

Mechanical and Electrical Properties of Hydrous Electrorheological Elastomers Based on Gelatin/Glycerin/Water Hybrid

Lingxiang Gao, Xiaopeng Zhao

Department of Applied Physics, Institute of Electrorheological Technology 141#, Northwestern Polytechnical University, Xi'an 710072, People's Republic of China

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ABSTRACT: Aimed at improving the stability of geometrical shape, mechanical performance, and particles dispersion of electrorheological (ER) hydrous elastomers, a new gelatin water-based elastic gels containing starch particles were prepared under an applied dc electric field, and their ER effects were described with the compression modulus and the electric resistivity. The result demonstrates that the mechanical and electrical properties of the ER elastomers are dominated by an externally applied electric field as well as the weight fraction of particles. On comparing with the same chemical composition, elastomers cured without a field and with barium titanate/gel-

atin water-based elastomer, some conclusions are suggested: the object elastomer has stronger responses to a field than the same chemical composition elastomer, especially with higher weight fractions of particles. The object elastomer has steady geometrical shape and mechanical performance because of the addition of glycerin into the matrix, and has a better dispersion of particles. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1738–1743, 2007

Key words: electrorheological effect; water-based elastomer; compression modulus; electric resistivity

INTRODUCTION

Electrorheological (ER) materials possess electrically controllable properties in mechanics, electrics, and optics.^{1–4} Owing to the fact that electric field can be obtained and controlled expediently, ER materials have many applications in actuators, dampers, clutches, high power vibrators, torque transducers, and artificial muscle.^{5–8} ER elastomer is a composite elastic gel, which consists of polarizable particles dispersed in chemical crosslinked network of organic macromolecule.^{7–9} In the network, as matrix's solid-like nature, particles are restricted and the congregation of particles are eliminated. Consequently, the instability of the ER effect, which is caused by the particles' congregation in ER fluid, is improved.^{10,11} At the same time, the interaction among the polarized particles under the applied electric field induces the elasticity change of the composite elastic gel, and then the elasticity change induces a notable ER effect. In addition, the shape

and size of ER elastomer can be designed for the practical requirement. Now, the advantages of ER elastomers have attracted a lot of attention to use them to produce mechanical devices.

In previous reports, a series of anhydrous macromaterials such as polysilicanes have been used as elastomer matrices,¹² but they have drawbacks e.g., long synthesis time and high-cost. ER elastomers with hydrous matrices have rarely been noticed. In our previous studies, we synthesized barium titanate/gelatin hydrous ER elastomers with gelatin/water hybrid as a matrix.¹³ Compared to anhydrous elastomers, the ER elastomers have some advantages, for instance, they are simple and convenient to synthesize, they have marked ER effect, low-cost, and are friendly to environment. On the other hand, they have some shortages as well, such as the low stability of geometrical shape and mechanical performance because of the water in matrix volatilizing, and low stability of particles in the matrix owing to particle's heavy density. In this study, an appropriate glycerin was added into the gelatin/water admixture matrix to improve the stability, and non-water soluble starch particles, a crude organic macromolecule with light density, were used to replace barium titanate particles to improve particle's dispersion. The aim is to produce water-based, crude organic ER elastomers, a sort of potential bionic intelligent material, which will be innocuous, friendly, and cost less.

Correspondence to: X. Zhao (xpzhao@nwpu.edu.cn).

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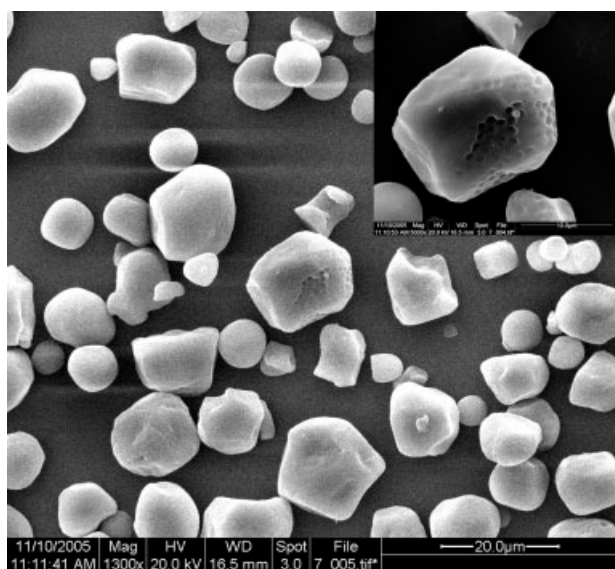


Figure 1 Scanning electron microscopy of starch particle.

