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Silicone Elastomers with High-Permittivity Ionic Liquids Loading

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Abstract

The most obvious challenge facing current dielectric elastomers (DEs) is the high driving voltages necessary to activate them, and so an effective way to overcome this shortcoming is to increase their dielectric permittivity. Herein, high-permittivity dielectric elastomer materials were prepared by synthesising silicone elastomer loaded with ionic liquids (ILs). The influence of the structure and the amounts of ILs on the material properties was discussed, and important properties for material applications as DEs, such as dielectric permittivity, gel fraction and mechanical properties, were also investigated. It was found that 1-butyl-3-methylimidazolium hexafluoroantimonate (BmimSbF₆) is the most suitable IL for the given system. The dielectric permittivity of the material with 90 phr BmimSbF₆ was 3.2 times higher than that of the pristine silicone elastomer, while the dielectric permittivity of pure silicone elastomer and elastomer loaded with ILs decreased in line with increased temperature in all cases. The Young's modulus decreased in line with the increasing amount of BmimSbF₆ in the elastomer, as expected. A simpler figure of merit (F_{om}^*) for actuators was used, and the F_{om}^* of the elastomer with a 90 phr IL loading was 10.40, thereby indicating that the material has a great advantage when used in actuators.

Keywords: Dielectric elastomer, Ionic liquids, Permittivity, Temperature-dependency

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Introduction

Dielectric elastomers (DEs), which consist of soft and thin elastomer films sandwiched between compliant electrodes, are well-known materials with a large variety of novel and advanced electromechanical applications, namely as actuators, sensors and generators.^[1-4] The popularity of DEs is due to their many favourable properties, which include flexibility, low weight, high electrical and mechanical breakdown strength and elasticity, as well as great stability with respect to a large range of chemicals.^[5, 6] Polydimethylsiloxane (PDMS) elastomers are one of the most commonly used materials for DEs, as they can be operated at a wide frequency range and offer high efficiency and fast response times.^[7-9] However, the most obvious challenge facing current PDMS elastomers is that they possess low dielectric permittivity and need high driving voltages to activate them.^[10, 11]

One effective way to overcome this shortcoming is to increase the dielectric permittivity of DE materials while keeping the Young's modulus constant.^[4] The most common method utilised to improve the dielectric permittivity of silicone elastomer involves blending a PDMS with high-permittivity fillers, the most common of which is in the form of metal oxide fillers, such as TiO_2 ,^[12, 13] Al_2O_3 ^[14] and BaTiO_3 .^[15, 16] A number of conductive fillers have also been employed, including carbon nanotubes,^[17] graphite^[18] and graphene,^[19] amongst other solutions, and they may also be blended with polymers. While these methods are certainly efficient ways of increasing dielectric permittivity, they can also lead to large dielectric losses and low breakdown strength. Furthermore, the Young's moduli of elastomers with fillers are always increased, which is often to a greater extent than dielectric permittivity, and thus no overall system improvement is forthcoming.^[4] It is therefore necessary to find new fillers to increase dielectric permittivity while ensuring losses remain constant.

Ionic liquids, as with polymer material fillers, have garnered interest in recent years, due

to their excellent properties, such as high dielectric permittivity, high conductivity, stability, nonvolatility and nonflammability.^[20-26] Promising results relating to ionic liquids as fillers for enforcing polymer materials have been published. Taylor et al.^{,[27]} for instance, synthesised fully-zwitterionic co-polymer scaffolds for ionogel electrolytes by using 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EmimTFSI) as a filler, resulting in high ionic conductivity. The results reported by Horowitz et al.^[28] also showed that the addition of EmimTFSI can increase capacitance and ionic conductivity, whilst Kusuma et al.^[29] found that ionic liquids with the least basic anion TFSI⁻ and aromatic cations containing an acidic proton provided the most stable and miscible ion gels. The PDMS-supported ion gels with ionic liquids as a filler exhibited favourable ionic conductivity and excellent mechanical behaviour.^[6] Although there have been extensive studies on ionic liquids as polymer fillers, very few articles report on applying ionic liquids in PDMS, in order to increase dielectric permittivity.

