Lead Magnesium Niobate-Filled Silicone Dielectric Elastomer with Large Actuated Strain

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Received 20 July 2011; accepted 31 October 2011
DOI 10.1002/app.36428

ABSTRACT: A silicone dielectric elastomer filled with lead magnesium niobate with a maximum actuated strain of 7.4% at 45 kV/mm was fabricated by optimizing the amount of dielectric filler, amount of plasticizing agent, and crosslink density of the elastomer. The actuated strain of dielectric elastomers (DEs) is determined by both the dielectric constant and the elastic modulus. Although the dielectric constant of the silicone elastomer increased with increasing loading amount of lead magnesium niobate, actuated strain did not increase as expected because the elastic modulus increased at the same time. The elastic modulus of silicone dielectric elastomer was decreased by reducing the crosslink density or adding plasticizing agent, leading to a visible increase in actuated strain. It was also revealed that actuated strain of silicone dielectric elastomer always goes up with increasing ratio of dielectric constant to elastic modulus. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2196–2201, 2012

Key words: actuated strain; dielectric properties; elastic modulus; crosslinking

INTRODUCTION

Dielectric elastomer actuators (DEAs), which consist of a dielectric elastomer (DE) film sandwiched between two compliant electrodes, are now considered as the most promising large-strain micro-actuator used in mini- and micro-robots, biomimetics, panel loudspeakers, artificial muscles, prosthetics devices, etc. In the past two decades, the researches on DEAs predominated in the field of micro-actuators.[1–8] For DEAs, the dielectric elastomer (DE) is the key issue to obtain a large strain, so it has attracted more and more attention.

Theoretically, the thickness strain s_z[1] is given by the following equation:

$$s_z = -\varepsilon\varepsilon_0 E^2/Y \tag{1}$$

where ε and ε_0 are the relative permittivity of the elastomer (dielectric constant) and the permittivity of free space respectively; E is the applied electric field strength and Y is the elastic modulus of the dielectric elastomer. The equation indicates that an ideal DE should have low elastic modulus, high dielectric constant as well as high electric breakdown strength, in order to obtain excellent electromechanical properties (large actuated force and strain). In previous studies, the dielectric constant of elastomers was improved by adding high dielectric constant fillers, such as inorganic particles (ceramic powder,[9,10] carbon nanotubes[5]) or organic particles (PANI,[3,11] CuPc[4,12]). However, the actuated strain of DE did not sufficiently increase as expected because those fillers increased the modulus, but limit the mechanical deformation. Besides, the addition of some semiconductive dielectric fillers, typically carbon nanotubes, could not only dramatically increase the elastic modulus but also decrease the electric breakdown strength even at very small loading amounts.[13] Therefore, in order to get a large ratio of dielectric constant to elastic modulus (ε/Y), it is important to balance these two incompatible key properties through material design.

Silicone elastomer has high flexibility, elasticity, and stability over a wide range of temperatures. Its dielectric loss and viscoelastic loss are independent of temperature and frequency. Besides, it has high filling capacity as well as electric breakdown strength (as large as several hundred kilovolts per millimeter).[1,3,14] So silicone elastomer is preferentially used as the matrix for DE.[1,5,10] However, its

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Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50933001, 51173007.

Contract grant sponsor: National Outstanding Youth Science Fund; contract grant number: 50725310.

Journal of Applied Polymer Science, Vol. 125, 2196–2201 (2012)

dielectric constant is only about 3. In this study, we aimed to develop ceramic–polymer (0-3) dielectric composites with balanced dielectric constant and modulus by modulating the loading amounts of dielectric filler and plasticizing agent, and the crosslink density of the elastomer. The relation of dielectric constant and elastic modulus and effects on the actuated strain were also discussed.

EXPERIMENT

Materials

A commercial poly(dimethyl siloxane) (PDMS) (type 110-2, Chenguang Research Institute of Chemical Industry, China) was used as the matrix. The filler was a commercial high-dielectric-constant (up to 4000) lead magnesium niobate (PMN) (Baoding Acoustic Electronic Equipment, China) with a particle diameter of about 1.5 μm. The crosslinking agent dicumyl peroxide (DCP), silane coupling agent A151 and the plasticizing agent silicone oil were commercial products. The composites containing 0, 10, 20, 30, 40, 50, and 60% (by volume) PMN were studied. Crosslinking agent DCP (2 phr) and coupling agent A151 (2 phr) were added to each of the composites. The 30 vol % PMN/PDMS composite with different contents of DCP (0.5, 1, 2, and 3 phr) and the 30 vol % PMN/PDMS composite with different contents of silicone oil (10, 20, 30, and 40 phr) were also studied.

