observed the distribution of the particles using microscopic techniques. Figure 3 shows the chemical composition distribution (CCD) micrographs.

Figure 3(a) shows the micrograph of particles in the elastomer cured without the externally applied electric field, and Figure 3(b) shows the elastomer cured under the field with $E = 1 \text{ kV/mm}$. It is observed that particles are randomly dispersed and aligned dispersed in Figure 3(a) and (b), respectively.

The reason may be that under an applied dc field, the particles are polarized and then the induced dipoles appear, between which the interaction induces obvious chain formation. According to dielectric polarization theory,^{18,19} BaTiO₃ particles are polarized by an applied field and there are positive/negative charges on the opposite tips of the particles, referred to as the induced dipole. An attractive interaction between dipoles in the field direction caused adjacent particles to draw near each other, and a repulsive interaction between identical charges, perpendicular to the field direction, caused the equatorial particles to repel each other. Two electrostatic forces together reduced the particles' aggregation in the field direction, which are like chains (so-called pearl chains). By comparing and analyzing the two elastomers, it is obvious that the particles have been aligned by the applied dc field during the curing process, whereas the particles disperse randomly without an applied field. Here we

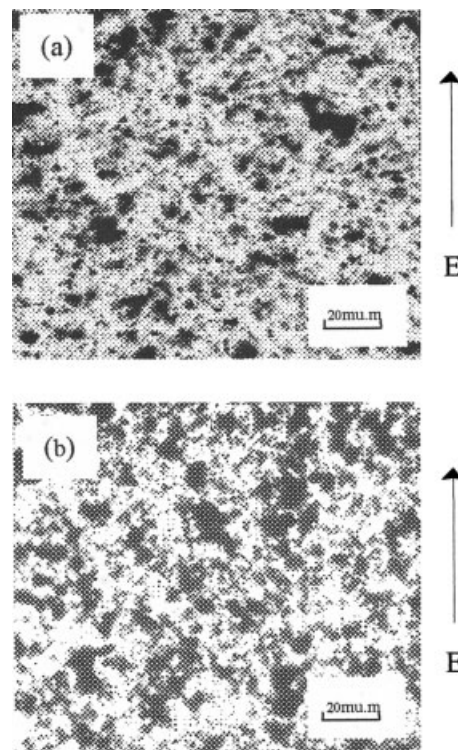


Figure 3 CCD micrographs of the elastomers cured in the absence/presence of the applied electric field.

call the aligned-particle elastomer A-elastomer for short; correspondingly, the random-particle elastomer is called R-elastomer.

Compression modulus of the elastomer as a function of the weight fraction of particle

The compression moduli of the two elastomers, mentioned earlier, were measured in both the absence and the presence of an applied dc electric field. The results, as a function of wt % BaTiO₃, are shown in Figure 4: the compression modulus of the A-elastomer is larger than that of the R-elastomer, measured whether in the absence or in the presence of the applied field. The reason is probably that the pearl chain of adjacent aligned particles, in the field direction, can resist compression better than randomly aligned particles.^{19,21}

In addition, Figure 4 shows that the compression moduli of A-elastomers generate a peak within the particle's weight fraction of 0–2.5%, that is BaTiO₃ = 1.5 wt %; it increases with the weight fraction when BaTiO₃ > 2.5 wt %. For R-elastomers, however, the moduli without application of the field increase concomitantly with the weight fraction of particles, whereas the corresponding moduli with application of the field generate a peak at BaTiO₃ = 1.5 wt %, similar to that of A-elastomers.

This can be expected that in the A-elastomer, the particles are polarized and form a pearl chain, and at

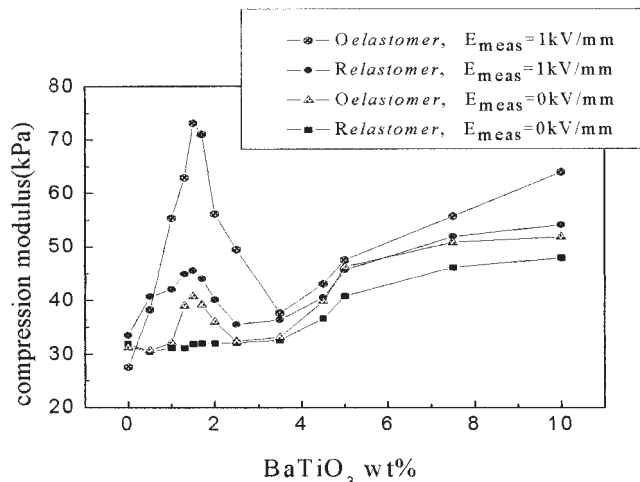


Figure 4 Compression moduli of the two elastomers measured in the absence/presence of the applied electric field ($E = 1 \text{ kV/mm}$) as a function of the weight fraction of particle.

the same time act as fillers, and so the stiffness of the elastomer is dominated by both pearl chain and fillers. When $\text{BaTiO}_3 < 1.5 \text{ wt } \%$, the particles disperse uniformly and can easily form a chain under a field, and the chain acts as a major resistance to the load-force. With increasing weight fraction of BaTiO_3 , the pearl-chain effect grows strong, whereas the filler effect increases only gradually. The two effects promote the obvious increment in the modulus. When $\text{BaTiO}_3 > 1.5 \text{ wt } \%$, the higher concentration of particles enhances the filler effect, but decreases the chain effect, because of increasing particle aggregation. The increasing filler effect and decreasing chain effect cause the compression modulus to decrease anteriorly and increase posteriorly with increasing wt % BaTiO_3 .^{22,23} Concomitantly, the random particles in the elastomer act only as fillers and the filler effect becomes stronger with increasing concentration of particles, so the modulus increase depends on the weight fraction of BaTiO_3 . When the electric field is applied to the system for measurement, particles are polarized and form a pearl chain; the moduli display a change similar to that of the aligned-particle system, as shown in Figure 4, which is also considered to be attributed to the cooperation of both chain effect and filler effect.