In this article, five ILs will be selected and added as fillers into silicone elastomers. The effects of the ILs' structure on the cross-linking efficiency of elastomer will then be analysed, and the dielectric properties of films with different amounts of IL loading, such as dielectric permittivity, dielectric losses and conductivity, will also be tested, to investigate the influence of IL amounts on dielectric elastomer properties. Dielectric permittivity and dielectric losses at different temperatures will also be investigated in this work, as well as the mechanical properties of films with IL loading. A simpler figure of merit for actuators will be used to evaluate the performance of elastomer materials as actuators.

2. Experimental

2.1 Materials and methods

Vinyl-terminated PDMS, DMS-V31 ($M_n = 28000 \text{ g mol}^{-1}$) and a cross-linker with hydride-functional HMS-301 ($M_n = 1950 \text{ g mol}^{-1}$) were purchased from Gelest Inc, USA. The silicone dioxide amorphous hexamethyldisilazane-treated particles (SIS6962.0) were obtained from Fluorochem, Belgium, and the platinum cyclovinylnmethyl siloxane complex catalyst (511) was acquired from Hanse Chemie, Germany. 1-butyl-3-methylimidazolium hexafluoroantimonate (BmimSbF₆), 1-allyl-3-methylimidazolium chloride (AmimCl), 1-ethyl-3-methylimidazolium diethylphosphate (EmimDEP), 1-ethyl-3-methylimidazolium acetate (EmimAc) and 1-2-hydroxyethyl-3-methylimidazolium chloride (HOEmimCl) were purchased from Chengjie Chemicals Ltd, China. The inhibitor Pt88 was acquired from Wacker Chemie AG, Germany. The structure of the PDMS and ILs can be seen in **Figure 1** and **Figure S1**.

Figure 1 PDMS and IL structures used in this work.

2.2 Preparation of elastomer/ionic liquids films

Vinyl-terminated PDMS, DMS-V31 (5g, 0.18 mmol), 8-functional cross-linker (0.1045g, 0.0536 mmol) and treated silica particles (25 wt%) were mixed with an inhibitor (1 wt%, Pt88) on a FlackTek Inc. DAC 150.1 FVZ-K SpeedMixer™. The catalyst (511) (15 ppm) was then added and the mixture was speedmixed, following which the different phr ionic liquid

was added to the mixture and mixing was performed again. The phr (parts per hundred rubber) unit is often used due to its simplicity when formulating, since it states the weight of a given substance per 100 g of rubber.^[30] For the control, the ionic liquid was not added. The uniform mixture was divided into two parts: one poured into a 1 mm-thick steel mould, and the other coated as 200 μm films on a glass substrate, using a film applicator (3540 bird, Elcometer, Germany). The films were cured in an oven at 80 °C.

2.3 Characterisation analysis

Dielectric properties determination. Dielectric relaxation spectroscopy (DRS) was carried out using a Novocontrol Alpha-A high-performance frequency analyser (Novocontrol Technologies GmbH & Co) operating in the frequency range 10^{-1} to 10^6 Hz at different temperatures and with a low electrical field (about 1 V mm^{-1}). The thickness of the tested samples was 1 mm, and the diameter was 20 mm.

Determination of gel fractions. The gel fractions were determined from the previously reported procedure.^[31] The film sample (about 200 mg) was immersed in chloroform (10 mL) at room temperature for 48 h, and the chloroform was then replaced every 24 h. The solvent was decanted off and the films were washed several times with fresh solvent. Finally, the samples were dried for 48 h under ambient pressure at room temperature. The BmimSbF₆ is immiscible with chloroform. It is evident from the FT-IR spectra of the extraction solutions that the release of BmimSbF₆ during the extraction can be neglected. The FT-IR spectra of the elastomers after extraction also show that BmimSbF₆ still loaded into the elastomers. The details can be seen in **Figure S2** and **Figure S3**. Gel fractions were calculated using the following equation:

$$W_{gel} = \frac{m_e - m_{IL}}{m_0 - m_{IL}} \quad (1)$$

where m_e is the weight after extraction and drying, m_0 is the initial weight of the sample and m_{IL} is the weight of IL in the initial sample. It is assumed that BmimSbF₆ is not released during the extraction. The amount of bonded and non-bonded species in the silicone networks can be elucidated by the gel fraction.