Methods

The composites consisting of PMN and PDMS with and without plasticizer were prepared through physical mixing on a 6-inch two-roll mill. The compounds were cured in a Chelsea mold for their respective T_{90} times at 160°C to obtain the corresponding cured composites, i.e., vulcanizates.

The commonly used compliant electrode material for dielectric elastomers was powdered carbon graphite dispersed in silicone oil. Each side of the DE was coated with the compliant electrode material by an air gun, and then the DE was put into an electric blast bellows at 60°C until the compliant electrodes were cured.

Measurements

The morphology of the PMN/PDMS composites was analyzed through a scanning electron microscope (S-4700, Hitachi, Japan). The elastic moduli of neat and filled silicone elastomers were determined by the slope of the stress–strain curves obtained by a tensile apparatus (CMT4104, Shenzhen SANS Testing Machine, China) at 25°C using rectangular strips (original length 40 mm) according to Chinese Standard GB/T528—1998. The strain rate was 50 mm/min. The electrodes, in the form of conductive silver paste, were painted on the surface of the cured composites for dielectric measurements. The dielectric properties of the samples were measured by an impedance analyzer (HP4294A, Agilent, USA) over the frequency range of 100 Hz to 10^7 Hz and the temperature range of 20–150°C. The actuated plane strain of the dielectric elastomer was measured under a high voltage supplied by an intelligent DC high voltage generator (Wuhan Dotek Electric, China). A schematic diagram of the equipment for measuring actuated strain is shown in Figure 1. A voltage (in the range 20 kV/mm to 55 kV/mm) was loaded on the DE to obtain the plane strain. During actuation, video images were captured by a camera (Canon Ixus 80, Japan) fitted with a wide-angle lens. Under isochoric deformation conditions, the in-plane strains (s_x and s_y) and the transverse strain (s_z) are related by $(1 + s_x)(1 + s_y)(1 + s_z) = 1$. If the actuation-induced in-plane deformation is isotropic, $s_x = s_y = s_{xy}$. The thickness strain s_z can be obtained as follows.[15]

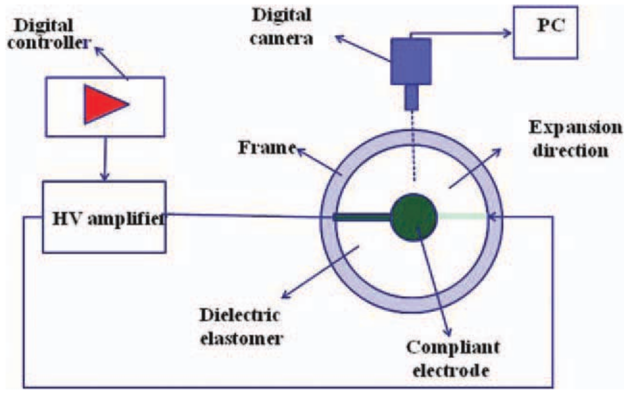

Figure 1 Schematic diagram of equipment for measuring actuated strain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$s_z = (1 + s_{xy})^{-2} - 1 \quad (2)$$

In all electromechanical actuation testing, we used the thickness strain which is negative to represent the actuated strain.

RESULTS AND DISCUSSION

Effect of dielectric filler amount

Microstructure

Figure 2 shows the SEM micrographs of the fractured surfaces of PMN/PDMS composites filled