EXPERIMENTAL

Materials

Gelatin (B.R. $\overline{M}_w = 77,970$, $\overline{M}_w/\overline{M}_n = 1.16$), was bought from the Third Chemical Factory of Tianjin, China. Glycerin (98%) and formaldehyde solution (A.R. 40%, diluted to 4% when used) were from the Chemical Factory of Xi'an, China. Nonwater soluble corn starch $\overline{M}_w = 1.28 \times 10^6$, $\overline{M}_w/\overline{M}_n = 15.14$) was from the Starch Factory of Xi'an, China. Its density is 1.5213 g/cm^3 and its particle size is about 6–12 μm , and mostly about 8–10 μm , which is confirmed by scanning electron microscopy (SEM) in Figure 1. Barium titanate was synthesized in our laboratory,¹³ and its density is 3.5984 g/cm^3 . Deionized water was used in all procedures.

Sample preparation

A 30% gelatin of aqueous solution was prepared at 60–70°C, and then added an appropriate glycerin. The specific amounts of starch particles, with weight fractions of 0, 5, 10, 15, 20, and 25%, respectively, were dispersed in gelatin/glycerin/water solution with grinding, in an agate mortar at 70°C. After 30 min, each mixture was transferred into the custom-made casting cell (Fig. 2) and cured with a parallel dc field (2 kV/mm) for an hour. For curing, the temperature was retained at 70°C for 30 min and then naturally cooled down to 25°C. The temperature at which the dc field was carried out was about 70–25°C. Under the temperature of 25°C, the composite physical gel was obtained after 8 h and then dipped into the chemical crosslinking agent (formaldehyde solution, 4%). After 16 h, a chemically crosslinked gel, A-elastomer, was obtained. The elastomer, B-elastomer, was prepared in

the absence of an applied electric field, which the chemical composition was the same as the object elastomer. The mechanisms of the gel chemical crosslinking accounting for the action of formaldehyde is described as follows



The barium titanate/gelatin water-based elastomer was prepared by the reported method.¹³

Mechanical and electrical property measurement

Compression modulus measurement

The elastic modulus of elastomer is a primary mechanical property. It can be performed with shear stress and compression stress. In this article, we describe it with compression modulus. According to the elasticity theories, the compression modulus (E) could be explained by the following formulas:

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

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

where F is the uniaxial force applied to a sample over its corresponding area A , A_0 is the sample's original area, L_0 is the original height of the sample, and ΔL is the change in width of the sample induced by the externally applied force.¹¹

The continuous static-state loading measurement was carried out with the custom-made apparatus, as shown in Figure 3. The dc electric fields (varying from 0 to 2.7 kV/mm), across a 3-mm gap with dc high-voltage generator (WYZ-010, China), were applied to the sample. The sample was compressed slightly to ensure it is in good contact with the copper electrode pieces, which were in the same area of the sample and

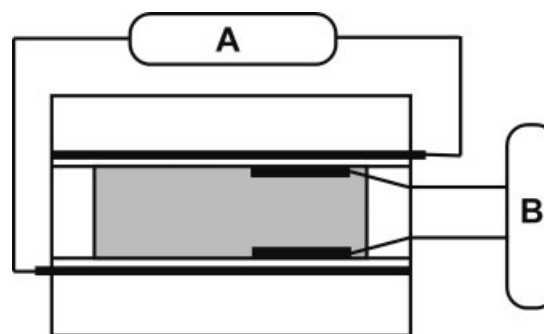


Figure 2 Schematic equipment for cure an elastomer and measure its electric resistivity. A: HV power source, B: multimeter.

