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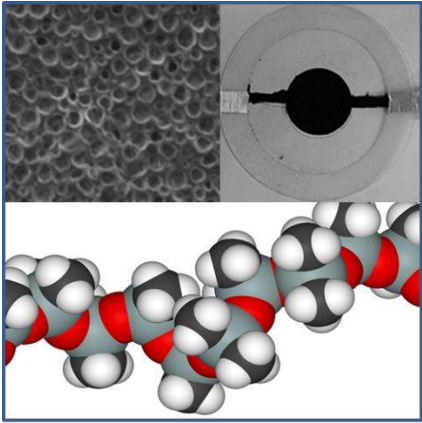
Review

The current state of silicone-based dielectric elastomer transducers

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Silicone elastomers are promising materials for dielectric elastomer transducers (DETs) due to superior properties such as high efficiency, reliability and fast response times. DETs consist of thin elastomer films sandwiched between compliant electrodes, and they constitute an interesting class of transducer due to their inherent lightweight and potentially large strains. For the field to progress towards industrial implementation, a leap in material development is required, specifically targeting longer lifetime and higher energy densities to provide more efficient transduction at lower driving voltages. In this review the current state of silicone elastomers for DETs is summarised and critically discussed, including commercial elastomers, composites, polymer blends, grafted elastomers and complex network structures. For future developments in the field it is essential that all aspects of the elastomer are taken into account, namely dielectric losses, lifetime and the very often ignored polymer network integrity and stability.



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1. Introduction

The search for materials that exhibit properties similar – or even superior – to the human muscle has been the focus of engineers and researchers for several decades. The challenge lies in the many excellent properties of human muscles, such as high energy densities and large, obtainable strains. Furthermore, human muscles generate linear motion, whereas currently used electric motors generate rotational motion.^[1-3] Another feature of human muscles is that they have self-repairing properties, which is also highly desired for soft transducers.

Polymers offer interesting prospects as smart materials for artificial muscles, as they are lightweight, noiseless and low in cost. Electroactive polymers (EAPs) consist of soft polymeric materials with relatively large energy densities, relatively fast response times and the ability to undergo large deformations when stimulated by electrical fields.^[4,5] EAPs can be divided into two main groups: ionic and electronic. Ionic EAPs respond to an electrical field through the diffusion of ions in a material. In addition, they generally require low driving voltages (as low as 1-2 V) but require an electrolyte, which means that encapsulating the aqueous environment is necessary. Furthermore, there is a need to maintain wetness, and it is difficult to maintain DC-induced displacements.^[6-9] However, recent developments^[10] have proven it possible to create semi-interpenetrating networks from polyionic liquids, which eliminates the need for an aqueous environment and thereby opens up the possibility of a wide range of applications where large forces are not needed. The advantages of electronic EAPs over their ionic counterparts include higher energy density, that they can be operated in air without major constraints, large actuation forces, rapid response times and long lifetimes. Their major disadvantage is that they require high driving voltages to actuate (typically 500 V to 10 kV),^[4,11] and so a great deal of research focuses on reducing this issue. Electronic EAPs can be divided further into subclasses, such as polymer electrets,^[12-14] electrostrictive graft elastomers^[15] and dielectric elastomers. In the field of electronic EAPs, dielectric elastomers are a very interesting class of material, due