FT-IR properties determination. FT-IR spectra of the samples were acquired in the wavenumber range 400-4000 cm⁻¹, using a PerkinElmer Spectrum One model 2000 Fourier Transform Infrared apparatus equipped with a universal attenuated total reflection accessory on a ZnSe/diamond composite. Spectra were obtained via 32 scans and at a resolution of 4 cm⁻¹. All the spectra were baseline-corrected.

Electrical breakdown strength determination. Electrical breakdown tests were performed on an in-house-built device which was manufactured based on international standards (IEC 60243-1 (1998) and IEC 60243-2 (2001)). Film thicknesses were measured by using microscopy of cross-sectional cuts. An indent of less than 5% of sample thickness was applied to ensure that the spherical electrodes were in contact with the sample. The breakdown strength was measured by applying a stepwise increasing voltage (50-100 V step⁻¹) at a rate of 0.5 s⁻¹ steps s⁻¹. Each sample was tested 12 times in parallel and an average of these values was given as the breakdown strength of the sample.

Mechanical properties determination. The tensile stress-strain behaviour of the elastomers was measured using a material tester (Instron 3340 materials testing system, INSTRON, US). Samples 60 mm in length and 6 mm width were placed between two clamps and initially separated by a distance of 30 mm. The test specimen was elongated uniaxially at 50 mm min⁻¹ with respect to length. Each composition was subjected to three tensile measurements, which were then averaged.

Figure of merit. The performance of dielectric elastomer actuators (DEAs), when a constant potential is applied, is expressed in a single parameter, a so-called ‘figure of merit’, which

provides guidance for the elastomer performance optimisation of dielectric elastomer actuators. In the work by Sommer-Larsen et al.,^[32] the figure of merit for a given dielectric elastomer was described as:

$$F_{om}^{traditional}(DEA) = \frac{3\varepsilon_r\varepsilon_0 E_B^2}{Y} \quad (2)$$

where ε_0 is vacuum permittivity (a constant equal to approximately 8.854×10^{-12} F m⁻¹), ε_r is the dielectric permittivity of the elastomer, Y is the Young's modulus and E_B is electrical breakdown strength, which is the maximum applicable voltage for a film of a given thickness. But, in many instances a given voltage will be used for a given product, for example a particular battery. Therefore, a simpler figure of merit for actuators was used in this work. The equation for the simpler figure of merit is given by:^[30]

$$F_{om}^*(DEA) = \frac{\frac{\varepsilon_r}{Y}}{\frac{\varepsilon_{r,0}}{Y_0}} = \frac{\varepsilon_r}{\varepsilon_{r,0}} \frac{Y_0}{Y} \quad (3)$$

where $\varepsilon_{r,0}$ is the dielectric permittivity of the reference material value and Y_0 is the Young's modulus of the reference material value. The equation for the simpler figure of merit states the actuation strain improvements for a certain applied electrical field below the electrical breakdown strength of the given elastomer.

Scanning electron microscopy (SEM) observation. The morphology of the samples was investigated with an FEI Quanta 200 ESEM (Thermo Fisher Scientific, USA) scanning electron microscope, equipped with a field emission gun. The samples were coated in 5 nm-thick gold by means of a sputter coater (Q150R ES, Quorum Technologies, UK) under vacuum condition and a current of 40 mA for 10 seconds. The sample's cross-section was detected with a secondary electron detector (SE) for an incident electron beam of spot 3.5 accelerated to 5 k eV. The samples were first immersed in liquid nitrogen for a few minutes then broken and deposited on the aluminium SEM holder.

3. Results and discussion

3.1 Effect of ionic liquids on elastomer materials

As reported previously, the addition of a chlorine functional group can increase the dielectric permittivity of elastomer materials.^[10] The ionic liquids AmimCl and HOEtMimCl were selected herein as fillers for the elastomer materials. EmimDEP, EmimAc and BmimSbF₆ were considered based on the work of Kusuma et al.^[29] and Horowitz et al.^[6] From **Table S1**, it is evident that a cured film was only obtained upon adding BmimSbF₆ as a liquid filler to the elastomer material. The films with AmimCl, HOEtMimCl, EmimDEP and EmimAc loading did not cure at 80 °C, which may be due to the halogen ions and acetate ions causing the catalyst to deactivate.^[33, 34] The amount of ionic liquid in the system is 1 phr. The effect of ionic liquid on dielectric properties of elastomer materials was investigated in this article by using BmimSbF₆ as the liquid filler.

