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Incorporation of liquid fillers into silicone foams to enhance the electro-mechanical properties

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ABSTRACT

Silicone foams with and without liquid fillers (silicone oils of various types and glycerol, respectively) are synthesized and analyzed to be used as dielectric layers in capacitive sensors. A simple fabrication technique involving only four components i.e. Sylgard 184, glycerol, sodium hydroxide and ethanol is used to make these silicone foams after which they are filled with silicone oil or glycerol by soaking the foam in respective liquid. Mechanical and dielectric properties of the foams are examined. The oil reinforces the foam’s dielectric properties, softens the foam and improves its capacitive response, making it a very good dielectric material for fabricating capacitive pressure sensors. Compared to dry silicone foams, foams filled with – and swollen by – chloropropyl-functional silicone oil, show a low Young’s modulus (31 kPa), a high and stable relative dielectric permittivity of around 5, and a high capacitive response of 132% for an applied pressure of 12 kPa. The presence of oil stabilizes the soft foam and ensures that it does not buckle under high pressure.

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Supplemental data for this article can be accessed here.
1. Introduction

Dielectric elastomeric transducers (DETs) are versatile and constitute a promising technology for fabricating soft and stretchable actuators, generators, and sensors [1–3]. Crosslinked silicones, such as in particular polydimethylsiloxane (PDMS), are a popular dielectric material for fabricating DETs due to their high efficiency, reliability, and fast response times [4–6]. Silicone materials have been widely used in soft and flexible sensing technologies because of their low Young’s modulus, superior mechanical flexibility, biocompatibility, dielectric nature, and high transparency [7–9]. Lately, silicone foams with embedded pores are widely researched due to their many additional attractive features, such as light weight, high flexibility, superior insulating capabilities [10], and their highly sensitive capacitive response to an applied pressure [11, 12]. Such unique properties have promoted silicone foams as the new alternative for fabricating soft, flexible, and wearable pressure sensors and as human-machine interfaces [13]. Silicone foams possess excellent mechanical, thermal, and structural properties, in comparison with conventional foams [14, 15]. However, the responsiveness of silicone foams is related to multiple variables. The compressibility is a very important property when the silicone foams are used in sensing applications, as the changes in their dielectric properties under compression increase when the flexibility of the foam is preserved [16]. Moreover, in reality other factors, e.g. microstructure and mechanical properties, also affect the foams’ sensitivities.

Silicone foams are expensive compared to conventional foams due to the high production costs and hence are not used as widely as e.g. polyurethane foams [17]. Lately, 3D printable silicone foams from viscoelastic inks prepared by simply mixing sodium chloride with PDMS precursor gel have been introduced [18]. Using this technique, PDMS foams with unprecedented hyper elasticity, compressibility, and hierarchical porosity can be produced after salt leaching and solvent removal [18]. Nonetheless, this technique involves sacrificial particles and the process is not conducive for mass production. A facile way to make silicone foams by use of glycerol [17, 19] is used in the current study, which does not involve the usage of sacrificial particles like sugar or salt [11, 12, 20], hence making the process less tedious and suitable for large scale and economic production.

As a dielectric layer in a sensor, silicone foams are more sensitive in comparison to silicone elastomers [21]. Silicone elastomers exhibit non-linear deformation and are incompressible, due to which their surfaces are either patterned or micropores are introduced, to improve their sensitivity when used as a dielectric layer in sensors [21]. Addition of liquid fillers can act as a softener that effectively decreases the elastic modulus of the elastomer materials [22–25]. Recently, the studies on silicone foams filled with pharmaceutical products and citric acid monohydrate (CAM) solution have been reported [26, 27]. Based on this notion, liquid fillers are added to the silicone foam in the present study to soften them further and to improve their sensitivity. The foams are filled with either silicone oil, or chloropropyl functional silicone oil or glycerol and their effect on the foam’s Young’s modulus (Y), relative dielectric permittivity ($\varepsilon_r$) and breakdown strength ($E_{\text{BD}}$) is analyzed. We also show that apart from softening the foams, the fluid fillers can also modify the dielectric properties of the foam. Recently, silicone foams were modified with carbon nanotube (CNT) fillers to fabricate piezo resistive pressure sensors [20]. Apart
from sensor application, dielectric elastomer foams can also be applied as actuators. Lately, an electromechanical foam (EFOAM) material (Expancel microsphere 031DUX 40) capable of acting as an electromechanical transducer with integrated functions has been investigated [28]. Polyurethane foams have also been used to fabricate soft pneumatic actuators applied in a direct cardiac compression (DCC) device design, a type of implanted mechanical circulatory support for cardiac compression [29].

