

Composition Dependence of Dielectric Properties, Elastic Modulus, and Electroactivity in (Carbon Black-BaTiO₃)/Silicone Rubber Nanocomposites

Hang Zhao,^{1,2} Yu-Juan Xia,² Zhi-Min Dang,^{1,2} Jun-Wei Zha,¹ Guo-Hua Hu³

¹Department of Polymer Science and Engineering, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China

²Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China

³Key Laboratory of Reactions and Process Engineering, CNRS-Nancy Université, ENSIC-INPL, BP 20451, Nancy 54001, France
 Correspondence to: Z.-M. Dang (E-mail: dangzm@ustb.edu.cn)

ABSTRACT: The dielectric properties, elastic modulus, and electromechanical responses of dielectric elastomers (DEs) consisting of silicone rubber and carbon black (CB) incorporated with BaTiO₃ (BT) were studied. When compared with single filler/rubber composites, the resulting three-component nanocomposites yielded very abnormal phenomena. They might be attributed to the interactions between the two kinds of fillers. The increase in concentration of CB (BT) would play a destructive role to the network structure formed by BT (CB) particles. The maximum electromechanical strain of the nanocomposites achieved at mass fraction $m_{CB} = 0.03$ and $m_{BT} = 0.06$. The resultant electromechanical strain would be attributed to the large dielectric permittivity in the three-component nanocomposites, in which the BT particles themselves have a high dielectric permittivity and the electrical networks of CB particles have a contribution on the increase in dielectric permittivity of the three-component nanocomposites. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: dielectric elastomer; electromechanical response; network structure; nanocomposites

Received 5 April 2011; accepted 19 April 2012; published online

DOI: 10.1002/app.38044

INTRODUCTION

Laid between two compliant electrodes, dielectric elastomers (DEs) are capable of being used as electromechanical actuators according to their electromechanical response.^{1–5} In recent years, a great deal of efforts has been focused on developing DEs due to their large deformation, fast response speed, heavy load driving, and giant energy density when exposed to electric fields.^{6–16} Originating from electrostatic force, it has been shown that the electromechanical response is related to dielectric constant, elastic modulus, and electric field strength. However, the unfortunate drawback for DEs materials is the incredibly high operating voltages (order of 100 MV/m), and therefore, it blocks their commercial viability. Theoretically, based on the assumptions that DE film is an ideal rubber (incompressible and has a Poisson's ratio of 0.5) with constant modulus and free boundary, and the active area covers the entire surface of the film, the electric field-induced strain of the DEs should follow the relation expressed by

$$S = \epsilon_0 \epsilon_r E^2 / Y \quad (1)$$

where Y is the elastic modulus, ϵ_r is the relative dielectric permittivity of the materials, and E is the applied electric field strength.¹⁷ Generally, increasing the dielectric permittivity of the elastomer films is an effective way to reduce the required electric field strength for the same strain.^{18–21}

The most commonly followed approach to increase dielectric permittivity involves loading the elastomer matrix with high-permittivity ceramic powders.^{22–26} In some cases, these composites can lead to significant improvement in dielectric permittivity, but their efficient enhancement of dielectric permittivity can be achieved only if the loading of fillers is high enough. Because of the network structure formed by high loading of fillers, the unintended consequence is the dramatic increase in elastic modulus. This is a remarkable disadvantage for actuation, because the electromechanical strain resulting from the electrostatic pressure is inversely proportional to the elastic modulus of the material.

To decrease the filler volume fraction while improving the dielectric permittivity of the composite at the same time, filling the elastomer host with either organic or inorganic conductive particles has been adopted.^{27,28} The conductive filler/elastomer composites are usually associated with a sudden increase in dielectric permittivity at certain concentration of filler; this is attributed to the percolation network structures established by conductive clusters. However, the resulting composites simultaneously show a rapid increase in dielectric loss, follow reduction of dielectric strength and electromechanical transduction efficiency; such consequences play a negative role to the DEs deformation.

To overcome such limitations, in this work, both BaTiO₃ (BT) and acetylene carbon black (CB) are added to room temperature vulcanization silicone rubber. It is expected that two types of fillers have appreciable advantages over single filler on solving the contradiction between dielectric permittivity and elastic modulus. By adjusting the concentration of fillers, the composites are expected to have improved dielectric properties and appropriate elastic modulus as well, and their electromechanical strain responses are also prospected to have considerable improvement.