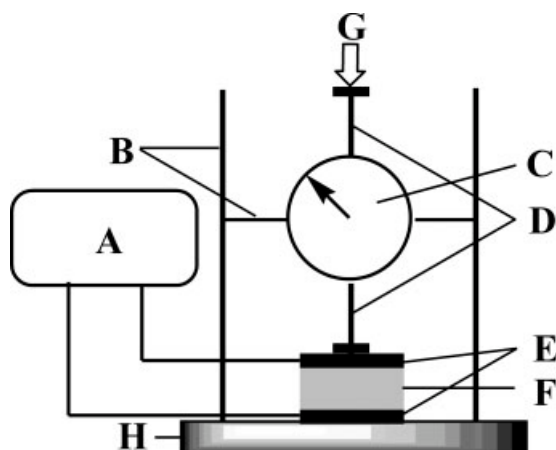


Figure 3 Sketch of measure instrument for compression modulus of the elastomer. A: HV power source; B: shore; C: mm meter (0.01 mm); D: force-transmitter; E: copper electrode; F: sample; G: loads; H: platform.

wrapped with the insulate film. The force was loaded onto the transmitter of a millimeter instrument (Harbin Axletree Factory, China) and then compressed to the sample of $20 \times 20 \times 3 \text{ mm}^3$ size, overlaid with a thin glass piece. The force was applied to the sample in the same direction of the field for curing and measurement. When the sample was compressed, the ΔL value was displayed in the millimeter instrument. With the force continuously increasing, a series of ΔL values were obtained. Based on the results, the stress-strain curve was drawn. From the drawing, the values of the stress and strain in elastic region were chosen and linear -fitted, following the formula $F/A = E(\Delta L/L_0)$. As a result, E of the elastomer sample was obtained. Measurements were performed at $25\text{--}30^\circ\text{C}$.

Electric resistivity measurement

Electric resistivities of composite systems were carried out by a multimeter in the direction of the applied field for curing, as depicted in Figure 2. The measurements were maintained for 90 min until the resistivities of the systems did not change any more.

RESULTS AND DISCUSSION

Mechanical properties of the starch/gelatin/glycerin elastomers

Response to an applied electric field on compression modulus of the elastomer

The starch/gelatin/glycerin elastomer, cured in the presence of electric field (2 kV/mm), was denoted A-elastomer, and the same chemical composition elastomer cured in the absence of electric field was denoted B-elastomer oppositely.

Compression modulus of the elastomers was measured in the absence and presence of field, referred as

E and E' , respectively. Figure 4 shows that compression modulus of both A and B-elastomers increases with the weight fraction of particles probably due to "particle's filler-effect".¹⁴ The effect increases with particle's concentration and induces the elastomers' stiffness to increase. In addition, a noticeable phenomenon is found from the figure: the modulus of A-elastomer in the absence of field (E_A) is larger than that of B-elastomer in the presence of field (E'_B). For a determinate chemical composition system, E_A is the result induced by the field for curing, and E'_B is induced by the field for measuring. According to the dielectric polarization theory,^{10,11} the particles dispersed in the matrix are polarized as dipoles under an applied dc field and the attractive/repulsive interactions between dipoles make the particles aggregate as pearl chains.¹⁵ The particles in A-elastomer align easily because they have been polarized before the matrix is cured as colloid. Consequently, the A-elastomer possesses higher modulus, whereas the particles in the B-elastomer have been restricted in the cured matrix before they are polarized. Hence, they are difficult to move and form particle chains under the applied field for measuring.^{11,16,17} As a result, the B-elastomer possesses lower modulus. That is why E'_B is lower than E_A . This phenomenon indicates that the effect of the applied field for curing is stronger than that for measuring.

Also from Figure 4, it is found that particle concentrations at 0 and 5%, the modulus of A-elastomer in the presence of a field (E'_A) is smaller than that in the absence of the field (E_A). But E'_A is much larger than E_A when the particle concentration increases over 10%. The reason is probably because the macromolecules of the matrix are polymerized anisotropically under an applied dc electric field for curing, and the anisotropic structure of the matrix makes the stiffness of elastomer decrease under an applied field for measuring. When particles are dispersed orderly in the elastomer

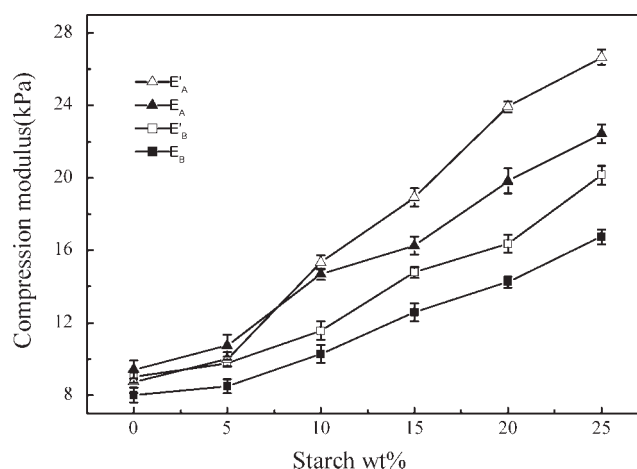


Figure 4 Compression modulus of A and B-elastomer as a function of the weight fraction of starch.