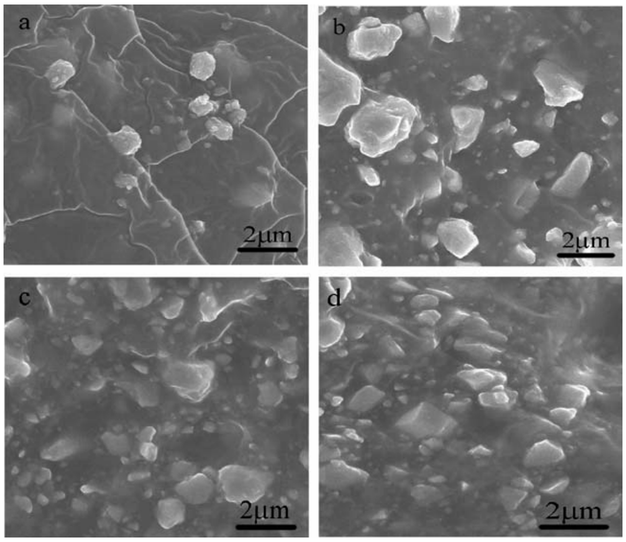

Figure 2 SEM micrographs of fractured surfaces of PMN/PDMS composites filled with different volume fractions of PMN (a) 10 vol % PMN/PDMS composite, (b) 30 vol % PMN/PDMS composite, (c) 50 vol % PMN/PDMS composite, and (d) 60 vol % PMN/PDMS composite.

with different volume fractions of PMN. At PMN volume fractions of 30% and below, the PMN particles are well dispersed in the silicone elastomer. At volume fractions of PMN between 50 and 60%, most of the PMN particles aggregate to form filler–filler networks, probably leading to a high modulus.[16] Whatever the loading amount of PMN is, the compatibility between PMN and PDMS is very good, as indicated by the smooth fractured surfaces and the absence of bonded rubber on the filler.

Elastic modulus and dielectric properties

Figure 3(a) displays the elastic modulus of PMN/PDMS composites filled with different volume fractions of PMN. As seen in Figure 3(a), the silicone elastomer used in this study had a very low elastic modulus. As expected, the addition of rigid PMN particles increased the elastic modulus of the composites. When the volume content of PMN exceeded 40%, the elastic modulus increased more rapidly than before. The material became too brittle to have any elasticity, thus limiting the deformation of DE. As mentioned above, a very high loading amount of PMN could form a strong filler-network, causing a sudden rise in elastic modulus, but a sharp decline in elongation.

Figure 3(b) presents the frequency dependence of the dielectric constant of the composites. With the increase of PMN amount, the dielectric constant increased significantly, especially when the PMN loading amount was more than 40%. It can be seen that the composite filled with 60 vol % PMN has a dielectric constant of 27.5 at 1 kHz, much higher than that of pure silicone elastomer (~ 3.0). The high