EXPERIMENTAL

Materials

It has been proved that silicone rubber is one of the most promising elastomers among the explored DEs during the last 20 years. Their low modulus, biocompatibility, thermal adaptability, and high elongation stress–strain properties are of significant interest.^{15,16,22–27} Here, room temperature vulcanized polydimethyl siloxane (107 silicone rubber) provided by GE Toshiba with viscosity of 3600 cSt was used as elastomer host. Acetylene CB particles were provided by Beijing Calcium Carbide Manufactory with about 50 nm in diameter and 60–70 (m²/g) in surface area. BT powder with about 100 nm in diameter was received from Guo Teng Ceramic Co. Before use, all the particles were dried at 100°C for 24 h to eliminate water.

Fabrication of the (CB-BT)/Silicone Rubber Nanocomposites

The CB and BT powders were mixed with silicone rubber using a three-roll grinding mill at room temperature for 30 min. Curing agent and activator were subsequently added into the composites for further mixing. Then, the (CB-BT)/silicone rubber nanocomposites obtained were compressed with a panel under 15 MPa pressure at room temperature for 6 h. The final samples were composite sheets with a thickness of about 100 μm and length of 7 cm. To limit the unexpected decrease in the dielectric strength of the (CB-BT)/silicone rubber nanocomposites, only low contents of CB (from mass fraction $m_{CB} = 0.01$ to $m_{CB} = 0.05$) could be exploited.

Measurement of Microstructures, Dielectric Properties, Mechanical Properties, and Electromechanical Strain Responses of the Nanocomposites

The microstructures of the fractured surface of the nanocomposites were characterized by scanning electron microscopy (SEM, Hitachi S-4700). The strips tailored SEM samples were first quenched in liquid-nitrogen, and then, the fractured cross sec-

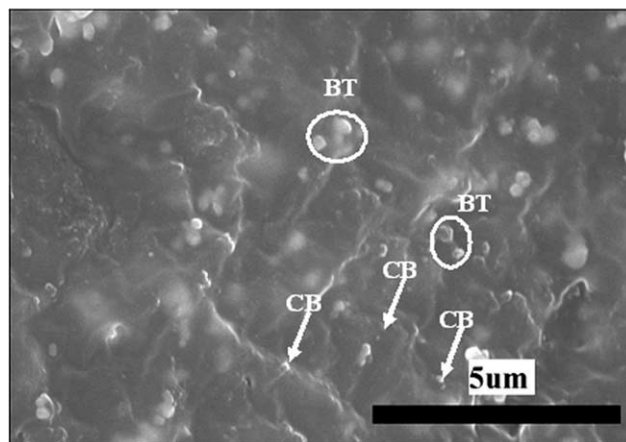


Figure 1. SEM micrograph of fractured cross section of the (CB-BT)/silicone rubber nanocomposites at $m_{BT} = 0.60$ and $m_{CB} = 0.01$.

tion was sprayed by gold. The dielectric properties were measured by an impedance analyzer (Agilent 4294A), demanding samples with an area of 1 cm² and two sides with silver electrode. The mechanical properties, in particular the elastic modulus, were gained by means of a tensile apparatus (type Instron1185) at room temperature and with test velocity of 20 mm/min, requiring dumbbell-shaped samples. The actual electromechanical strain responses perpendicular to the applied field of the planar sheets were recorded with a Canon SX100 at sixfold zoom. Before use, the planar sheets were coated with carbon-powder compliant electrodes with a diameter of 2.5 cm. Considering the safety and utility, the applied electric field strength to the samples was below 30 MV/m. The results of mechanical properties and electromechanical strain response presented in this work are the average from at least three samples with the same compositions.

RESULTS AND DISCUSSION

Microstructure of Fractured Cross Section of the Nanocomposites

Figure 1 displays the SEM micrograph of the fractured cross section of the (CB-BT)/silicone rubber nanocomposites at $m_{BT} = 0.60$ and $m_{CB} = 0.01$. It was observed that both BT and CB particles were homogeneously dispersed in the rubber host without serious aggregation, and the blurry interfaces supported a strong interaction between the nanosized particles and the rubber matrix.