2. Experimental

2.1. Materials

The silicone elastomer used in this study is the two-component Sylgard 184 silicone (abbreviated as S184), consisting of polymer base (vinyl-functional PDMS and platinum catalyst) and curing agent (vinyl-functional PDMS and crosslinker), purchased from Dow Corning, US. Glycerol was provided by Emmelev A/S, Denmark. Sodium hydroxide (NaOH) was purchased from Sigma Aldrich, Denmark. Chloropropyl-functional silicone oil (Cl-silicone oil), LMS-152 ($M_n \approx 8750$ g mol$^{-1}$), was acquired from Gelest Inc., US. Linear silicone oil (Powersil Fluid TR50) and conductive liquid silicone rubber (ELASTOSIL® LR 3162 A/B) were purchased from Wacker Chemie AG, Germany. Ethanol was purchased from VWR, Denmark. All products were used as received.

2.2. Sample preparation

The varied preparation parameters of the investigated samples are listed in Table S1 in the Supplementary Information (SI). Consequently, an optimized foam with homogeneous micromorphology prepared through the below optimized parameters was chosen for the subsequent studies. The optimized foam was prepared as follows. Glycerol with 1 wt.% NaOH and 1 wt.% ethanol was first prepared by uniformly dissolving 0.1 g NaOH and 0.1 g ethanol in 10 g glycerol. Then, 1.2 g of the above glycerol solution was mixed with 9.09 g of S184 polymer base and 0.91 g of S814 curing agent using a dual asymmetric centrifuge SpeedMixer (DAC 150.1 FVZ-K, Synergy Devices Ltd, UK) at 3500 revolutions per minute (rpm) for 25 s. High shear forces produced by the speed-mixer resulted in the formation of glycerol-in-silicone emulsion, which was subsequently poured into a round aluminum dish of approximately 50 mm diameter and 15 mm thickness and cured for 30 min at 120 °C. The obtained foam was then left at room temperature for two days, in order for eventual post-curing to take place. The foam with glycerol of approximately 50 mm diameter and 15 mm thickness was immersed in deionized water (~500 mL) at room temperature for 48 h. The deionized water was replaced after 24 h. Afterward, the foam was washed several times with deionized water, subsequently dried in oven at 80ºC for 48 h until the weight was constant. The obtained dry foam was immersed in glycerol or linear silicone oil or Cl-functional silicone oil (~100 mL) for a total of 48 h (the glycerol or oil was replaced after the first 24 h). Subsequently the excess glycerol or oil was removed after 48 h. Then the foam with glycerol, foam with silicone oil, or foam with Cl-silicone oil was obtained.


2.3. Methods

Optical characterization of the foams was performed using an optical microscope (Leica DMLB, Germany) connected to a microscope camera (Leica MC190 HD, Germany).

The Young’s moduli of the various foams were obtained from compression measurements at room temperature by using an ElectroForce mechanical test machine (ElectroForce 3200, TA Instruments, USA) using a load cell of 50 N. A sample of 20 mm diameter and 15 mm thickness was placed between two stainless steel parallel plates of 20 mm. The uniaxial compression rate was applied in a manner of displacement control. The test specimen was compressed up to 15% strain at constant frequency of 1 Hz and compressive strain rate of 0.15 s$^{-1}$. Young’s moduli@5% (the slope of the stress-strain curve of the test specimen within the linear elastic regime of its uniaxial deformation) were obtained from the tangent of the stress-strain curves at 5% strain. Each sample was subjected to three measurements, which were then averaged.