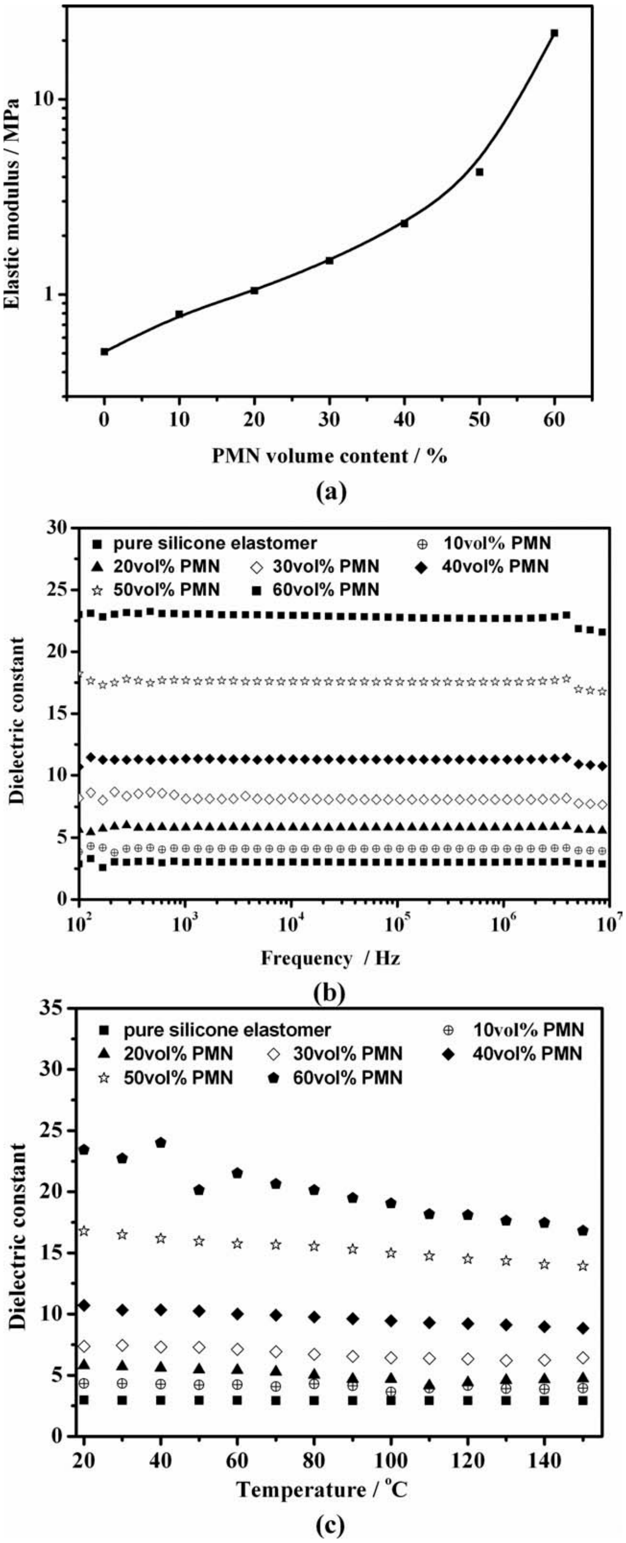

Figure 3 (a) Elastic modulus of PMN/PDMS composites filled with different volume fractions of PMN filler, (b) Frequency dependence of dielectric constant for PMN/PDMS composites filled with different volume fractions of PMN filler at room temperature, (c) The dependence of the dielectric properties of the PMN/PDMS composites on temperature at 1 kHz.

dielectric constant was mainly attributed to the interface polarization between the PMN and silicone matrix.[17] The Maxwell-Wagner polarization mechanism was probably responsible for this phenomenon.[18] On the other hand, when the volume content of PMN exceeded 40%, the filler–filler distances became smaller and the dipole polarization between the PMN particles in the matrix was solidified, leading to a rapid increase in dielectric constant.[19] Figure 3(b) also shows the high frequency stability of dielectric constant over a wide range of frequencies ranging from 100 Hz to 10^7 Hz.

The dependence of the dielectric properties of the composites on temperature at 1 kHz is shown in Figure 3(c). At PMN contents below 30 vol %, the dielectric constant of the composites is quite high and exhibits a weak temperature dependence over a relatively broad range of temperatures, mainly because of the high thermal stability of the dielectric behavior of the nonpolar polymer matrix with temperature.[9] However, the dielectric constant of the composites hardly decreased with increasing temperature when the volume content of PMN exceeded 30%, which can be explained by the polarity of PMN. The dielectric constant of PMN decreases with increasing temperature after it reaches a maximum value dielectric constant ($\varepsilon_{\max}$) at about room temperature.[20]

Actuated strain

The actuated strain of PMN/PDMS composites as a function of electric field at different contents of PMN is shown in Figure 4(a). To get the largest strain, the actuation voltage was increased until an electric breakdown occurred. The composite with 20 vol % PMN exhibited a maximum thickness strain of 7.89% at an electric breakdown field of 53 kV/mm. Also we found that with increasing content of PMN, the electric breakdown strength decreased as a result of the increasing number of defects in the composites, in agreement with phenomenon in the literature.[21] A comparison of the actuated strains of various composites at a constant electric field of 40 kV/mm is shown in Figure 4(b). The composite with 20 vol % PMN has the largest actuated strain. This result reconfirmed that the electromechanical behavior of DE was controlled by the competing effects of elastic modulus and dielectric constant, as indicated by eq. (1). As the PMN amount increased, the insulation of the composites decreased, and at the same time the number of cavities which were caused by the poor interface between the filler and rubber in the composites increased. Both effects led to an electric breakdown. As seen from Figure 4(c), the actuated strain increased with increasing ε/Y, but the trend was nonlinear. That maybe a small amount of electrical work might dissipate because of electrical loss and viscoelastic loss. And the actuated response of the composites also depends on the electrode, and the structure of the actuator.