Dielectric Properties of the Nanocomposites

Figure 2(a) shows the dependence of the dielectric permittivity of the nanocomposites on mass fraction of CB at room temperature and 10³ Hz. In general, the dielectric permittivity increased with the increase in m_{CB} at fixed m_{BT} . However, at fixed m_{CB} , the dielectric permittivity did not change uniformly with increase in m_{BT} . The curves indicate that at lower m_{CB} , namely $m_{CB} < 0.03$, the increasing amount of BT caused an increase in dielectric permittivity, whereas at higher m_{CB} , namely $m_{CB} \geq 0.03$, the increasing amount of BT induced an initial increase and subsequent decrease in dielectric permittivity.

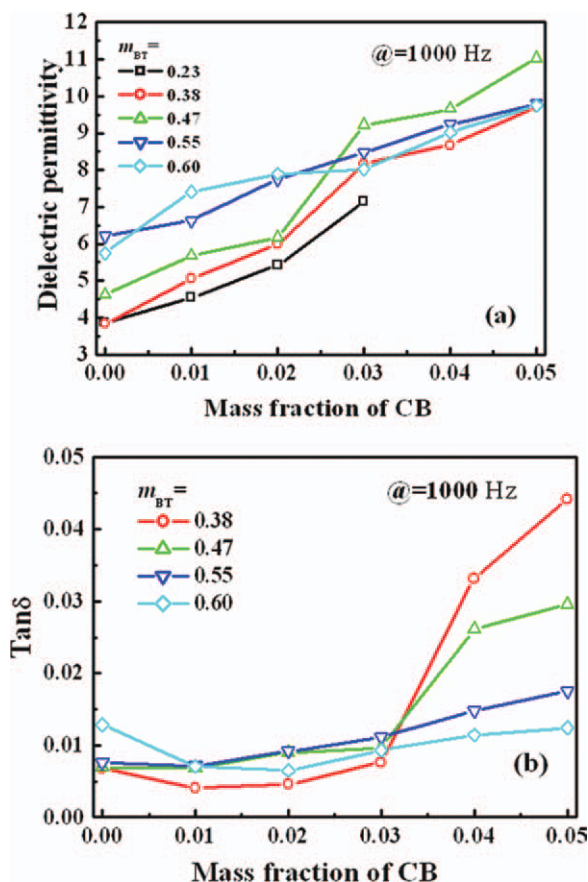


Figure 2. Dependences of (a) dielectric permittivity and (b) loss of the (CB-BT)/silicone rubber nanocomposites on m_{CB} measured at room temperature and 1000 Hz, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2(b) displays the dependence of the dielectric loss of the (CB-BT)/silicone rubber nanocomposites on m_{CB} at room temperature and 10^3 Hz. It can be observed that the dielectric loss of the nanocomposites increased with increasing m_{CB} . It is worth noting that at lower mass fraction of BT, namely $m_{BT} \leq 0.47$, the dielectric loss increased dramatically when m_{CB} was higher than 0.03. At lower mass fraction of CB ($m_{CB} \leq 0.03$), the dielectric loss was below 0.02, which was beneficial for highly efficient electromechanical response of the nanocomposites.

The dependences of the dielectric permittivity and loss of the nanocomposites with $m_{BT} = 0.55$ on frequency at room temperature are shown in Figure 3(a, b), respectively. With increasing frequency, the dielectric permittivity of all samples displayed a slight drop as presented in Figure 3(a). However, the dielectric permittivity increased with increasing m_{CB} at the same frequency, which would be attributed to the gradual formation of percolation in the composites. In addition, it could be seen that the dielectric loss of all samples were below 0.03 from 10^2 Hz to 10^6 Hz, which was valuable to electrostriction of composites. Of course, the dielectric loss increased with increasing m_{CB} at the same frequency, showing the effect of CB concentration.

Mechanical Properties of the Nanocomposites

Figure 4(a) shows the elastic modulus of the (CB-BT)/silicone rubber composite with different mass fractions of BT as a function of m_{CB} . Differing from the general consideration that CB fillers loading would inevitably stiffen the filler/polymer composites,^{29,30} the overall tendency of elastic modulus of the three-component nanocomposites revealed unusual phenomena. As shown in Figure 4(a), the elastic modulus first decreased and subsequently increased with increase in m_{CB} . The phenomena may be related to the interaction between CB and BT particles. Additionally, the elastic modulus increased with an increase in m_{BT} at given m_{CB} , and the lowest values of the elastic modulus were achieved at different m_{CB} for different m_{BT} . Figure 4(b) also shows the stress–strain curves of the pure matrix and the three-component nanocomposites with $m_{BT} = 0.55$ and different m_{CB} .