Rheological characterization of the prepared foams was performed with a hybrid rheometer (Discovery HR-1, TA Instruments, US) set to 1% controlled strain mode, thus ensuring that measurements are within the linear viscoelastic regime. Measurements were performed with a parallel plate geometry of 20 mm at 25 °C, with a normal force of 1 N and in the frequency range 100–0.01 Hz.

Dielectric relaxation spectroscopy (DRS) was performed on a Novocontrol Alpha-A high-performance frequency analyzer (Concept 40 Top Class System, Novocontrol Technologies GmbH & Co, Germany) operating in the frequency range $10^{-1}$-$10^6$ Hz at room temperature and low electrical field (~1 V/mm). The diameter of the tested 15 mm thick samples was 20 mm.

Electrical breakdown tests were performed on an in-house-built device based on international standards (IEC 60243–1 (1998) and IEC 60243–2 (2001)) [30]. Sample thicknesses were measured using vernier caliper. The distance between the spherical electrodes was set accordingly using a micrometer stage and gauge. An indent of less than 5% of sample thickness was then applied to ensure that the spheres were in contact with the sample. The test specimen was slid between the two spherical electrodes (diameter of 20 mm), and the electrical breakdown strength ($E_{BD}$) was measured at the point of contact.

Figure 1. Experiment setup for measuring the impedance of the foam with applied force at 1 V applied voltage for 1 minute at room temperature.
by applying a stepwise increasing voltage (50–100 V step\(^{-1}\)) at a rate of 0.5–1 steps s\(^{-1}\). Each sample was subjected to 6 breakdown measurements at room temperature, and an average of these values was given as the \(E_{BD}\) of the sample.

For each test specimen, the impedance signature was measured using KEYSIGHT E4990A impedance analyzer (Keysight Technologies, US) operated at 20 Hz (the lowest available frequency of this analyzer). Figure 1 shows the experimental setup of the test specimen connected to the impedance analyzer during the impedance measurement. All the foams were cut out to the same dimensions of approximately 40 mm diameter and 15 mm thickness. The conductive elastomer mixtures (ELASTOSIL® LR 3162 A/B, premixes A and B were uniformly mixed in the mass ratio 1:1) were coated on both top and bottom surfaces of the foam using a film applicator (3540 bird, Elcometer, Germany) with a 100 µm blade, and subsequently the specimen was cured at 80 °C for 2 hours. The dimension of the cured compliant electrodes was approximately 40 mm diameter and 100 µm thickness determined by optical microscope. Copper wires were used to connect the impedance analyzer to the test specimen. Multiple weights (0 to 1500 g at intervals of 250 g) were vertically fixed on the top of the test for applying axial pressure. Each specimen was tested at 1 V applied voltage for 1 minute at a specific applied pressure at room temperature.

3. Results and discussion

Schematic diagram of the chemical and physical processes taking place during foaming of the glycerol-silicone compositions and the post-treatment of silicone foams is shown in Figure 2. The optical micrographs of the 5 different foams (a) foam-original (abbreviated as Foam-ori), (b) foam-glycerol wash out (abbreviated as Foam-w), (c) foam-filled silicone

![Figure 2. Schematic diagram of the foaming processes of the glycerol-silicone compositions and the post-treatment of silicone foams.](image-url)
oil (abbreviated as Foam-sioil), (d) foam-filled Cl-silicone oil (abbreviated as Foam-cloil) and (e) foam-filled glycerol (abbreviated as Foam-gly) are shown in Figure 3 and are explained in the SI.