3.2 Ionic liquid in elastomer materials

FT-IR spectra were investigated to verify if BmimSbF₆ loaded successfully into the elastomer materials. As illustrated in **Figure 2**, all films with a BmimSbF₆ loading show distinctive C-H and N-H stretchable peaks at approximately 3200 cm⁻¹ and 3180 cm⁻¹, respectively, and all of them display the characteristic peaks of an imidazole ring at 1580 cm⁻¹. Enlarged FT-IR spectra at the wavenumber region running from 3300 cm⁻¹ to 3100 cm⁻¹, and from 1700 cm⁻¹ to 1500 cm⁻¹, are also shown in **Figure 2**. The imidazole peaks of 90 phr BmimSbF₆ are sharper than those of 1 phr BmimSbF₆, thereby confirming the higher amount of BmimSbF₆ in this material. Furthermore, the SEM images show that the ionic liquid well dispersed in the silicone network (**Figure S4**).

Figure 2 FT-IR spectra of films with different amounts of BmimSbF₆ loading.

3.3 Effect of ionic liquid on dielectric properties

Effect of ionic liquid content. Dielectric spectroscopy tests over a wide frequency range, from 10^{-1} Hz to 10^6 Hz, were performed in order to determine the effect of ionic liquid content on dielectric properties. In **Figures 3**, the dielectric relaxation spectra are shown along with details on the frequency-dependent storage permittivity, loss permittivity, conductivity and loss tangent of films with different BmimSbF₆ loadings, as well as the pure film. The storage permittivity and loss tangent at 10^6 Hz and 10^{-1} Hz are presented in **Table 1**.

Compared to the pure PDMS film, a significant increase in dielectric permittivity for all films with BmimSbF₆ loading is observed. The dielectric permittivity of elastomers with BmimSbF₆ loading increased in line with an increasing amount of BmimSbF₆, while dielectric permittivity at 10^6 Hz increased from 2.37 for the pure film up to 7.53 for the

sample with 90 phr BmimSbF₆ loading. This means that the dielectric permittivity of an elastomer with 90 phr BmimSbF₆ loading has increased by 2.2 times compared with the pure PDMS. It should be noted that the dielectric permittivity of all samples exhibited no significant changes when the frequency was changed, one possible explanation for which may be that the dielectric response depends mainly on bulk polarisation processes in materials with ILs.^[7] The dielectric loss of elastomers with BmimSbF₆ loading is slightly more pronounced in the frequency range 10⁰ Hz to 10⁻¹ Hz, which is due to Maxwell polarisation.^[35] In line with this more severe loss, an increase of Tan δ occurs in the same frequency region. It is notable from **Figure 3** that the conductivity of elastomer film is not changed significantly by increasing the content of ionic liquid. Furthermore, samples with BmimSbF₆ loading show slightly higher electric conductivity at a low frequency, albeit overall conductivity is considered to be exceptionally low for all of the investigated samples.

Figure 3 Storage permittivity (a), loss permittivity (b), conductivity (c) and tan δ (d) of films

with different amounts of BmimSbF₆ loading at room temperature.

Table 1 Dielectric properties of elastomer materials at room temperature.