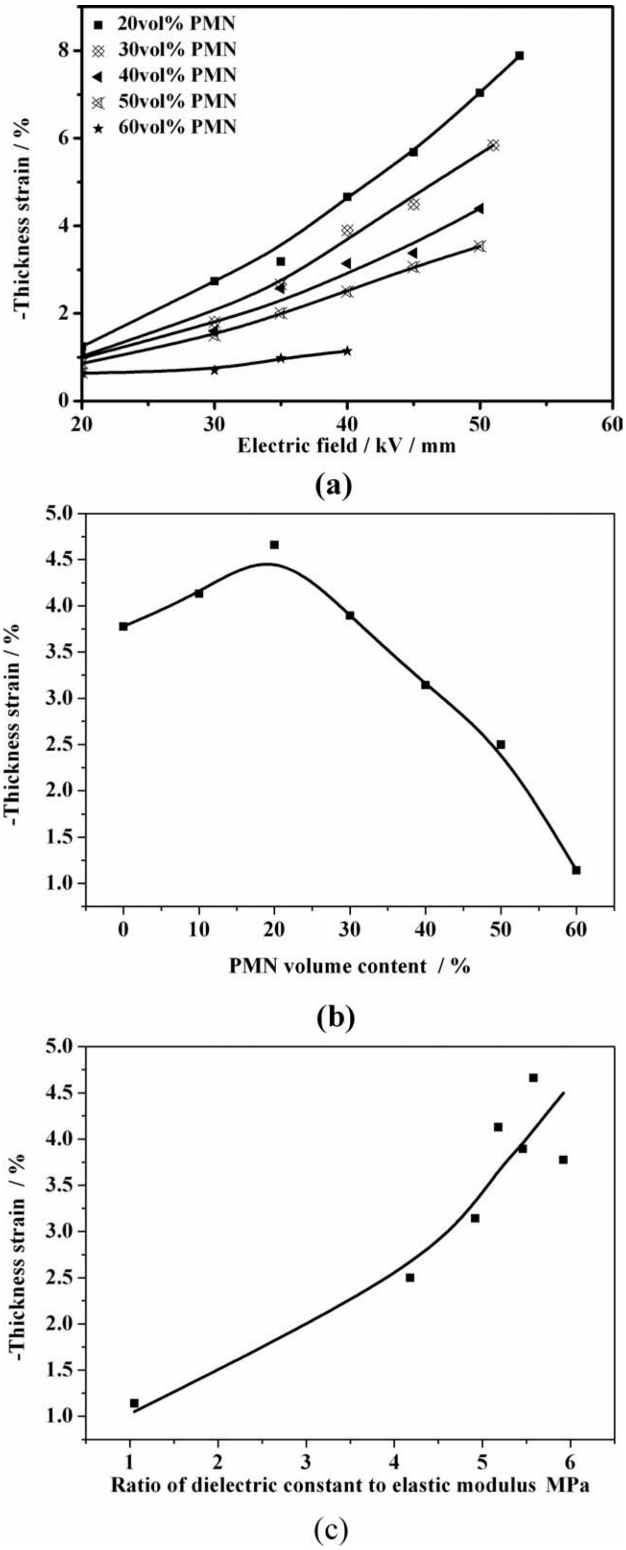

Figure 4 (a) Thickness strain of composites versus electric field at different volume fractions of PMN filler, (b) Thickness strain of composites versus PMN content at an electric field of 40 kV/mm, (c) Thickness strain of composites versus ε/Y at an electric field of 40 kV/mm.