Schematic Diagram of the Network Formed by Various Mass Fractions of BT and CB Particles

As mentioned above, all the obtained results of (CB-BT)/silicone rubber nanocomposites, whether dielectric permittivity or elastic modulus, behave quite differently compared with the monotonic behavior of composites loaded with single fillers. The interpretation of this phenomenon is shown in Figure 5.

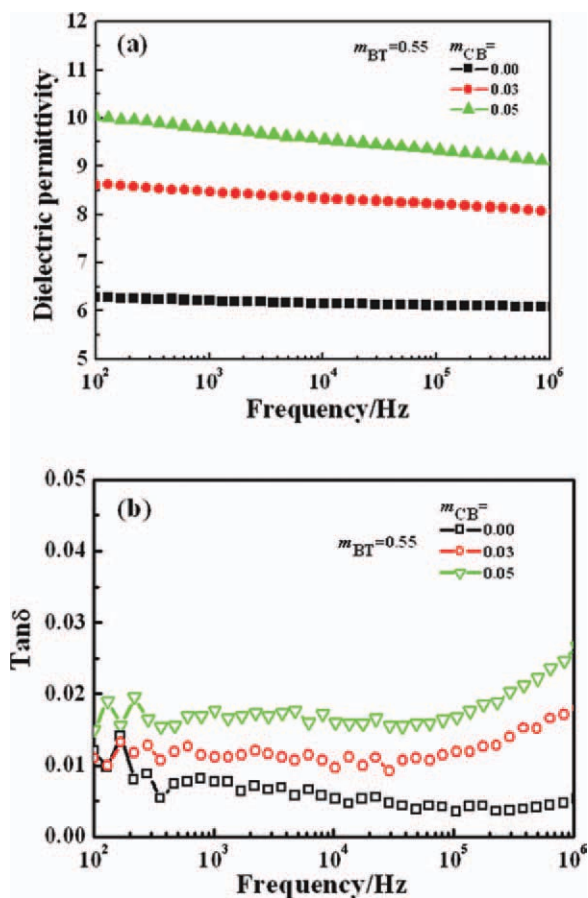


Figure 3. Dependences of (a) dielectric permittivity and (b) dielectric loss on frequency of the nanocomposites with different compositions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

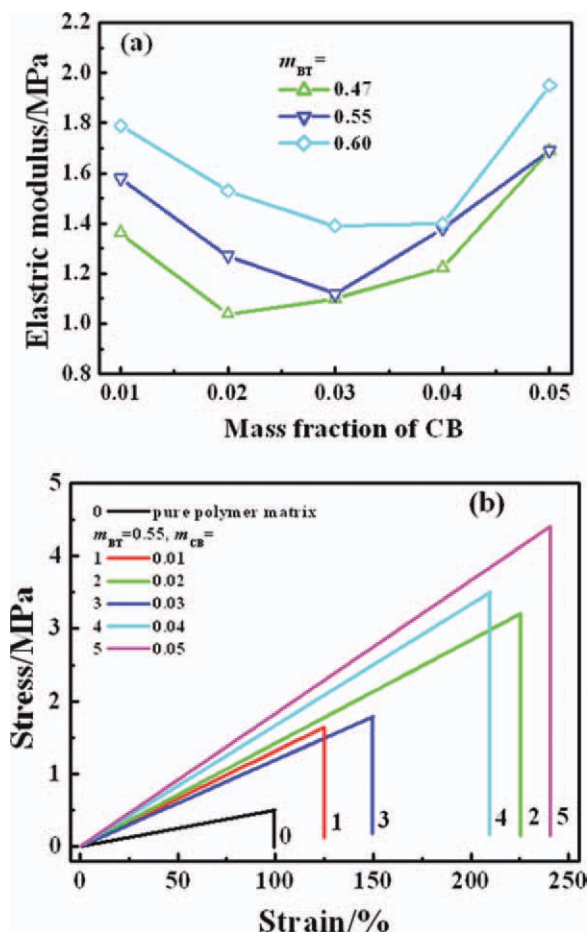


Figure 4. (a) Dependence of elastic modulus on m_{CB} with various m_{BT} ; (b) stress–strain curves of the pure matrix and the three-component nanocomposites with $m_{BT} = 0.55$ and different m_{CB} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Here, the gray grain represents BT particle, black grain represents CB particle, the gray line vividly shows the network formed by BT particles, and black line means network formed by CB particles.