Response of the elastomer to the applied electric field

Also in Figure 4, for the A-elastomer, the compression modulus measured under the field is larger than that measured without the field. As in the $\text{BaTiO}_3 = 1.5 \text{ wt } \%$ system, the modulus measured without the applied field is $Y_c = 40.77 \text{ kPa}$, whereas that measured under the 1 kV/mm field is $Y'_c = 73.11 \text{ kPa}$; the increment between them is $\Delta Y_{cA} = Y'_c - Y_c = 32.34 \text{ kPa}$, $\Delta Y_{cA}/$

$Y_c = 79.32\%$. Accordingly, the modulus of the R-elastomer measured under the field is also larger: the increment of Y_c is $\Delta Y_{cR} = Y'_c - Y_c = 45.58 \text{ kPa} - 31.90 \text{ kPa} = 13.68 \text{ kPa}$, $\Delta Y_{cR}/Y_c = 42.57\%$.

This indicates that the compression modulus increment of A-elastomer is larger than that of R-elastomer. The result shows that (1) the field applied for measurement increases the moduli of the two elastomers, that is, both elastomers have positive responses to the applied field; and (2) the response of the A-elastomer to the applied field on modulus is larger than that of the R-elastomer. The reason for this phenomenon is that in the A-elastomer, the stronger attractive interaction between aligned particles induces them to connect much more closely, so the resistance to compression is stronger; as a result the higher incremental modulus appears.^{18,23}

To investigate the influence of the field intensity, applied for curing, on an elastomer's modulus, a series of elastomers ($\text{BaTiO}_3 = 1.5 \text{ wt } \%$) were prepared under different fields ($0, 0.5, 1.0, 1.5, 2.0$, and 2.7 kV/mm). Their moduli were tested without the field. Figure 5 shows that the modulus increases with the field applied for curing. This result is interpreted such that the stronger field causes higher particle polarity and thus attractive interactions of induced dipoles are greater, causing particles to form a more perfect pearl chain. Consequently, when the particles are closely arranged in the direction of the applied field, the elastomer modulus in this direction becomes larger.²⁴

In addition, for investigating the influence of the field intensity, applied for curing, on an elastomer's modulus, we tested the moduli of the A-elastomer ($\text{BaTiO}_3 = 1.5 \text{ wt } \%$), which cured in a 1.0 kV/mm field, under a series of fields ($0, 1.0, 2.0$, and 2.7 kV/mm). The result is shown in Figure 6.

The A-elastomer modulus was enhanced with increasing field applied for measurement. The reason may be that the aligned particles are polarized ulteriorly by the field for measurement, so the attractive

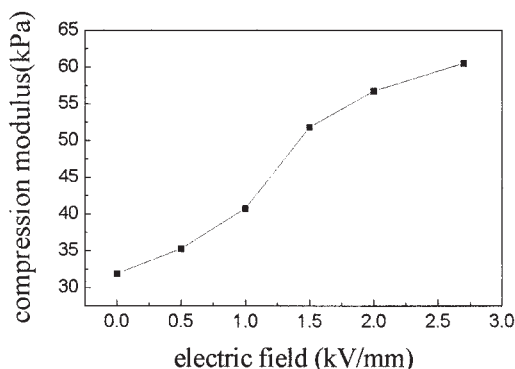


Figure 5 Compression moduli of the elastomers ($\text{BaTiO}_3 = 1.5 \text{ wt } \%$) as a function of the electric field intensity applied for cure.

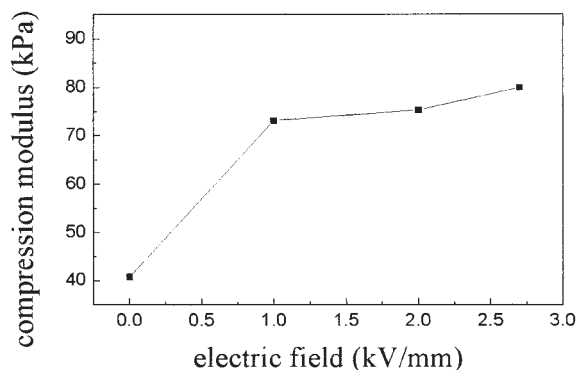


Figure 6 Influence of the electric field intensity applied to measure the compression moduli of the A-elastomer (BaTiO₃ = 1.5 wt %) cured in the field ($E = 1$ kV/mm).

interactions between the particles increase. Furthermore, the higher the field becomes, the greater the strength of the interactions, so that the particles arrange themselves much more closely in order. Consequently, the modulus becomes larger.²⁵

CONCLUSION

Electrorheological behaviors of the hydrogel composite ER elastomers, composed of gelatin polymer (continuous phase) and barium titanate (dispersed phase) were investigated. For the elastomer cured under an applied dc field, barium titanate particles are polarized and aligned, and their chain effect induced the large compression modulus of the elastomer and strong response to the field. Further, the particles' chain effect and filler effect together result in the modulus peak and the strongest response to the field at BaTiO₃ = 1.5 wt %. In addition, the modulus of this elastomer increases with the strength of the applied field for curing and measurement. The result shows that the ER behavior of the elastomer can be controlled by the electric field strength. ER hydrogel elastomers will have many potential applications in potential technologies as the investigative scope, concerning their production and use, widens.

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