1 to high obtainable actuation speeds, large strains and high work densities, a high degree of
2 electromechanical coupling and good overall performance.^[16,17] As a result of this unique
3 combination of properties, dielectric elastomers occupy a niche in transducer technologies,
4 mainly due to their low weight coupled with large strains. The focus of this review is therefore
5 exclusively on dielectric elastomers.
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10 Dielectric elastomers are promising materials for advanced electromechanical applications such
11 as actuators, generators and sensors, due to their simple and flexible working principle. They
12 consist of an elastomer film sandwiched between two thin and compliant electrodes, thereby
13 forming a capacitor capable of energy transduction. The electrodes can be made from a variety
14 of conducting materials such as silver and gold^[18,19] and carbon grease.^[17] For more details on
15 electrode systems an excellent recent review on electrode materials by Rosset and Shea^[20]
16 exists. In this review we refer to the system of elastomer and electrode as a ‘dielectric elastomer
17 transducer’ (DET). When an external voltage is applied to the electrodes, electrostatic forces
18 are created. Electrostatic pressure acting on the film squeezes the elastomer in thickness, and
19 as the elastomer is incompressible it consequently expands in planar directions. Electrical
20 energy, in this case, is thus converted into mechanical energy. The driving force for the
21 actuation process is the resulting reduction in charge density when the electrode area is
22 enlarged.^[21] When the external voltage is switched off, the elastomer film returns to its original
23 shape. The actuation working principle can be seen in **Figure 1**.
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46 Dielectric elastomers can also be used for generators to create electrical energy, if the DET is
47 stretched by an external force and electrical charges are placed on the film.^[22,23] When the DET
48 is allowed to relax, elastic stresses work against electrical field pressure, thereby increasing
49 electrical energy. In this process opposite charges on the two electrodes are pushed further apart
50 as the film contracts and increases in thickness, while similar charges are brought closer
51 together as a result of the decreasing area of the elastomer, thus increasing energy density.
52 These changes increase the voltage of the charge, and the created energy can be harvested.^[24]
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DETs have the potential to be used in novel applications which have not been possible previously or feasible through the use of other technologies. Especially within the actuator application area, DETs could provide novel solutions such as flat screen loud speakers,^[25] lightweight morphing structures and prosthetic-like actuation, especially due to the flexibility of the material, which offers the ability to be formed into complex shapes and still provide actuation.^[26–29] Other DET applications range from valves and pumps^[30] to (bio-mimicking) robotics,^[31–33] Braille displays,^[34–36] adaptable lenses and gratings,^[37] motion sensors,^[38] wave energy harvesting^[24] and active vibration control.^[39] The main advantage of DETs in these applications over other transducers, however, is their ability for large displacements. In **Figure 2** two examples are presented showing the extraordinary behaviour of dielectric elastomers, namely a flying fish by the Swiss Federal Laboratories for Materials Science and Technology, EMPA,^[40] illustrating the lightweight nature, and a wave-harvesting unit capable of large strains.^[41]

One of the most important components of a DET is the elastomer, as it governs dielectric permittivity, dielectric breakdown strength and (in combination with the electrodes) obtainable strain. Silicone elastomers are one of the most used materials for DETs due to their high efficiency, reliability and fast response times.^[4,42] Other materials commonly used include acrylic elastomers (such as VHBs from 3M) and polyurethane elastomers. The major advantage of silicone elastomers over other materials is that they produce repeatable, reproducible actuation upon activation, they show little tendency for Mullins (stress softening) and ageing effects and they have been shown to actuate (at low strains) to more than 4 million cycles, in some instances more than 10 million cycles, without failure.^[3,43,44] They also possess significantly lower viscous losses than acrylics, indicating that they can be operated at higher frequencies with lower losses and less heat generation. Furthermore, silicones can be operated at a broader temperature range^[4] and possess inherent softness and stability. The disadvantage

1 of silicone elastomers is that they possess relatively low dielectric permittivity, which means
2 that a higher electrical field is needed to actuate the DET to obtain a given strain.
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4 Generally speaking, the dielectric permittivities of current dielectric elastomers range from 2 to
5 8, while silicone elastomers typically have dielectric permittivity at around 2-3. This means that
6 silicone elastomers, despite possessing superior mechanical properties compared to other
7 dielectric elastomers, do not reach their full potential due to their energy density being too low
8 (i.e. too low dielectric permittivity). The practically obtained actuation strain of silicone DETs
9 is thus usually less than 15% (if not pre-strained), while elongations up to 300% should be
10 realisable, provided that the elastomer survives electrically.
11

12 The silicone elastomers currently used for DETs are off-the-shelf materials, and as such they
13 have not been developed for use in this specific application and are not the result of targeted
14 development. Therefore, recent years have seen a large increase in research on and the
15 development of silicone materials for DETs, namely where commercial silicone elastomers
16 have been modified and where new silicone elastomer formulations have been prepared.
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18 While several excellent reviews and overviews about EAPs exist,^[4,45-49] this review aims
19 specifically at providing a comprehensive overview of recent developments with silicone
20 elastomers for DETs. Silicone elastomers are often highlighted as the most suitable and
21 promising elastomer material for DETs; however, the benchmark for silicone dielectric
22 elastomers is still commercial silicone elastomers, such as RT625 from Wacker Chemie AG
23 and Sylgard 184 from Dow Corning. We hope that this review will pave the way forward in
24 order for the field to progress and handle great challenges, such as the often ignored lifetime
25 and electromechanical stability. Furthermore, the intent is that this overview will reduce the
26 number of repetitive studies performed within the field and promote research into silicone
27 elastomers in general by showing their strengths as dielectric elastomers.
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29 First, a discussion of important dielectric parameters is undertaken, followed by a brief
30 introduction to the chemistry and technology of silicones and silicone elastomers and a section-
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wise description of the research that has been conducted on the use of silicones as DETs, including: commercial silicone elastomers, silicone composites, silicone blends, chemically modified silicones and advanced network structures such as interpenetrating networks and bimodal networks. The review is summarised by an outlook describing the potential of silicone DETs and the suggested next steps for the research community within the area.