In (CB-BT)/silicone rubber nanocomposites, the existence of BT fillers may hinder the contact between CB particles. In compari-

son with lower BT mass fraction ($m_{BT} \leq 0.47$), the high content of BT particles ($m_{BT} \geq 0.55$) most likely leads to higher BT particles insertion between the adjacent CB particles and accordingly destroys the network formed by CB particles [as shown in Figure 5(a, c)]. This interacted structure impeded the long-range electronic transitions and minimized the leakage current and decreased the dielectric loss, which was undoubtedly proved by the loss measurements shown in Figure 2(b). Similarly, the abnormal behavior of dielectric permittivity of the nanocomposites shown in Figure 2(a) also provided proof of this structure. At higher concentration of CB ($m_{CB} \geq 0.03$), the dielectric permittivity initially increased but subsequently decreased with increase in m_{BT} and in mathematical sense 0.47 shows a maximum for permittivity versus m_{BT} .

In view of mechanical properties, previous studies on ceramic/polymer composites have reported a dependence of elastic modulus on the type of the ceramic and elastomeric polymer matrices.^{22–26} For CB/elastomer composites, an increase in elastic modulus is reported.^{28,29} In this study, the elastic modulus showed an increase with increasing m_{BT} at given m_{CB} as shown in Figure 4(a). However, with increasing m_{CB} at given m_{BT} , an initial decrease followed by an increase in elastic modulus was observed. This unusual phenomenon could also be interpreted by schematic diagram displayed in Figure 5. When comparing Figure 5(b) with Figure 5(c), it is noted that with the increase in mass fraction of CB, more and more insertion of CB particles may destroy the network formed by BT fillers. Moreover, the particles with varying size ($d_{CB} = 50$ nm, $d_{BT} = 100$ nm) would enlarge the packing volume fraction of the fillers.³¹ Because of these mentioned reasons, the elastic modulus would decrease with increase in m_{CB} . Of course, by further increase in CB fillers, the CB network would be reformed gradually and would raise the elastic modulus again.

Electromechanical Strain Response of the Nanocomposites

As evidenced by the results gained from the independent dielectric and mechanical tests, it is worth noting that the content adjustment of m_{CB} and m_{BT} seems to be responsible for the abnormal trend of dielectric permittivity and elastic modulus. High values of dielectric permittivity along with low elastic modulus were acquired at a particular content of CB located between $m_{CB} = 0.02$ – 0.04 (around 0.03), and they happened to

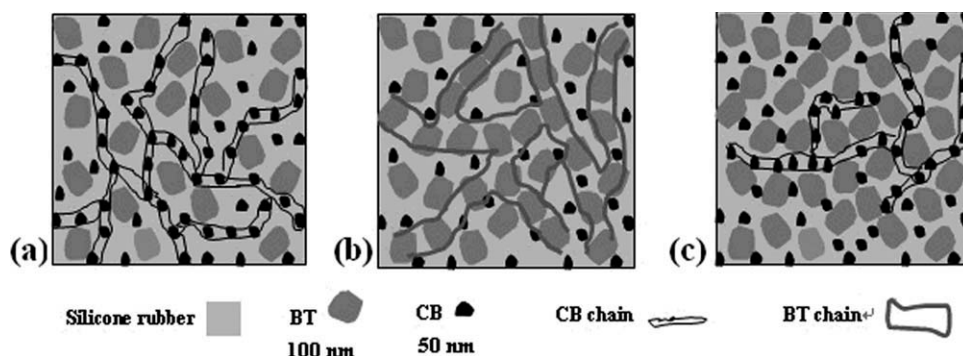


Figure 5. Schematic diagram of the network formed by various mass fractions of BT and CB particles with (a) $m_{BT} \leq 0.47$, $m_{CB} \geq 0.03$, (b) $m_{BT} \geq 0.55$, $m_{CB} < 0.03$, and (c) $m_{BT} \geq 0.55$, $m_{CB} \geq 0.03$.