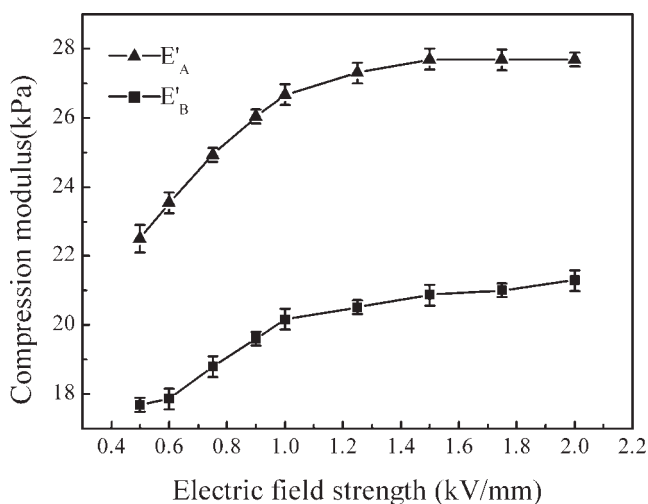


Figure 5 Compression modulus of *A* and *B*-elastomers as a function of dc electric field strength.

the elastomer's stiffness increases. However, the stiffness increases slightly when the particle concentration $\leq 5\%$. The small increment is not able to counteract the stiffness decrement from the anisotropic matrix, and then E'_A is still low.^{13,18} When the particle concentration increases up to 10%, the stiffness increment, which is induced by ordered particles, strongly counteracts the stiffness decrement, and eventually E'_A is much larger than E_A . The result suggests that the elastomer has great response to the field with the particle concentration.

Influence of the applied field strength for measuring the elastomer's modulus

As the best response of the elastomer appears at 25 wt % starch, as shown in Figure 4, the modulus of *A* and *B*-elastomers with 25 wt % starch were chosen and tested under the field ranging from 0.5 to 2.0 kV/mm. The results are shown in Figure 5: (1) E'_A and E'_B are enhanced by increasing field strength, indicating the positive ER effects of *A* and *B*-elastomers; (2) E'_A does not increase anymore with increasing the field strength when the strength larger than 1.5 kV/mm. Whereas, E'_B increases continuously with increasing the field strength till 2 kV/mm. The phenomena are probably interpreted as following: the previously polarized particles in *A*-elastomer are polarized ulteriorly by the measuring field, and the attractive interaction increases. With an increase of the field strength, the interaction becomes stronger and induces the particles to aggregate closer in lines. Consequently, the modulus of the elastomer becomes larger. When the measuring field reaches 1.5 kV/mm, the polarization of particles rise to the top, and the interaction of particles does not increase any more with the increase of the field strength,¹⁹ so E'_A approximately remains

steady. However, for *B*-elastomer, the polarization of particle can not reach the top under 1.5–2.0 kV/mm measuring field, and then E'_B increases continuously with the increase of field strength.

Actually in experiments, the field of the application apparatus could not be applied more than 2.0 kV/mm. We will discuss the modulus increment under the field of >2.0 kV/mm in the future.

Comparison in response to an electric field with the barium titanate/gelatin elastomer

Both barium titanate/gelatin and starch/glycerin/gelatin elastomers are gelatin–water based. The response to an applied electric field on compression modulus of the anterior elastomer was reported in Ref. 13.

It is noticed that there are a few similar phenomena for the two elastomers. One is that their compression moduli increase with increasing the applied field strength, and the other is that they both have modulus peaks with the weight fraction of particles.