1.1 Dielectric elastomer parameters

The equation for the actuation strain of DETs valid for small strains (usually less than 10%), developed by Pelrine et al.^[50], correlates electrostatic pressure, p_{el} , to thickness strain, s , and the Young's modulus, Y , according to:

$$s = \frac{p_{el}}{Y} = \frac{\epsilon_r \epsilon_0}{Y} \left(\frac{U}{d} \right)^2 \quad (1)$$

where $\epsilon_0 = 8.854 \times 10^{-12}$ F/m is vacuum permittivity, d is the thickness of the material, U is the voltage and ϵ_r is the relative dielectric permittivity of the elastomer film defined as $\epsilon_r = \epsilon' / \epsilon_0$, where ϵ' is the real part of the dielectric permittivity of the material.

From Equation 1 it is clear that three material properties, namely dielectric permittivity, the Young's modulus and the maximum applicable voltage (the dielectric breakdown strength, $E_B = (U/d)_{max}$), govern the performance of a DET. It is important, however, to keep in mind that several other essential parameters remain unexposed in the actuation equation.

In particular, Equation 1 is valid for small strains only, since the Young's modulus depends not only on the applied strain for larger strains (usually higher than 10-30%, depending on the elastomer), but also on the applied strain rate, i.e. $Y(s, \delta s / \delta t)$. In the linear regime, which for silicone elastomers is up to approximately 15% in strain,^[51] elastic and viscous properties are well described by the shear storage modulus, G' , and the shear loss modulus, G'' , defined from the complex shear modulus $G^* = G'(\omega) + iG''(\omega)$. Due to the incompressibility of silicones (Poisson's ratio (ν) close to 0.5), the Young's modulus can be determined as $Y = 2(1 + \nu)G$,

