# A Novel Electric Elastomer Based on Starch/Transformer Oil Drop/Silicone Rubber Hybrid

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**ABSTRACT:** The electrorheological fluid composed of starch particles and silicone oil/transformer oil was dispersed into 107 silicone rubber, and then two types of electric elastomers were prepared in the absence and presence of a curing electric field, respectively. The storage modules were measured using dynamic mechanical analysis with the round disk compression clamp. The results indicate that the storage modulus sensitivity of electric elastomers composed of pure transformer oil is the highest, that of electric elastomers composed of pure silicone oil takes second place, and that of electric elastomers composed of mixture oil is the smallest. For the given starch concentration, the storage modulus sensitivity attains a maximum value of 3.88 when the mass ratio between the transformer oil and 107 silicone rubber is 1. For the given mass ratio of 1, the effects of starch concentration and the presence or absence of the curing electric field on the storage modulus of electric elastomers were studied. When the starch concentration is 5 wt %, the storage modulus of the elastomer without the electric field (denoted as A-elastomer) is 20.1 kPa, whereas that of the elastomer with the electric field (denoted as B-elastomer) is 101.8 kPa. The storage modulus sensitivity attains a maximum value of 4.07. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2991–2995, 2011

**Key words:** electrorheological elastomer; silicone rubber; storage modulus; storage modulus sensitivity; liquid phase

## INTRODUCTION

As a type of intelligent soft matter, electrorheological (ER) materials have been extensively investigated.[1–4] ER materials include electrorheological fluid (ERF) and electrorheological elastomer (ERE). ERF may be applied in actuators, dampers, clutches, hydraulic valves, high power vibrators, chucks, and torque transducers because its rheological properties can be changed suddenly with the application of an electric field.[4–10] Although many materials with high ER activity have been prepared,[5–10] the problems such as sedimentation, aggregation, attrition, and leakage limit the potential applications.[7]

ERE is composed by dispersing particles with a high dielectric constant into a polymer matrix. When an electric field is applied, the particles are polarized and form chain or column structures in the direction of the electric field. Therefore, the elastic modulus can be controlled by applying an electric field, which induces a notable ER effect. In addition, ERE does not need to be sealed under service conditions, and the shape and size can be designed for the practical requirements. ERE is superior to ERF in the aspect of sedimentation and coagulation. Furthermore, ERE is more flexible, light, and easily prepared, all desirable properties in their applications.[11] The preparation and performance of ERE have recently attracted considerable attention in the research community.[12–21]

For ERE, one of key problems is that storage modulus sensitivity is low. Many types of ERE are investigated to improve the storage modulus sensitivity. Gao and Zhao[16] developed a type of barium titanate/gelatin hydrogel hybrid elastomer, and the elastic modulus sensitivity of the hydrogel elastomer with 1.5 wt % barium titanate is 79.36% at the measuring electric field of 2 kV/mm. For the starch/glycerin/gelatin hydrogel hybrid elastomer, it was found that the concentration of the dispersed particles can be improved to an optimum value of 20 wt %, but the elastic modulus sensitivity is only 21.04% at the measuring electric field of 2 kV/mm.[18] Sirivat and coworkers[19,20] prepared the poly (*p*-phenylene)/acrylic elastomer and polythiophene/polyisoprene elastomer and found that the storage modulus sensitivity attained the maximum values of 97% and 110% at the measuring electric field of

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2 kV/mm. In addition, the ER effect is closely related to the matrix's elasticity. The smaller a value of elastic modulus is, the stronger the ER effect is.[13,14,21] On the other hand, the viscosity of polymer matrix should be low in order that the particles move freely in the matrix during the curing process.

In our previous work,[21] the starch/silicone oil/silicone rubber hybrid electric elastomer was prepared, and the storage modulus sensitivity was improved to 2.44 by adding silicone oil. Here, to further decrease the matrix viscosity, the transformer oil, keeping a liquid phase in the whole curing process, was added into the electric elastomer, and the storage modulus sensitivity was enhanced to 4.07. Two types of starch/transformer oil/silicone rubber hybrid electric elastomers were prepared in the absence and presence of the curing electric field, respectively. The effects of various concentrations of the starch particles, the mass ratio of silicone oil to transformer oil, and the presence or absence of the curing electric field on the elastic modulus were investigated in detail.