3.1. Comparison of mass and volume of the foams

Cylindrical samples of size 40 mm diameter and 15 mm thickness were cut out of the different foams and are compared to the original foam’s mass, volume, thickness and
The results are shown in Figure 4. The Foam-w is lighter by 50% compared to Foam-ori, which is predictable as the glycerol (100 phr) is washed out. As expected, the mass of foams filled with oils are higher than the Foam-ori. The Foam-sioil has a 100% increase in mass and Foam-cloil shows an 87% increase in mass compared to the Foam-ori as the oils swell the foam homogenously, besides filling up the pores. The Foam-gly shows a 37% higher mass compared to the Foam-ori. The other parameters like diameter, thickness and volume are subject to changes depending on the shrinkage of Foam-ori and oil leakage from the foams.

### 3.2. Young’s modulus

The Young’s moduli (Y) of the foams were determined through the tangent of the stress-strain loading curves at 5% strain in Figure 5, and the details on the prepared foams are listed in Table 1. Figure 5 contains the stress-strain curves from a cyclic loading-unloading test, indicating all the prepared foams have relatively low stress-strain hysteresis. The

![Figure 5. Compression stress-strain curves of the prepared silicone foams compressed up to 15% strain at constant frequency of 1 Hz at room temperature. The measurement was terminated at 15% strain since some of the foams started leaking oil/glycerol at higher strains due to the buildup of internal stresses in the foam structure.](image-url)

![Table 1. Properties of the prepared silicone foams. Young’s modulus was obtained from the tangent of the stress-strain curves at 5% strain. Compressive strength was the stress at 15% strain. Sensitivity was expressed as the relative capacitance change to an applied pressure of 12 kPa.](table-url)
Foam-ori shows a $Y$ of 109 kPa, which is still much lower than silicone foams made using other methods [20]. The Foam-cloil shows the smallest $Y$ of 31 kPa, as the oil self-lubricates resulting in the softest network. The presence of Cl-silicone oil swells and softens the Foam-cloil and decreases the $Y$ by almost 3 times compared to the Foam-ori [31]. The glycerol is insoluble in silicone and it does not soften the foam, therefore, Foam-gly has a higher stiffness ($Y \approx 82$ kPa). Moreover, when subjected to strain, the glycerol droplets oppose the movement due to the droplets getting a larger surface upon deformation. Silicone foams with low stiffness, like Foam-sioil and Foam-cloil will deform easily at small applied pressures. Thus, when this foam is used as a dielectric layer in a sensor it makes the sensor more sensitive. Surprisingly, the original foam remains the most rigid of all samples but this is believed to stem from small unblown glycerol compartments that introduces liquid stiffening. Upon washing and subsequent soaking not all structures are filled up.

### 3.3. Linear viscoelasticity

The storage modulus ($G'$) and loss factor ($\tan\delta$) of the fluid foams were determined. The results are presented in Figure 6. The Foam-sioil shows the highest $G'$ at lower frequencies and toward the higher frequencies Foam-w shows a higher $G'$. Though the $G'$ curves for all the foams are more or less similar, Foam-sioil and Foam-cloil show a lower $\tan\delta$, and lower viscous loss compared to the other foams indicating that Foam-sioil and Foam-cloil exhibit a more elastic behavior. The silicone oil and Cl-silicone oil swell the foam, making the foam-oil matrix act as a monolithic structure with more mechanical integrity/stability compared to Foam-gly (glycerol is insoluble in foam), Foam-w (foam contains air) and Foam-ori (foam is filled with glycerol and air). The data of $G'$ and $\tan\delta$ at 0.01 Hz is shown in Table S2 in the SI. At higher frequencies the $\tan\delta$ increases slightly indicating that the foam is more dissipative. During the shear rheology measurements, the glycerol leaks from the foam, increasing the air pockets, which changes the modulus behaviors of the tested foams.
3.4. Dielectric permittivity and electrical breakdown strength