Also, some differences between them are noticed. The matrix, which improved with an appropriate glycerin addition, makes the object elastomer's geometrical shape and mechanical performance steady. Figure 6 shows relative change in modulus $((E' - E)/E)$ of BaTiO₃ and starch of *A*-elastomer as a function of the weight fraction of particle. Under the measuring electric field, the BaTiO₃ elastomer's largest value of $(E' - E)/E$ was 79.36% at 1.5 wt % BaTiO₃. Oppositely, the starch elastomer's largest value of $(E' - E)/E$ was only 21.04% at about 20 wt % starch. The dominating factors of this result are probably the differences in density and relative permittivity of the two particles. Low density of particle is an advantage to reduce sedimentation and is a foundation of good ER effect. The density of the BaTiO₃ and starch particle is 3.5984 and 1.5213 g/cm³, respectively. Sedimentation of the BaTiO₃ particle, due to its heavier density, induces its

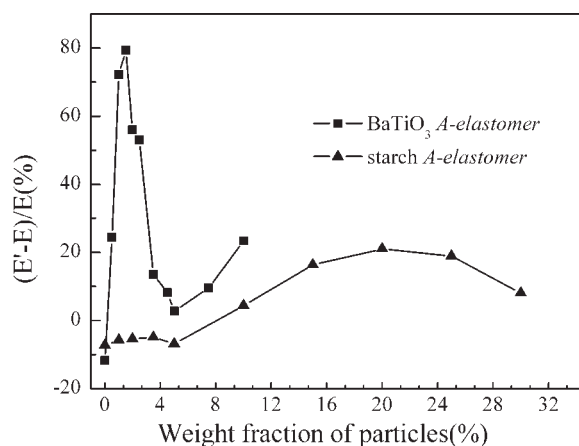


Figure 6 Relative change in modulus of BaTiO₃ and starch *A*-elastomer as a function of the weight fraction of particle.

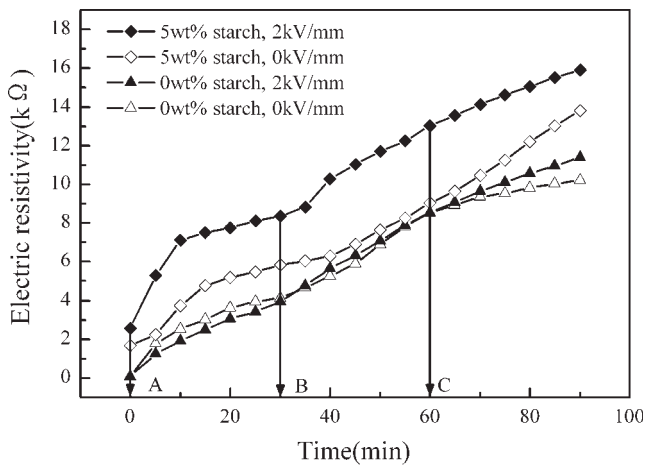


Figure 7 Electric resistivity of the systems cured in the absence/presence of dc electric field, with the weight fraction of starch particle of 0 and 5 wt %.

poor dispersion in the matrix at $\text{BaTiO}_3 > 1.5$ wt %. Contrarily, the lower density of starch particle makes particle disperse well in the matrix, and then the weight fraction of particle extends to 25 wt %. As a result, the starch elastomer's largest response to the applied field appears at 20–25 wt % starch, and the BaTiO_3 elastomer's largest response only appears at 1.5 wt % BaTiO_3 .

Furthermore, the relative permittivity of BaTiO_3 is about 2000.²⁰ Whereas, the relative permittivity of the starch is about 2–5.²¹ According to the dielectric polarization theory, the BaTiO_3 particles that possess higher relative permittivity are strongly polarized under an electric field. The strong interactions between the polarized particles induce strong ER response. On the other hand, starch particle possesses lower relative permittivity and is weakly polarized. The interactions between the polarized particles are weak, and there-

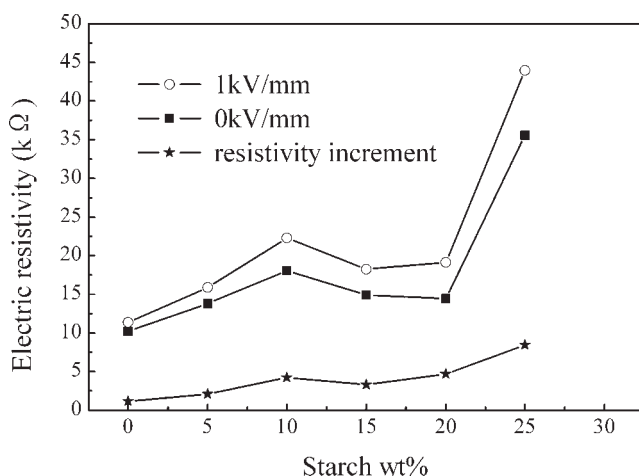


Figure 8 Resistivity and resistivity increment as a function of the weight fraction of starch.