## EXPERIMENTAL SECTION

### Materials

In our experiment, 107 silicone rubber ($\eta$ = 2000 mPa s at 25°C) was obtained from Shandong Duoweiqiao CO. LTD, China. The catalyst was dibutyltin dilaurate, the crosslinking agent was tetraethyl silicate, and their mixture was used as the curing agent with the mass ratio of 0.9. The silicone oil ($\eta$ = 50 mPa s at 25°C) was manufactured by Asahikasei CO. LTD, Japan. 25# transformer oil ($\eta$ = 20 mPa s at 25°C), commercial grade, was filtered and dryed. A nonsoluble sweet potato starch with the density of 1.47 g/cm$^3$ was obtained from the Chengdu Yangtian Food CO. LTD, China. Its particle size is about 10–20 μm, and it is approximately spherical, which was confirmed by scanning electron microscopy (SEM) in Figure 1. At the same time, as seen from Figure 2 of starch particle distribution, the average size of starch particles is 14.36 μm.

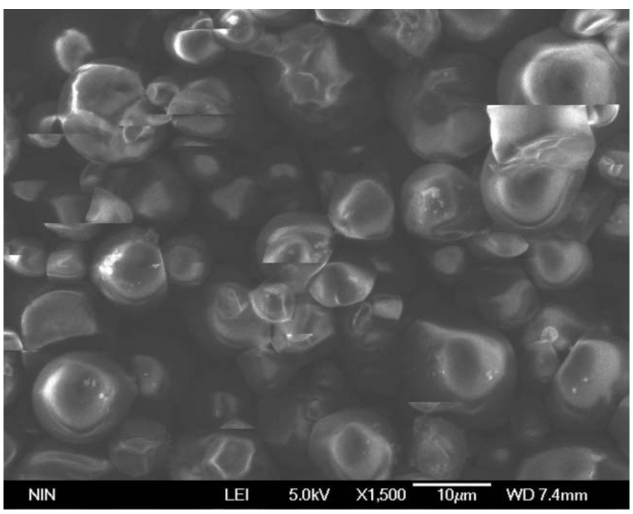


**Figure 1** SEM of starch particle.

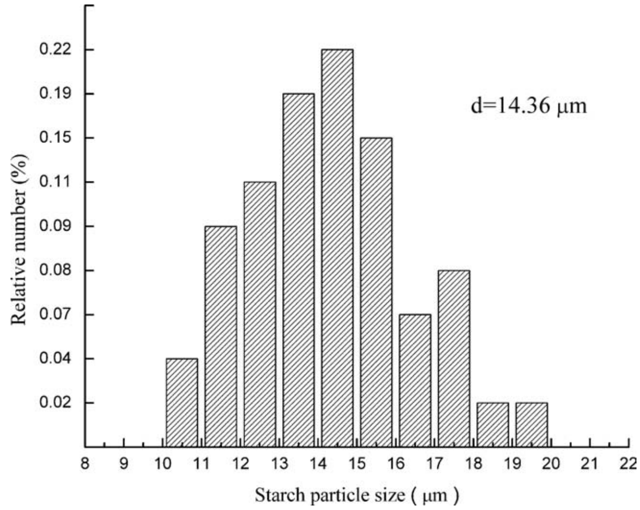


**Figure 2** Starch particle distribution.

### Preparation of starch/transformer oil/silicone rubber hybrid electric elastomer

First, the ERF was prepared by immersing the specific amounts of the starch particles into the transform oil and stirring for 30 min with a constant temperature magnetic stirrer. Second, silicone rubber prepolymer was dispersed in the obtained ERF under stirring until a uniform liquid-like mixture was obtained. Third, an curing agent was added, where the volume ratio between curing agent and silicone rubber was fixed as 1 : 20, and the mixture was stirred for 2 min to disperse the curing agent. Finally, the mixture was transferred to a glass-made casting box (40 mm long × 20 mm wide × 5 mm thick) and cured for 3 days at room temperature. As shown in Figure 3, bottom and top outer surface of the casting box were coated with ITO conductive layer, and a DC electric field of 0.6 kV/mm was applied to align an ordered chain or column structure in the matrix at the beginning 5 h of the curing process.[21] Consequently, a kind of starch/transformer oil/silicone rubber hybrid electric elastomer