The relative dielectric permittivity ($\varepsilon_r$) and dielectric loss tangents (tan$\delta$) of foams are shown in Figure 7. The Foam-cloil shows an enhanced and stable dielectric permittivity of approximately 5 over a large range of frequency ($10^{-1}$ to $10^6$ Hz). The Foam-gly shows an extremely high $\varepsilon_r$ at low frequencies. The Foam-ori also shows a high $\varepsilon_r$ of approximately 10 and a high tan$\delta$ at low frequencies. The $\varepsilon_r$ of the oil/glycerol filled foams presented here is higher than the $\varepsilon_r$ of dry silicone foams reported in previous studies, because the oil/glycerol has a higher dielectric permittivity than that of air [11,12]. Thus when used as the dielectric layer in a pressure sensor, the oil filled silicone foam with a higher $\varepsilon_r$, provides higher capacitance to the sensor in comparison to an air filled silicone foam (dry foam) [12]. Higher $\varepsilon_r$ values are also crucial if the silicone foams should be actuated but this is not the scope of the current study.

The $E_{BD}$ of the foams are shown in Figure 8. The Foam-cloil has a higher $E_{BD}$ than the Foam-ori or those filled with glycerol or silicone oil. Air has a low $E_{BD}$ of $\approx 3$V/µm [32] while that of RTV silicone is $\approx 50$V/µm [30]. Hence dry silicone foams will break down at low
voltages. Filling the silicone foams with high breakdown strength fluids can improve the overall $E_{BD}$ of the foam, though this parameter is not usually of concern for sensor applications. Furthermore, filling with similar dielectric permittivity materials prevents the buildup of charges on the internal surfaces. The buildup of charges manifests itself as high dielectric losses at low frequencies as seen for Foam-ori (air and silicone have different dielectric permittivities) and Foam-gly (glycerol and silicone have different permittivities).

3.5. Impedance measurements

The relative capacitance change of the foam specimens under different pressures is calculated from the impedance data in Table S3. The results are illustrated in Table S4 and Figure 9. The Foam-ori and Foam-w show only a negligible change in capacitance at an applied pressure of 0–12 kPa due to the almost pure silicone nature of the samples. At the same applied pressure (12 kPa) the Foam-gly shows 58% relative change in capacitance, while the Foam-cloil shows 132% relative change in capacitance which is more than double the sensitivity of Foam-gly. The combination of low $Y$ and high $\varepsilon_r$ of the Foam-cloil reflects in its high capacitive response compared to other foams. The relative capacitance change of Foam-cloil is also better than the performance of the silicone foams in previous studies [11,12] for an applied pressure of 12 kPa. The Cl-silicone oil increased the $\varepsilon_r$ and softened the foam, thereby improving the sensitivity of the silicone foam.

To further the discussion, it can be added that the oil that is filled in the foam, apart from modifying the properties of the foam, can also carry some functional materials for imparting additional properties to the foam matrix like making the foam thermo-, chemically and/or electrically responsive [33]. Such silicone foam sensors can be applicable for advanced touch panels providing more tactile interfaces and skin sensors for noninvasive monitoring [34]. The functional silicone foams provide great potential for novel applications by allowing for tunable

Figure 9. Relative capacitance change versus applied pressure for the different foam specimens at room temperature.
foam materials for specific devices. We believe that such soft flexible silicone foams with good dielectric properties can be applied as soft, compliant and lightweight dielectric electroactive sensors to enrich the sensorization revolution.

4. Conclusions

A simple technique for making silicone foams filled with silicone oil and glycerol has been shown. For the purpose of making sensors and possibly actuators, silicone foams filled with silicone oil show excellent mechanical and dielectric properties and higher capacitive response compared to dry silicone foams. From the present study it has been concluded that the silicone foam filled with chloropropyl-functional silicone oil was the softest and had the best dielectric properties and exhibited the highest capacitive response to an applied pressure. It can be concluded that the solubility of the fluid filler in the foam matrix softens the foam while retaining its mechanical stability. The presence of a functional silicone oil in the silicone foam improved the dielectric permittivity which increased its capacitive response. This work can serve as a starting point for fabricating dielectric elastomeric foams filled with functional liquids to enhance the mechanical and other intrinsic properties. Such liquid fillers may also prevent the ambient fluids from percolating into the foam which could interfere with the functioning of the foams.

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