Samples	Permittivity at 10 ⁶ Hz	Permittivity at 10 ⁻¹ Hz	Tan δ at 10 ⁶ Hz	Tan δ at 10 ⁻¹ Hz
Pure	2.37	2.39	3.67×10 ⁻⁴	9.62×10 ⁻³
1 phr BmimSbF ₆	2.83	2.89	1.13×10 ⁻⁴	1.70×10 ⁻¹
5 phr BmimSbF ₆	3.23	3.31	5.86×10 ⁻⁴	1.41×10 ⁻¹
10 phr BmimSbF ₆	3.35	3.46	1.67×10 ⁻³	1.93×10 ⁻¹
30 phr BmimSbF ₆	4.52	4.64	1.64×10 ⁻³	1.97×10 ⁻¹
50 phr BmimSbF ₆	5.53	5.71	2.35×10 ⁻³	1.35×10 ⁻¹
70 phr BmimSbF ₆	6.32	6.43	2.74×10 ⁻³	2.97×10 ⁻¹
90 phr BmimSbF ₆	7.53	7.61	3.07×10 ⁻³	1.66×10 ⁻¹

Effect of temperature. The stability of the dielectric elastomer between -40 °C and 100 °C is important for advanced electromechanical applications, so the dielectric permittivity of pure PDMS-, BmimSbF₆- and 90 phr BmimSbF₆-loaded elastomers were tested, to study the effect of temperature on dielectric permittivity.

As shown in **Figure 4**, pure BmimSbF₆ has very high dielectric permittivity, which increased slightly in reaction to increased temperature. There is a characteristic peak of dipolar relaxation in dielectric loss in the frequency region between 10³ to 10⁶ Hz, and the higher the temperature, the steeper the relaxation step. From the results presented in **Figure 4**, it is evident that the dielectric permittivity of the pure PDMS film and the elastomer with 90

phr BmimSbF₆ loading decreased following a rise in temperature. Silicone elastomer materials have the opposite effect of pure BmimSbF₆, due to the different polarisation types of elastomer and BmimSbF₆, i.e. BmimSbF₆ possess ion displacement polarisation, while silicone elastomer has relaxation polarisation. Vucong et al.^[36] also reported that the dielectric permittivity of silicone elastomers decreased when the temperature increased. Although the dielectric permittivity of the elastomer with 90 phr BmimSbF₆ loading decreased in line with a rise in temperature, dielectric permittivity at 100 °C is still higher than for the pure PDMS. These results indicate that the addition of ionic liquid did not cause a change in the effect of temperature on dielectric permittivity. Furthermore, the DSC curves of pure PDMS, PDMS with 10 phr and 90 phr BmimSbF₆ respectively loading show that there are no phase transitions in the elastomers between -40 °C and 100 °C (**Figure S5**).

Figure 4 Dielectric permittivity of pure BmimSbF₆ (a), tan δ of pure BmimSbF₆ (b), dielectric permittivity of pure PDMS (c), tan δ of pure PDMS (d), dielectric permittivity of film with 90 phr BmimSbF₆ loading (e) and tan δ of film with 90 phr BmimSbF₆ loading.

3.4 Effect of ionic liquid on mechanical properties

Gel fraction. In order to illustrate the amount of bonded (gel fraction) and non-bonded (sol fraction) species in the elastomer network, the gel fractions of the films were investigated through swelling experiments with chloroform. Here, the release of BmimSbF₆ during the extraction can be neglected. The gel fractions were determined from **Equation 1**. It is notable in **Figure 5** that the gel fractions decreased in line with an increased amount of BmimSbF₆ in the elastomer. The gel fractions are summarised further in **Table 2**. The lowest gel fraction was obtained for the film with 90 phr BmimSbF₆ loading, possibly due to the slow curing of the film, thus indicating that not all reactive end groups on the PDMS react, which leaves larger fractions of non-bonded substructures in the networks. The result of the gel fraction also suggests that there is a slight inhibition in terms of cross-linking efficiency when adding BmimSbF₆.

Figure 5 Gel fractions of films with different amounts of BmimSbF₆ loading. Gel fractions were determined from **Equation (1)**.

Young's modulus and tensile strain. Samples with various amounts of BmimSbF₆ incorporated into PDMS were tested, in order to analyse the effect of ionic liquid on mechanical properties. The mechanical behaviour of V31 PDMS was investigated for reference purposes. The results are shown in **Figure 6**, where it can be seen clearly that the

pure elastomer exhibits the highest Young's modulus. The Young's modulus of elastomers with BmimSbF₆ loading decreased in line with the increasing amount of BmimSbF₆, as expected due to dilution of the network.

Figure 6 Young's modulus of films with different amounts of BmimSbF₆ loading at room temperature.