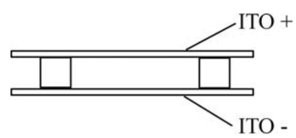


**Figure 3** Planform of container for curing the elastomer.

**TABLE I**
**The Compositions of All Samples**

| | Group 1 (1–5) | | | | | Group 2 (6–11) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Starch (wt %) | 10 | 10 | 10 | 10 | 10 | 0 | 5 | 15 | 20 | 25 | 30 |
| Silicone rubber (wt %) | 45 | 45 | 45 | 45 | 45 | 50 | 47.5 | 42.5 | 40 | 37.5 | 35 |
| Silicone oil (wt %) | 45 | 33.8 | 22.5 | 11.2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Transformer oil (wt %) | 0 | 11.2 | 22.5 | 33.8 | 45 | 50 | 47.5 | 42.5 | 40 | 37.5 | 35 |

was obtained (denoted as the B-elastomer). Using the same procedure, a hybrid electric elastomer, with the same chemical components as the B-elastomer, was also prepared without an applying electric field (denoted as the A-elastomer).

According to the chemical components, the hybrid electric elastomers were divided into two groups. For group 1, the starch concentration and the mass ratio of silicone rubber to the mixture of silicone oil and transformer oil were fixed, and the mass ratio between the silicone oil and transformer oil was varied. For group 2, the mass ratio of silicone rubber to transformer oil was fixed at 1, and the starch concentration was varied. The composition of each sample and its serial number is shown in Table I.

### Mechanical property measurement

The elastic modules were measured with dynamic mechanical analysis in the mode of multifrequency (Q800-DMA, TA instrument CO. LTD, USA). The samples with a diameter of 12 mm and a thickness of 5 mm were sandwiched in a round disk compression clamp. The strain sweep test was carried out to determine the suitable strain in the linear viscoelastic regime. The appropriate strain was determined to be 0.05%. Each measurement was carried out with a fixed strain of 0.05% at a temperature of 20°C and the frequency of 1 Hz and was repeated at least two or three times. The storage modulus of the A-elastomer samples was denoted by $G'_0$ and that of the B-elastomer samples by $G'$. The storage modulus sensitivity can thus be calculated as $\Delta G'/G'_0 = (G' - G'_0)/G'_0$.

## RESULTS AND DISCUSSION

### Effect of mass ratio between silicone oil and transformer oil

The blended transformer oil is used to further reduce the viscosity of the silicone rubber prepolymer under a zero electric field, which can enhance the electric field-induced storage modulus, or an ER effect. Group 1 is catalogued to study the optimal mass ratio of silicone oil to transformer oil.

Figure 4 shows the storage modulus versus the mass ratio of silicone oil to transformer oil. It can be seen that $G'$ for the B-elastomer is larger than $G'_0$ for the A-elastomer. The reason is that the polarized starch particles form chain or column structures, which strengthens the resistance of the elastomer to compression and enhances its storage modulus. It can also be found that $G'_0$ decreases with increasing concentrations of the transformer oil. This is mainly because the viscosity of the hybrid matrix is lowered, and the flexibility is improved as concentrations of the transformer oil increases, which reduces the storage modulus. In addition, as concentrations of the transformer oil is increased, $G'$ is decreased due to lowering the matrix's viscosity by adding the transformer oil keeping a liquid phase in the entire curing process. While, $G'$ enhances with further increasing concentrations of the transformer oil. An explanation for this enhancement is that the influence of a curing electric field on the storage modulus of the hybrid elastomer by adding the transformer oil was strengthened, and then this increase is larger than the decrease because of the lower matrix viscosity.

Figure 5 demonstrates the relationship between the storage modulus sensitivity and the mass ratio