1 where $G = G'(\omega \rightarrow 0)$. Viscous loss, i.e. energy lost as heat into the surroundings, can be
2 determined from G'' and is usually referred to via the loss tangent, $\tan \delta = G''/G'$. Silicone
3 elastomers usually possess significantly lower viscous losses than acrylic elastomers.
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6 The strain dependency of dielectric elastomers' permittivity is also often debated, but no
7 coherent conclusion has been drawn so far.^[52] Much of the inconsistency in dielectric data may
8 be caused by the complexity of obtaining reliable, reproducible data on thin, flexible films.
9
10 Nevertheless, the strain-dependency of the Young's modulus is usually significantly larger than
11 that of the observed dielectric permittivity, and therefore dielectric permittivity is usually
12 regarded as a constant. Since one of the major advantages of dielectric elastomers over other
13 transducer materials is the possibility of achieving high strains, the use of models taking large
14 strains into account is required for a satisfactory description of high-strain behaviour such as
15 the models proposed in the references.^[2,53-55] However, modelling is not discussed further in
16 this review.
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31 In principle a DET is a stretchable capacitor for which energy storage capacity is described by
32 its capacitance, which in turn is defined by the dielectric permittivity of the dielectric elastomer.
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34 As mentioned in the introduction, dielectric permittivity is an important – if not *the* most
35 important – factor for silicone elastomers that suffer from low dielectric permittivity compared
36 to, for example, acrylic elastomers and polyurethanes. When an electrical field is induced, all
37 materials become polarised. If the material is conducting, the electrical field will induce charge
38 transport. In an insulator, such as a silicone elastomer, the elastomer can be considered as
39 consisting of small dipoles with separate internal charges within an overall electrically-neutral
40 material. The dipolar species consists of molecules that carry dipole moments or negatively
41 charged species, such as electrons, anions and other chemical groups with negative partial
42 charges, and positive species, such as atomic nuclei, cations and groups with positive partial
43 charges. When subjected to an electrical field, the dipoles will align with the field, in order for
44 the negative part of the dipole to orient towards the higher potential, while the positive part of
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1 the dipole will orient towards the lower potential. Electrostatic energy created in the material is
2 then converted into mechanical energy through different mechanisms, the simplest of which is
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4 Maxwell stress, whereby stress is proportional to the dielectric constant.^[21]
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7 The driving voltage that can be applied to a dielectric elastomer is limited by dielectric
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9 breakdown strength, $E_B = (U/d)_{\max}$, which ideally is a material-specific constant, also denoted
10 the inherent breakdown strength. Electrical breakdown mechanisms are complex, as they are
11 dominated by extrinsic factors not inherent in the material, such as imperfections, as well as
12 statistical variations in morphology and microstructure.^[56–59] Recent modelling has focused on
13 determining intrinsic breakdown strengths,^[59] and a fundamental understanding thereof will
14 lead to improved materials. Based on this fundamental knowledge, combined with continued
15 progress in processing methods, electrical breakdown strengths closer to the intrinsic
16 breakdown will become realisable.
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19 High dielectric breakdown strength is desired so that the DET does not experience premature
20 failure. This means that it is important for the elastomer to be free from impurities or voids that
21 cause locally reduced dielectric strength. Since – in practice – it is impossible to avoid defects,
22 E_B depends strongly on elastomer film thickness, since the number of defects scales with
23 volume and thus thickness.^[60] Furthermore, it is important that the material exhibits low
24 dielectric losses, which continuously contribute to the generation of heat in the material. If heat
25 generated by these dielectric losses exceeds heat dissipated in to the surrounding area, the
26 temperature in the elastomer will rise, which in turn could lead to thermal breakdown.^[61] The
27 structural order of the polymer network also influences dielectric breakdown strength. This is
28 obtained through pre-straining the elastomer,^[62] whereby the polymer chains are aligned and
29 the maximum applicable electrical field is greatly increased.^[57] Pre-straining is crucial for the
30 actuation performance of, for example, acrylic elastomers,^[62,63] since it simultaneously
31 facilitates at least two properties favourable for improved actuation, namely reducing thickness
32 and significantly increasing breakdown strength,^[57] while the Young's modulus may decrease
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1 significantly for strain-softening elastomers such as VHB and many soft silicone elastomers. In
2 **Figure 3**, pre-straining devices are illustrated. In general, silicone elastomers do not show the
3 same strong tendency to strain-softening as acrylics, and they are naturally soft from the un-
4 stretched state. Therefore, pre-straining is not a prerequisite for the actuation of silicone
5 elastomers. However, several studies have shown pre-straining to be very favourable for
6 silicone elastomers.^[62,64] A recent study by Zakaria et al.,^[65] for instance, showed that the
7 breakdown strength of two types of silicone elastomers was greatly improved by pre-straining,
8 even when accounting for the reduction in thickness. It is therefore obvious that pre-straining
9 introduces a favourable orientation for silicone elastomers and allows for the diffusion of
10 volatile cyclic silicones out of the elastomer.^[65] Pre-straining is also a common way to avoid
11 electromechanical instability (EMI),^[66] a matter which will be discussed later.

12 A factor not accounted for in the actuation equation is dielectric loss, ε'' , which is commonly
13 stated as the loss tangent, $\tan \delta = \varepsilon''/\varepsilon'$, where ε'' is the imaginary part of dielectric permittivity
14 attributed to, among other things, dipole relaxation phenomena, which in turn gives rise to
15 energy loss. Dielectric losses also influence the conductivity (σ) of the elastomer, where
16 conductivity for insulating dielectric materials is dependent on dielectric loss and frequency (ω)
17 as $\sigma = 2\pi\omega\varepsilon''\varepsilon_0$. Silicones are in general electrically insulating materials, though no material
18 can be considered as ideally insulating. Upon changing the molecular structure of the elastomer
19 or adding high dielectric constant fillers, unwanted conductive paths – and thereby possible
20 means of charge transport – can occur in the elastomer. Undesired conductivity, which can lead
21 to large dielectric losses, results in the formation of conducting pathways and σ becoming
22 independent of frequency below a critical frequency ω_c .^[67]

23 Tear strength, especially for inherently soft silicone elastomers, is a very important material
24 parameter which is not considered in the equation for actuation strain. It becomes crucial in
25 processing, as the thickness of the elastomer films is reduced to increase transducer
26 performance. In the commercial film coating process of Danfoss PolyPower the major