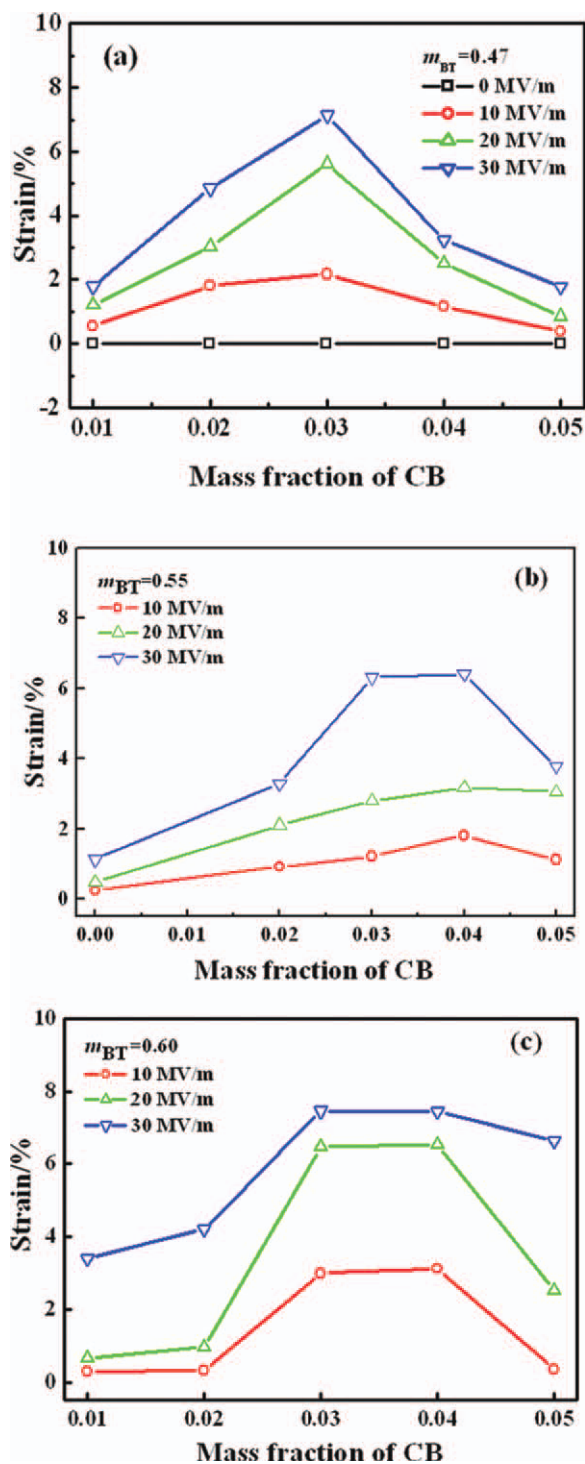


Figure 6. Electromechanical strain response at different electric fields as a function of mass fraction of CB with (a) $m_{BT} = 0.47$, (b) $m_{BT} = 0.55$, and (c) $m_{BT} = 0.60$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be two advantageous features for an energy transduction material to achieve larger strains. Here, the actual electromechanical strain response of the (CB-BT)/silicone rubber nanocomposites with $m_{BT} = 0.47, 0.55,$ and 0.60 were reported in Figure 6(a–c) as a function of m_{CB} . In fact, due to the leakage current raised

by the CB network structure, at lower content of BT ($m_{BT} < 0.47$), the dielectric strength was so small that the nanocomposites failed to provide any measurable deformation.

According to eq. (1), it is obvious that at the same electric field, the higher is the quotient ϵ_r/Y , the larger would be the theoretical strain response (s). Or in other words, the ϵ_r/Y has the same trend with the s . Hence, the ϵ_r/Y was used to represent the theoretical strain response. Considering that dielectric permittivity had a weak dependence on frequency, it is reasonable to think that the ϵ_r/Y might have similar tendencies at different frequencies. In this work, the used value of ϵ_r was at 1000 Hz. When comparing the curves in Figures 6 and 7, it is found that the values of ϵ_r/Y first increased but subsequently decreased with the increase in m_{CB} , and the actual strain responses also showed the same trend. Additionally, the trend became more and more significant as the electric field strength increased. The maximum values of ϵ_r/Y were found at around $m_{CB} = 0.03$ – 0.04 with specific m_{BT} , namely $m_{BT} = 0.47, 0.55,$ and 0.60 . As reasonably expected, the actual maximum strains were also reached at around $m_{CB} = 0.03$ – 0.04 for each given m_{BT} . For instance, at $m_{BT} = 0.47$ and 30 MV/m, a strain of 7.13% was observed at $m_{CB} = 0.03$, and it was four times higher than at $m_{CB} = 0.01$ or $m_{CB} = 0.05$, as shown in Figure 6(a). Figure 6(b, c) showed the maximum strain of 6.42% and 7.46% at ($m_{BT} = 0.55, m_{CB} = 0.04$) and ($m_{BT} = 0.60, m_{CB} = 0.03$), respectively.