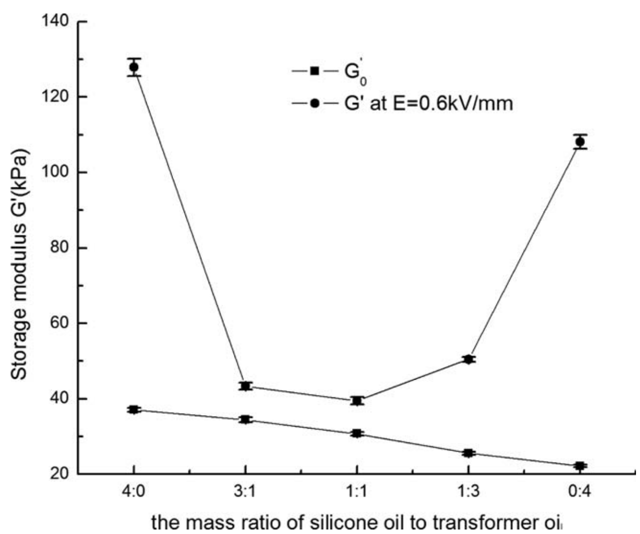


**Figure 4** Storage modulus as a function of the mass ratio of silicone oil to transformer oil.

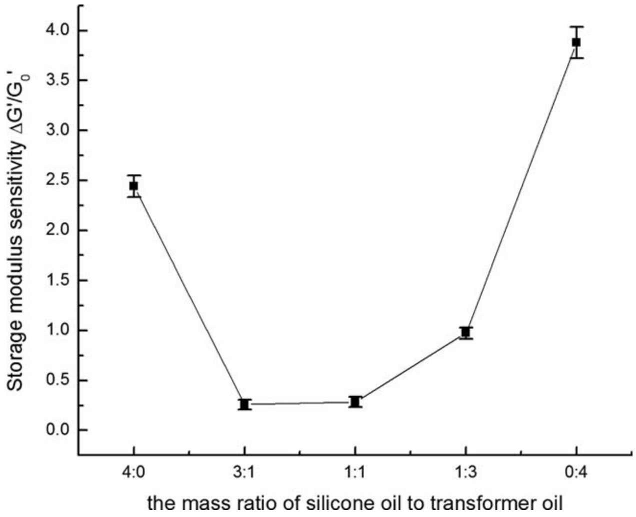


**Figure 5** Storage modulus sensitivity as a function of the mass ratio of silicone oil to transformer oil.

of silicone oil to transformer oil. The storage modulus sensitivity ($\Delta G'/G'_0$) of the hybrid elastomer including a pure oil is larger than that of a mixed oil. The reason is that the dispersion of starch particles in a pure oil system is superior to that of a mixed oil system, and then the effect of a curing electric field on a pure oil system is stronger than that of a mixed oil system.

It is worth noting that $\Delta G'/G'_0$ of hybrid elastomer with transformer oil is larger than that of silicone oil. It is thought that although either silicone oil or transformer oil belongs to a liquid, the silicone oil is gradually cured with the curing time, whereas the transformer oil is not cured and keeps a liquid phase in an entire curing process. Thus, during the curing process, the viscosity of hybrid elastomer with the transformer oil is lower than that of the silicone oil in the corresponding condition, and the effect of a curing electric field on the transformer oil system is stronger than that of the silicone oil system. Furthermore, its ER effect is better than that of the silicone oil system, which is in agreement with the conclusion of Refs. 13 and 14. Therefore, $\Delta G'/G'_0$ is enhanced by the addition of the transformer oil with a liquid phase, and $\Delta G'/G'_0$ attains a maximum value of 3.88 in a pure transformer oil system, that is, the mass ratio between the transformer oil and the silicone rubber is equal to 1. Therefore, in the following section, the mass ratio is fixed at 1.

## Effect of starch

Group 2 is catalogued to obtain the maximum storage modulus sensitivity.

Figure 6 shows the storage modulus as a function of the starch concentration. First, the values of $G'_0$ and $G'$ for the samples with starch particles are both higher than those for the samples without starch particles. The storage modulus increases due to the "particle filler-effect". Second, as the concentration of the starch increases, $G'_0$ enhances because of the presence of the starch particles as filler particles. Third, with increasing the concentration of the starch particles, the value of $G'$ enhances at first, then suddenly decreases, and rises again. This first increase is caused by the "particle filler-effect" and an ordered chain or column structure in the matrix, and this ordered structure is gradually enhanced with increasing the starch content. When the starch content is 10 wt %, the electric response of the elastomer is the strongest due to the best dispersion of starch in the elastomer, which lead to the increment of storage modulus. Although when the starch content is 15 wt %, the electric response became weaker due to the worse dispersion, and the weak effect on storage modulus is stronger than the filler's enhanced effect. So, when the starch content increases from 10 to 15 wt %, the storage modulus suddenly drops. The value of $G'$ finally increases as a result of the presence of the filler particles and an weaker ordered structure in the elastomer, where the electric response on the storage modulus has no obvious change. In addition, $G'$ is higher than $G'_0$; for example, when the concentration of starch particles is 5 wt %, $G'_0$ is 20.1 kPa, while $G'$ is 101.8 kPa.