1 processing issue was high surface energies related to the release of the thin films with micro-
2 structural corrugations from the carrier web.^[68–70] Unsuccessful release usually caused the
3 detrimental tearing of films. Also, when considering product reliability, the tearing of elastomer
4 films after electrical breakdown is a crucial problem. Silicone elastomers may be partly self-
5 healing upon electrical breakdown, but if they are torn, the film cannot, with current materials,
6 be restored in a simple way.
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14 With the vast number of important parameters, a direct comparison of different elastomers is
15 difficult. Therefore, Sommer-Larsen and Larsen^[71] defined a universal expression which,
16 through a single parameter, the *figure of merit*, F_{om} , can be used to evaluate the performance of
17 a DET at a constant potential. The figure of merit depends on the dielectric constant, dielectric
18 breakdown strength and, for actuators, the elastic modulus (Young's modulus) of the elastomer
19 material. The equations for figures of merit, to assess elastomer performance as a dielectric
20 elastomer actuator (DEA),^[71] and a dielectric elastomer generator (DEG)^[72] are defined as
21 follows:
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$$33 F_{om}(\text{DEA}) = \frac{3\varepsilon'\varepsilon_0 E_B^2}{Y} \quad (2)$$

$$34 F_{om}(\text{DEG}) = \frac{\varepsilon'\varepsilon_0 E_B^2}{2\varphi} \quad (3)$$

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40 where φ is the strain energy function of the elastomer.
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43 Of course, a more realistic figure of merit would also include maximum extensibility, tear
44 strength, excessive heat dissipation (from losses), etc. In other words, the figure of merit should
45 account for whichever failure occurs first. However, for silicone elastomers the maximum
46 elongation is currently not the limiting factor for dielectric elastomer performance regardless
47 of whether applying pre-straining or not.
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1.2 Failure modes of dielectric elastomers

The failure modes of dielectric elastomers are not included in the actuation equation. Models have been used extensively to study the failure modes and instabilities present in DETs, including thermodynamic electromechanical instability (pull-in, EMI),^[66,73–78] wrinkling and/or buckling,^[74,75] mechanical rupture^[75,76] and dielectric breakdown,^[75,76] for varying actuator configurations. Silicone elastomers very rarely fail due to mechanical rupture as the initial failure mode, but they may tear easily upon dielectric breakdown. This tearing usually arises from a pinhole formed in the elastomer after electrical breakdown, due to the resulting inhomogeneous stress fields. An improved understanding of these failure modes is required for the design of actuators capable of operating in a safe regime, thus prolonging actuator lifetime. Various safety factors (β), for example presented as a percentage of the intrinsic breakdown strength, $U_{\max} = \beta E_B$, have been assumed, but obviously the safety margin is not a universal parameter and depends rather on the configurations of both the dielectric elastomer with electrodes as well as the type of actuator. The highly deformable, capacitive elastomer exhibits complex nonlinear behaviour, and in voltage-controlled actuation the electrical field increases as the thickness of the elastomer reduces. Instabilities may result in inhomogeneous deformation due to bi-stable conditions, also denoted as snap-through.^[79] In **Figure 4**, the electromechanical responses of three types of elastomers with different chain extensibility are shown. The plots illustrate stresses, namely elastic and Maxwell stress, across the film as a function of strain, alternatively represented as an electrical field at constant voltage. The physical interpretation of this voltage-stretch response is as follows: as voltage (U) increases, the DET responds to the applied voltage through an increase in strain (λ). When U becomes sufficiently high, the same voltage induces an even higher electrical field; positive feedback then develops between a thinning dielectric elastomer and an increasing electrical field, indicating the onset of EMI. In voltage-controlled actuation, at EMI, the deformation of the elastomer will ‘jump’ locally from a small λ to a very high λ . The elastomer may not survive