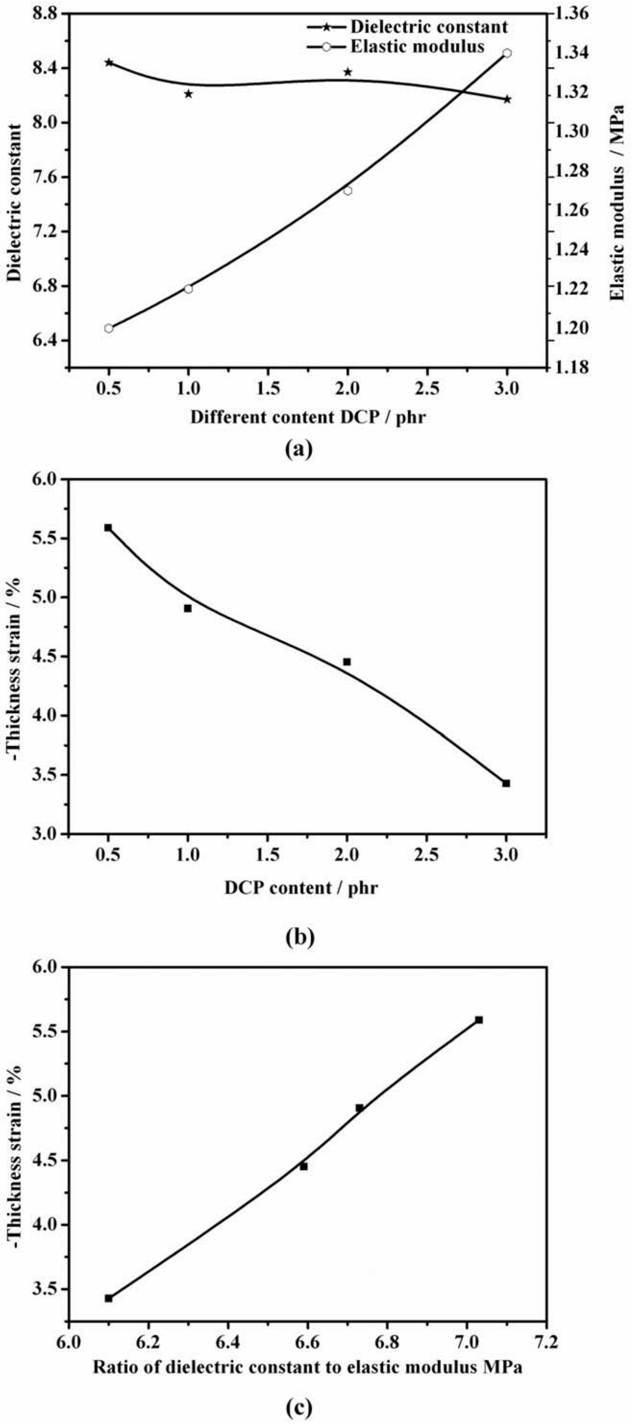

Figure 5 (a) Dielectric constant (1 kHz) at room temperature and elastic modulus of 30 vol % PMN/PDMS composite versus content of DCP, (b) Thickness strain of 30 vol % PMN/PDMS composites versus DCP content at an electric field of 45 kV/mm, (c) Thickness strain of 30 vol % PMN/PDMS composite versus value of ε/*Y* of dielectric elastomer at an electric field of 45 kV/mm.

Effect of crosslink density

Besides the dielectric constant, the elastic modulus is another important factor determining actuated strain of DE. We intended to improve the actuated strain of DE by reducing the elastic modulus. To study the effect of elastic modulus, we chose the PMN/PDMS composite filled with 30 vol % PMN and reduced its