As illustrated in **Figure 7**, the tensile strain of elastomer changes only slightly compared to the pure PDMS film when the loading amount of BmimSbF₆ is below 50 phr. The tensile strains of elastomers with 70 phr and 90 phr BmimSbF₆ loading exhibit a small decrease. The Young's modulus and tensile strain of elastomers are summarised further in **Table 2**. All of the films display typical linear elastic behaviour up to strains of around 20%, as shown in **Figure S6**.

The dielectric and tensile properties of the elastomers after extracting the sol fraction were investigated. As shown in **Figure S7**, the dielectric permittivity of the pure PDMS and elastomer with 10 phr BmimSbF₆ loading before and after extracting the sol fraction exhibited no significant changes within the measured frequency range 10⁻¹ to 10⁶ Hz. Similarly, the dielectric permittivity of the elastomer with 90 phr BmimSbF₆ loading before

extracting the sol fraction showed almost frequency-independent. While it can be noted that an obvious relaxation appeared for the elastomer after extracting the sol fraction in the low frequency range 0.1-10 Hz, which is due to the enhancement of the dipolar group mobility after extracting the larger sol fraction that increases the polarization in the network at low frequency. The Young's modulus, tensile stress and strain of all the elastomers were increased after extracting the sol fraction (**Figure S8**). This is due to the removal of the sol fraction in the network which makes the elastomer tougher and leads to the enhanced tensile properties.

Figure 7 Tensile strain of films with different amounts of BmimSbF₆ loading at room temperature.

Figure 8 Viscous losses of films with different amounts of BmimSbF₆ loading at room temperature.

Table 2 Young's modulus, tensile strain, viscous losses and gel fraction of films with different amounts of BmimSbF₆ loading.

Samples	Young's modulus (MPa)	Tensile strain (%)	Tan δ_{visc} at 10 ⁻¹ Hz	Gel fraction (%)
Pure PDMS	0.49 ± 0.07	318 ± 30	0.02	100
1 phr BmimSbF ₆	0.45 ± 0.04	315 ± 20	0.02	97
5 phr BmimSbF ₆	0.42 ± 0.09	301 ± 9	0.03	92
10 phr BmimSbF ₆	0.40 ± 0.01	297 ± 10	0.04	86
30 phr BmimSbF ₆	0.34 ± 0.06	295 ± 20	0.07	79
50 phr BmimSbF ₆	0.27 ± 0.06	299 ± 9	0.09	77
70 phr BmimSbF ₆	0.2 ± 0.05	267 ± 22	0.11	70
90 phr BmimSbF ₆	0.15 ± 0.03	240 ± 10	0.13	64

The viscoelastic properties of the films were measured by linear shear rheology, and the resulting viscous losses ($\tan \delta_{\text{visc}}$) are shown in **Figure 8** and **Table 2**. The elastomers became increasingly softer in line with an increasing amount of BmimSbF₆, and the viscous losses also increased in line with an increasing amount of BmimSbF₆. This was expected, due to the larger amounts of non-bonded structures in the networks giving rise to viscoelastic relaxation. These viscous losses, however, remained very low with the amount of BmimSbF₆ up to 90 phr.

3.5 Effect of ionic liquid on the figure of merit for actuators

In order to evaluate the performance of elastomers with BmimSbF₆ loading as actuators, the electrical breakdown strength (E_B) and Sommer-Larsen figure of merit (F_{om}) were tested in this work. In **Table 3**, the E_B and F_{om} of elastomers with BmimSbF₆ loading decreased with an increasing amount of BmimSbF₆. But, in many instances a given voltage will be used for a given product, for example a particular battery. Therefore, a simpler figure of merit (F_{om}^*) for actuators was used in this work. From the F_{om}^* equation, the elastomer performance as an actuator depends on dielectric permittivity and the Young's modulus, i.e. higher dielectric permittivity and a low Young's modulus will be more advantageous in this regard.

Figure 9 Figure of merit of films with various amounts of BmimSbF₆ loading.

Table 3 Figure of merit of films with various amounts of BmimSbF₆ loading.