Based on the data originated from the independent dielectric and mechanical tests, the maximum theoretical value of strain response should have achieved at filler concentration combination of $m_{CB} = 0.03$ and $m_{BT} = 0.47$ as shown in Figure 7. However, the experimental maximum strain response obtained from the electromechanical strain response deviated from theoretical values and shifted to new filler concentration combination of $m_{CB} = 0.03$ and $m_{BT} = 0.60$. The differences between theory and test may be attributed to the dielectric loss. In fact, besides Y, ϵ_r and E , the electromechanical strain response of DEs is related with several other factors, such as the dielectric

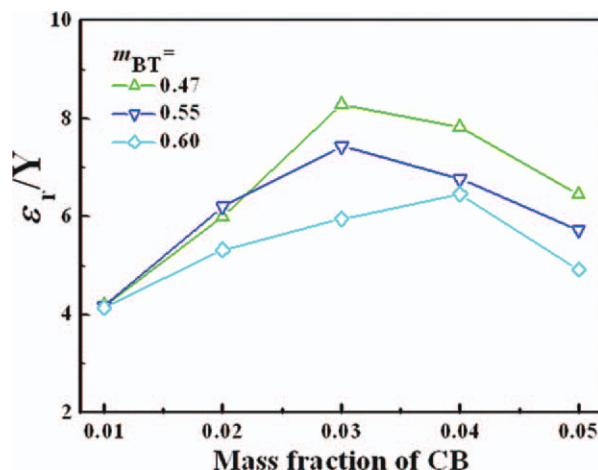


Figure 7. Dependence of ϵ_r/Y on the mass fraction of CB in the (CB-BT)/silicone rubber nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

loss, type of electrode, structure of the actuator, and so on. It is easy to find in Figure 2(b) that the dielectric loss value of the nanocomposites with $m_{CB} > 0.03$ and $m_{BT} = 0.47$ was higher than that with $m_{CB} > 0.03$ and $m_{BT} = 0.60$, which illustrated that the energy transferred by electric field might be dissipated as heat rather than being stored in the form of elastic energy. In brief, according to the results from Figures 6 and 7, $m_{CB} = 0.03$ and $m_{BT} = 0.60$ seem to represent the optimal concentration of fillers of the nanocomposites according to the electromechanical strain response.

CONCLUSIONS

Different from previous reports that both the dielectric permittivity and the elastic modulus would increase inevitably with the increase in concentration of inorganic fillers, this work demonstrated an increase in dielectric permittivity and a decrease of elastic modulus in the (CB-BT)/silicone rubber nanocomposites. The interesting results were attributed to the interaction between two different types of fillers, which played a negative role to the network formed by each other. The varying size of the particles further enlarged the packing volume of the fillers. Both, dielectric loss and elastic modulus, decreased by the disruption of the network structure. All of these factors synergistically contributed to a remarkable increase in the electromechanical strain response. The maximum strain response was found at $m_{CB} = 0.03$ and $m_{BT} = 0.60$. Although the result disagreed with the optimal concentrations of fillers calculated theoretically, this is acceptable by further considering the dielectric loss. The approach proposed in this work can be extended to different kinds of conductive-ceramic fillers and elastomer matrices. These improvements may lead to the development of functional materials with improved electromechanical response.

ACKNOWLEDGMENTS

This work was financially supported by Beijing Natural Science Foundation (No. 2122040), NSF of China (No. 50977001, 51073015), the Ministry of Sciences and Technology of China through China-Europe International Incorporation Project (No. 2010DFA51490), State Key Laboratory of Power System (SKLD11KZ04), and the Fundamental Research Funds for the Central Universities (06103012, 06103011).