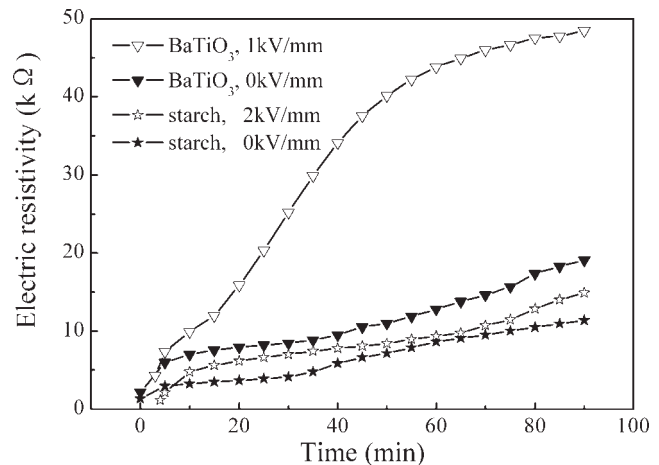


Figure 9 Electric resistivity of BaTiO_3 and starch elastomers in the absence/presence of dc electric field.

fore induce weak ER response. So it was possible that the large difference in the relative permittivity induces the obvious difference in the ER response, as described in the previous paragraph.

The electric resistivity of the water-based systems

Electric resistivity of the starch/gelatin/glycerin system

To compare the properties of *A* with *B-elastomer* ultimately, the electric resistivity of the two corresponding systems was tested in the course of cure. Figure 7 shows electric resistivity of the systems cured in the absence/presence of dc electric field, with the weight fraction of starch particle of 0 and 5 wt %. In the figure, the temperature of the systems remained at 60–70°C in section AB, and cooled down spontaneously from 70 to 25°C in section BC. The 2 kV/mm field was applied for 1 h in section AC (section AB + section BC).

In Figure 7, the two electric resistivity curves of the nonstarch system, cured in the absence and presence of the field (2 kV/mm) respectively, show similar behavior. This phenomenon indicates that the 2 kV/mm electric field for curing has little influence on nonstarch system.

Also in Figure 7, for 5 wt % starch system, there is a distinct increment of electric resistivity between the system cured with the 2 kV/mm field and without the field. This is the evidence that the 5 wt % starch system has an obvious response to the applied field. It is presumed that the curing field aligns particles in the matrix and induces an additional electric resistivity in the system.

In a series of systems with weight percent of 10, 15, 20, and 25, the electric resistivity increments are similar to that of the 5 wt % one. Evidently, the electric re-

sistivity with an applied field is larger than the one without a field. But the value of increment varies with the particle contents, as shown in Figure 8. The largest increment appears in the 25 wt % starch system. This result matches with the results shown in Figure 4—the maximum values of E_A and E_B appears at 25 wt % starch.

Comparison in the electric resistivity with barium titanate/gelatin elastomer

Figure 9 shows the electric resistivity curves of BaTiO₃ and starch elastomer (both weight fraction of particles are 1.5%) with and without an electric field. In the figure, the electric resistivity of BaTiO₃ elastomer is larger than that of starch elastomer, and its resistivity increment, influenced by the dc electric field, outclasses that of starch elastomer. This phenomenon indicates that the two elastomers have obvious difference in response to the field. Perhaps it is because the particles have the apparent difference in the relative permittivity and density, as mentioned earlier. This result matches the fact, which was described in section “Comparison with the barium titanate/gelatin elastomer,” and reveals the difference in response of the two elastomers to an applied field.

CONCLUSIONS

The starch/gelatin/glycerin composite hydrous ER elastomers were prepared under an applied dc electric field, and a series of tests on compression modulus and electric resistivity were carried out. It is found that the mechanical and electrical properties of the elastomers are controlled by an applied electric field and the weight fraction of particles. Compared to the

elastomer cured without a field, it is found that the response to an applied field for curing is stronger than that for measuring. And compared to the barium titanate/gelatin elastomer, the results indicate that the differences of ER response of gelatin water-based elastomers are mainly induced by the difference in particle's density and relative permittivity.

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