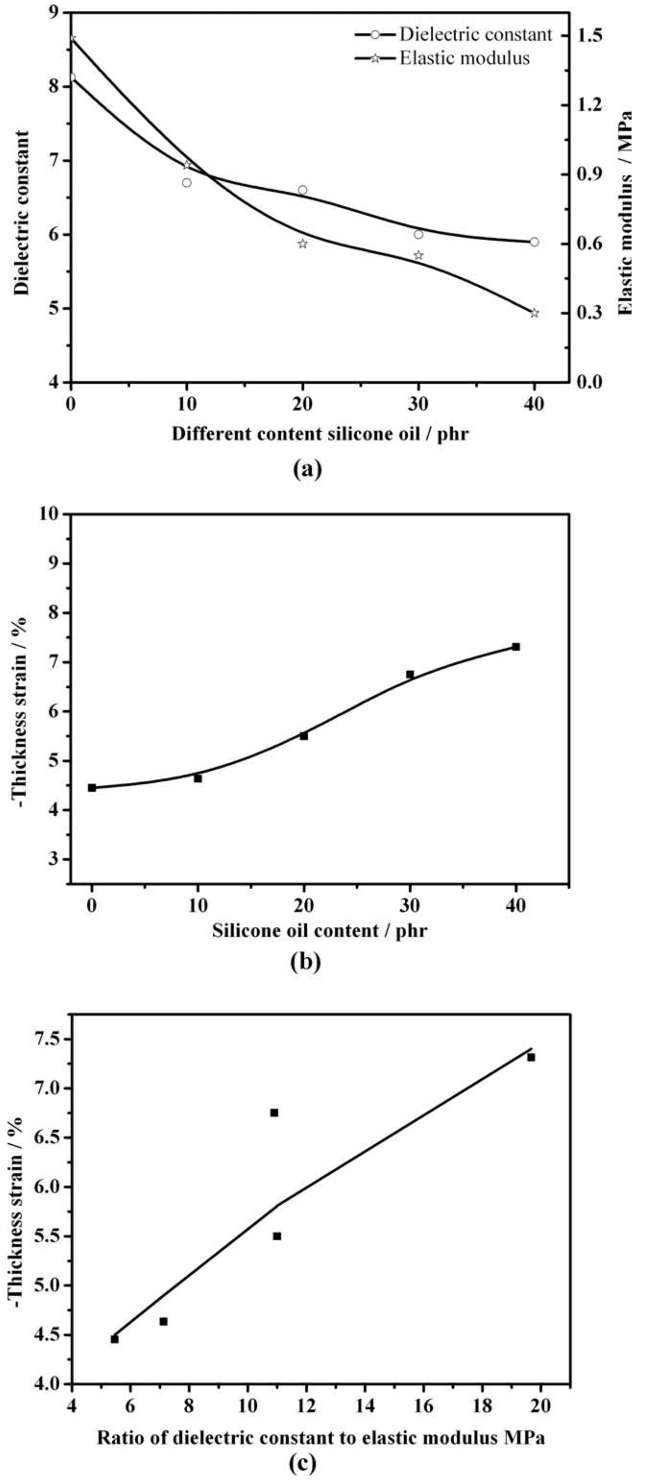

Figure 6 (a) Dielectric constant (1 kHz) at room temperature and elastic modulus of 30 vol % PMN/PDMS composite versus content of silicone oil, (b) Actuation strain of 30 vol % PMN/PDMS composite versus content of silicone oil at an electric field of 45 kV/mm, (c) Thickness strain of 30 vol % PMN/PDMS composite versus value of ε/*Y* of dielectric elastomer at an electric field of 45 kV/mm.

elastic modulus by decreasing the crosslink density and adding a plasticizing agent.

Figure 5(a) shows the dielectric constant at 1 kHz and elastic modulus as functions of the content of the crosslinking agent dicumyl peroxide (DCP). We can see that the dielectric constant changed little, but the elastic modulus dramatically increased with increasing content of DCP. As a result, the actuated strain of the composite decreased with increasing DCP content, as shown in Figure 5(b). The composite containing 0.5 phr DCP exhibited an actuated strain of 5.92% at an electric field of 45 kV/mm, whereas the one containing 3 phr DCP had an actuated strain of only 3.55% at the same electric field. A high concentration of crosslink agent results in a high crosslink density, which will reduce the elongation and increase the modulus of the elastomer. We can see from Figure 5(c) that the actuated strain of the composite increased linearly with increasing ε/Y value. For highly filled rubber composites, the viscoelastic loss is mainly dominated by the filler amount rather than the crosslink density.

Effect of plasticization

From Figure 6(a), not only the elastic modulus but also the dielectric constant decreased significantly with increasing content of silicone oil. The elastic modulus of the composite containing 40 phr silicone oil was just 20% of that of the composite without plasticizer. With increasing content of silicone oil whose dielectric constant is only 2.6–2.8, the volume fraction of PMN was accordingly decreased, so the dielectric constant of the composites decreased. Even so, we can see that the actuated strain of the composite increased significantly with increasing silicone oil content, with the largest strain reaching 7.4%, as shown in Figure 6(b). In Figure 6(c), we can see that in ε/Y value of DE range of 5.46 to 19.67, the actuated strain increased almost linearly with increasing ε/Y value. In conclusion, the ε/Y ratio is a crucial parameter determining the actuated strain of dielectric elastomers.

CONCLUSIONS

We confirmed that the actuated strain of DEs is determined by both the dielectric constant and the elastic modulus. Although the dielectric constant of silicone elastomer increased with increasing loading amount of lead magnesium niobate, the actuated strain did not increase as expected because the elastic modulus increased at the same time. The elastic modulus of silicone elastomer was decreased by reducing the crosslink density or adding plasticizing agent, leading to a visible increase in actuated strain. The optimized silicone dielectric elastomer filled with lead magnesium niobate gave a maximum actuated strain of 7.4% at 45 kV/mm, which is much larger than the literature value of 0.1% for piezoceramic.[22]

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