REFERENCES

- Brochu, P.; Pei, Q. B. *Macromol. Rapid Commun.* **2010**, *31*, 10.
- Carpi, F.; De Rossi, D.; Kornbluh, R.; Pelrine, R.; Sommer-Larsen, P. *Dielectric Elastomers as Electromechanical Transducers: Fundamentals, Materials, Devices, Models and Applications of an Emerging Electroactive Polymer Technology*; Elsevier Science, 2008 (USA).
- Biddiss, E.; Chau, T. *Med. Eng. Phys.* **2008**, *30*, 403.
- Pelrine, R.; Kornbluh, R.; Pei, Q. B.; Joseph, J. *Science* **2000**, *287*, 836.
- Pelrine, R.; Kornbluh, R.; Joseph, J.; Heydt, R.; Pei, Q. B.; Chiba, S. *Mater. Sci. Eng. C* **2000**, *11*, 89.
- Heydt, R.; Kornbluh, R.; Prlrine, R.; Mason, V. J. *Sound Vib.* **1998**, *215*, 297.
- Delille, R.; Urdaneta, M.; Hsieh, K.; Smela, E. *Proc. SPIE* **2006**, 6168, 61681Q.
- Kofod, G.; Paajanen, M.; Bauer, S. *Appl. Phys. A* **2006**, *85*, 141.
- Wissler, M.; Mazza, E. *Sens. Actuators A* **2007**, *134*, 494.
- Wissler, M.; Mazza, E. *Sens. Actuators A* **2007**, *138*, 384.
- Plante, J. S.; Dubowsky, S. *Sens. Actuators A* **2007**, *137*, 96.
- Patrick, L.; Gabor, K.; Silvain, M. *Sens. Actuators A* **2007**, *135*, 748.
- Carpi, F.; Migliore, A.; Serra, G.; De Rossi, D. *Smart Mater. Struct.* **2005**, *14*, 1210.
- Mockensturm, E. M.; Goulbourne, N. *Int. J. Non-Linear Mech.* **2006**, *41*, 388.
- Kofod, G.; Sommer-Larsen, P. *Sens. Actuators A* **2005**, *122*, 273.
- Goulbourne, N. C.; Mockensturm, E. M.; Frecker, M. I. *Int. J. Solids Struct.* **2007**, *44*, 2609.
- Zhang, Q. M.; Li, H. F.; Poh, M.; Xia, F.; Cheng, Z. Y.; Xu, H. S.; Huang, C. *Nautre* **2002**, *419*, 284.
- Zhang, Q. M.; Wissler, M.; Jaehne, B.; Broennimann, R.; Kovacs, G. *Proc. SPIE* **2004**, 5385, 78.
- Huang, C.; Zhang, Q. M. *Adv. Mater.* **2005**, *17*, 1153.
- Xu, H. S.; Bai, Y.; Bharti, V. Z.; Cheng, Y. J. *Appl. Polym. Sci.* **2001**, *82*, 70.
- Bar-Cohen, Y.; Zhang, Q. M. *MRS Bull.* **2008**, *33*, 173.
- Gallone, G.; Carpi, F.; De Rossi, D.; Levita, G.; Marchetti, A. *Mater. Sci. Eng. C* **2007**, *27*, 110.
- Carpi, F.; De Rossi, D. *IEEE Trans. Dielectr. Electr. Insul.* **2005**, *12*, 835.
- Khastgir, D.; Adachi, K. J. *Polym. Sci. Part B: Polym. Phys.* **1999**, *37*, 3065.
- Popierlarz, R.; Chiang, C. K.; Nozaki, R. *Macromolecules* **2001**, *34*, 5910.
- McCarthy, D. W.; Mark, J. E.; Schaefer, D. W. *J. Polym. Sci. B* **1998**, *36*, 1167.
- Carpi, F.; Gallone, G.; Galantini, F.; De Rossi, D. *Adv. Funct. Mater.* **2008**, *18*, 235.
- Guiffard, B.; Seveyrat, L.; Sebald, G.; Guyomar, D. *J. Phys. D* **2006**, *39*, 3053.
- Medalia, A. L. *Rubber Chem. Technol.* **1972**, *45*, 1171.
- Qian, S. Y.; Huang, J. F.; Guo, W. H.; Wu, C. F. *J. Macromol. Sci. Phys.* **2007**, *46*, 453.
- Aharony, A.; Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London, **1993**.