Figure 7 depicts the storage modulus sensitivity as a function of the starch concentration. As shown in Figure 7, $\Delta G'/G'_0$ increases from 0.07 for the samples without starch particles to 4.07 for the samples with 5 wt % starch particles. The reason is that the increment of the storage modulus due to an ordered chain or column structures is greater than that due to the "particle filler-effect." When the starch

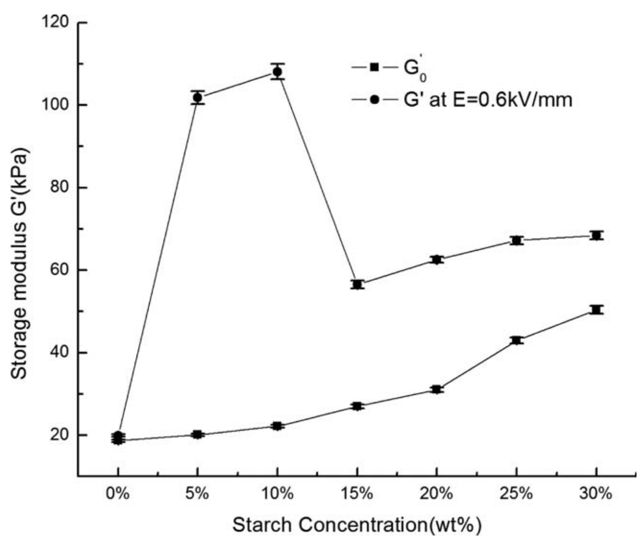


**Figure 6** Storage modulus as a function of starch concentration.

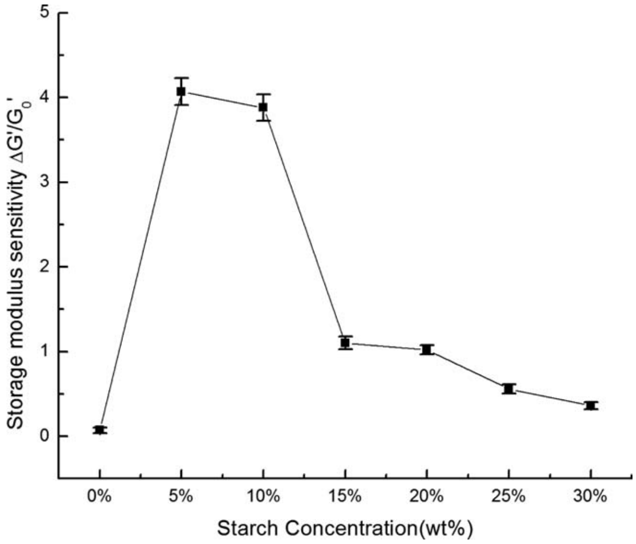


**Figure 7** Storage modulus sensitivity as a function of starch concentration.

concentration increases from 10 to 15 wt %, $\Delta G'/G'_0$ decreases slowly. The reason is that although the value of $G'$ increases, the increment of $G'$ is weaker than that of $G'_0$, where an ordered structures is gradually weakened due to the worse dispersion. As the starch concentration further increases, $\Delta G'/G'_0$ decreases as a result of a weaker ordered constructure for the poor dispersion and the increase of $G'_0$.

## CONCLUSIONS

Based on the idea of an ER fluid, the effect of a curing electric field on the storage modulus of hybrid elastomer was enhanced by adding transformer oil keeping a liquid phase in the entire curing process. Two types of hybrid electric elastomers, with random and ordered dispersion phases, were prepared by controlling the distribution of the particles in the curing electric field. The value of $G'$ is larger than $G'_0$. The storage modulus sensitivity of electric elastomers composed of pure transformer oil is the highest, that of electric elastomers composed of pure silicone oil takes second place, and that of electric elastomers composed of mixture oil is the smallest. It attains a maximum value of 3.88 at a mass ratio of 1 between the transformer oil and the silicone rubber with the fixed starch concentration. Furthermore, when the concentrations of the starch, the transformer oil, and the silicone rubber are 5 wt %, 47.5 wt %, and 47.5 wt %, respectively, $G'_0$ is 20.1 kPa, while $G'$ is 101.8 kPa, and $\Delta G'/G'_0$ attains a maximum value of 4.07.

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