Samples	Permittivity at 10 ⁻¹ Hz	Young's modulus (MPa)	E _B (V/μm)	F _{om}	F _{om} [*]
Pure PDMS	2.39	0.49	55	1.00	1.00
1 phr BmimSbF ₆	2.89	0.45	40	0.70	1.32
5 phr BmimSbF ₆	3.31	0.42	30	0.48	1.62
10 phr BmimSbF ₆	3.46	0.40	24	0.34	1.77
30 phr BmimSbF ₆	4.64	0.34	19	0.33	2.80
50 phr BmimSbF ₆	5.71	0.27	13	0.24	4.33
70 phr BmimSbF ₆	6.43	0.2	10	0.22	6.59
90 phr BmimSbF ₆	7.61	0.15	7.5	0.19	10.40

The figures of merit of elastomers with different amounts of BmimSbF₆ can be seen in

the **Figure 9**. The detailed data for F_{om}^* can also be found in **Table 3**. It is clear that the F_{om}^* of elastomers with BmimSbF₆ loading increased in line with the increasing amount of BmimSbF₆. The F_{om}^* of the elastomer with 90 phr BmimSbF₆ is 10.40, which means this material has high potential for use as an actuator.

Conclusions

In summary, IL structures affect the cross-linking reaction of PDMS, and Cl⁻, DEP⁻ and Ac⁻ can deactivate the catalyst. Dielectric permittivity increases in line with increasing amounts of BmimSbF₆, while the dielectric permittivity of a film with 90 phr BmimSbF₆ loading was 3.2 times higher than that of the pristine silicone elastomer. Dielectric losses and conductivity also experience a slight increase compared with the reference film, albeit they remain low. Compared to the reference elastomer, elastomers with IL loading became increasingly softer, in line with an increasing amount of BmimSbF₆. The gel fraction of the elastomer decreased with an increase in ionic liquid content. The simpler figure of merit of an elastomer with 90 phr BmimSbF₆ loading is 10.40, thus indicating that this material has high potential for use as an actuator.

The dielectric permittivity of pure silicone elastomer and elastomers with IL loading decreased in all cases when the temperature increased, while the dielectric permittivity of a film with 90 phr BmimSbF₆ loading was still higher than that of the pristine silicone elastomer, which means this elastomer can be used over a wide range of temperatures.

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Supporting information

Supporting information is available.

Conflict of interest

The authors declare no conflict of interest.

References

- [1] S. Bauer, S. Bauer-Gogonea, I. Graz, M. Kaltenbrunner, C. Keplinger, R. Schwödiauer, *Adv. Mater.* **2014**, 26 (1), 149-162.
- [2] D. Chen, Q. Pei, *Chem. Rev.* **2017**, 117 (17), 11239-11268.
- [3] S. Rosset, H. R. Shea, *Appl. Phys. Rev.* **2016**, 3 (3), 031105.
- [4] R. Pelrine, R. Kornbluh, Q. Pei, J. Joseph, *Science* **2000**, 287 (5454), 836-839.
- [5] F. B. Madsen, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Macromol. Rapid Commun.* **2016**, 37 (5), 378-413.
- [6] A. I. Horowitz, M. J. Panzer, *Angew. Chem. Int. Ed.* **2014**, 53 (37), 9780-9783.
- [7] F. B. Madsen, L. Yu, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Polymer* **2014**, 55 (24), 6212-6219.
- [8] C. Löwe, X. Zhang, G. Kovacs, *Adv. Eng. Mater.* **2005**, 7 (5), 361-367.
- [9] P. Brochu, Q. Pei, *Macromol. Rapid Commun.* **2010**, 31 (1), 10-36.
- [10] F. B. Madsen, L. Yu, P. Mazurek, A. L. Skov, *Smart Mater. Struct.* **2016**, 25 (7), 075018.
- [11] L. Yu, F. B. Madsen, S. Hvilsted, A. L. Skov, *RSC Adv.* **2015**, 5 (61), 49739-49747.
- [12] H. Liu, L. Zhang, D. Yang, Y. Yu, M. Tian, *Soft Mater.* **2013**, 11 (3), 363-370.
- [13] S. Vudayagiri, S. Zakaria, L. Yu, S. S. Hassounah, M. Benslimane, A. L. Skov, *Smart Mater. Struct.* **2014**, 23 (10), 105017.

- [14] Y. Liu, L. Liu, Z. Zhang, J. Leng, *Smart Mater. Struct.* **2009**, 18 (9), 95024-95010.
- [15] G. Gallone, F. Galantini, F. Carpi, *Polym. Int.* **2010**, 59 (3), 400-406.
- [16] P. Lotz, M. Matysek, P. Lechner, M. Hamann, H. F. Schlaak, *Proceedings of SPIE - The International Society for Optical Engineering* **2008**, 6927, 692723-692723-10.
- [17] S. K. Yadav, I. J. Kim, H. J. Kim, J. Kim, S. M. Hong, M. K. Chong, *J Mater. Chem. C* **2013**, 1 (35), 5463-5470.
- [18] S. S. Hassouneh, A. E. Daugaard, A. L. Skov, *Macromol. Mater. Eng.* **2015**, 300 (5): 542-550.
- [19] A. Javadi, Y. Xiao, W. Xu, S. Gong, *J. Mater. Chem.* **2011**, 22 (3), 830-834.
- [20] S. K. Ameri, P. K. Singh, A. J. Angelo, M. J. Panzer, S. R. Sonkusale, *Adv. Electron. Mater.* **2016**, 2 (5), 1500355.
- [21] J. L. Bideau, L. Viau, A. Vioux, *Chem. Soc. Rev.* **2011**, 40 (2), 907-925.
- [22] S. J. Park, O. S. Kwon, H. L. Sang, H. S. Song, H. P. Tai, J. Jang, *Nano Lett.* **2012**, 12 (10), 5082-5090.
- [23] S. K. Ameri, P. K. Singh, S. R. Sonkusale, *Carbon* **2014**, 79 (1), 572-577.
- [24] N. Terasawa, *Sens. Actuators, B* **2018**, 257, 815-819.
- [25] S. Zhang, H. Feng, *Green Energy Environ.* **2016**, 1 (01), S2468025716300176.
- [26] Z. Zhang, X. Zhang, Y. Nie, H. Wang, S. Zheng, S. Zhang, *Sci. China Chem.* **2017**, 60 (7), 934-941.
- [27] M. E. Taylor, M. J. Panzer, *J Phys. Chem. B.* **2018**, 122(35), 8469-8476.
- [28] A. I. Horowitz, M. J. Panzer, *J. Mater. Chem.* **2012**, 22 (32), 16534-16539.
- [29] V. A. Kusuma, M. K. Macala, L. Jian, A. M. Marti, R. J. Hirsch, L. J. Hill, D. Hopkinson, *J. Membr. Sci.* **2017**, 545, 292-300.
- [30] A. L. Skov, L. Yu, *Adv. Eng. Mater.* **2018**, 20 (5), 1700762.
- [31] P. J. Madsen, L. Yu, S. Boucher, A. L. Skov, *RSC Adv.* **2018**, 8 (41), 23077-23088.

- [32] P. Sommer-Larsen, A. L. Larsen, *Smart Structures and Materials 2004: Electroactive Polymer Actuators and Devices (EAPAD)*, International Society for Optics and Photonics, **2004**, 5385, 68-78.
- [33] P. Forzatti, L. Lietti. *Catal. Today*. **1999**, 52 (2-3), 165-181.
- [34] E. B. Maxted. *Adv. Catal.* **1951**, 3, 129-178.
- [35] K. Goswami, F. Galantini, P. Mazurek, A. E. Daugaard, G. Gallone, A. L. Skov, *Smart Mater. Struct.* **2013**, 22 (11), 208-210.
- [36] T. Vucong, C. Jeanmistrail, A. Sylvestre, *Smart Mater. Struct.* **2012**, 21 (10), 5036.

A short summary

High-permittivity dielectric elastomer materials were prepared by synthesising silicone elastomer loaded with ionic liquids (ILs). The influence of the structure and the amounts of ILs on the material properties was discussed, and important properties for material applications as DEs were also investigated. The elastomer with IL loading has high potential for use as an actuator.

Silicone Elastomers with High-Permittivity Ionic Liquids Loading

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Table of content