1 this instability due to dielectric breakdown. As such, maximum actuation strain may be severely
2 limited by EMI. Hence, to increase maximum actuation strain, it is desirable to avoid the snap-
3 through phenomenon, or to move the phenomenon to low strains, such that the EMI can be
4 utilised as a favourable instability.^[79]
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9 Another often overseen failure mode is space charge (SC) accumulation, which is an important
10 characteristic of a direct current (DC) insulator and can be detrimental to the performance and
11 reliability of an insulating elastomer.^[80] Space charging can result from a range of phenomena,
12 but most importantly they include 1) charge injection from electrodes and from electrical stress
13 enhancement, 2) a combination of current density and spatially inhomogeneous resistance, 3)
14 the ionisation of species within the dielectric to form a hetero-charge and 4) polarisation in
15 structures such as water treeing. Due to the large water permeability of silicone elastomers it is
16 very hard to avoid water within the silicone elastomer in humid environments, so all four
17 phenomena are relevant for silicone dielectric elastomers.
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31 Good materials for DETs are those less susceptible to SC accumulation, i.e. elastomers,
32 amongst other things, should preferably be dry and have similar levels of electrical resistance.
33 This is a major obstacle for hygroscopic materials such as polyurethane-based elastomers.^[47]
34 Furthermore, it is also desirable that any accumulated SC will deplete as quickly as possible
35 when electrical stress is removed.^[80]
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1.3 Chemistry and technology of silicone polymers and elastomers

As mentioned previously, several classes of elastomers are applied for DETs, such as acrylics, polyurethanes and silicones. Of these three main types of elastomer, the silicones have the most promising potential for DETs, due in particular to increased long-term stability and reliability, which are the areas where the greatest development has to take place in order for the field to progress from the current state of the art.

In order to exploit advantages from the use of silicones, continued development, taking all the different aspects of the polymer system into account, is required. Silicone polymers (polysiloxanes) are an interesting and important class of polymer in which polydimethylsiloxane (PDMS) is the most widely used.^[81] Polysiloxanes are based on the repeating unit $RR'SiO$, where R groups can be different organic groups such as vinyl, phenyl, hydride and alkanes, with the most common group being the methyl groups, such as those found in PDMS.^[82]

Polysiloxanes have many interesting properties, such as high thermal stability, chemical and biological stability and inertness, ozone and UV resistance, hydrophobicity, transparency, high gas permeability, low glass transition temperature and low surface tension.^[83] Polysiloxanes do not, however, possess good mechanical properties, and they are therefore often used as components in other systems or cross-linked and solidified into three-dimensional polymer networks, namely elastomers, which are usually formed by end-linking telechelic polymer chains in cross-linking reactions. When the siloxane polymer chains are linked together in networks, they are no longer able to diffuse by reptation, and the network has the ability to return to its original shape after stress is applied, i.e. they possess elasticity. Silicone elastomers are viscoelastic materials and therefore exhibit properties as both elastic solids and viscous fluids, where usually the elastic contribution dominates. In general, this viscous behaviour results in the materials becoming more sticky and adhesive-like, and it also causes heat dissipation within the material, which may have a strong impact on electrical properties and

1 thus lead to premature failure. Additionally, mechanical stability and reliability will be strongly
2 affected.
3

4 Polysiloxanes, and in particular PDMS elastomers, have found widespread use as adhesives,^[84]
5 membranes,^[85] sealants^[86] and surface treatments^[87,88] for soft lithography^[89] and as dielectric
6 elastomers. The PDMS elastomers utilised in these diverse applications are usually prepared by
7 hydrosilylation, radical or condensation reactions which form a PDMS network. The most
8 commonly applied preparation technique is the hydrosilylation reaction, also known as an
9 ‘addition reaction’, where –Si-H groups react with –CH=CH₂ groups, as seen in **Scheme 1**.
10 Hydrosilylation reactions are usually catalysed by a platinum catalyst and have the advantage
11 over, say, a condensation reaction, in that they are very efficient and do not form by-products,
12 which means that voids – in principle at least – can be avoided during elastomer synthesis.
13 Condensation reactions are usually slower than hydrosilylation reactions, and curing rates
14 depend strongly on the atmospheric humidity level. Furthermore, there seems to be a tendency
15 for condensation cure elastomers to have lower dielectric breakdown strengths, most likely due
16 to residual low molecular weight compounds and voids left in the elastomer from the
17 condensation reaction.
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19 Polysiloxanes are usually prepared through the nucleophilic substitution of chlorosilanes, which
20 leads to low molecular weight linear and cyclic siloxanes. These are reacted further into high
21 molecular weight polymers by an acid- or base-catalysed equilibrium reaction. Thus, silicone
22 polymers commonly contain small amounts of low-molecular weight residuals which usually
23 remain in the final elastomer if precautions against this issue are not taken.^[90] The most
24 commonly utilised method for this is so-called ‘post-curing’, where the elastomers – after
25 curing at normal conditions – are heated in an oven at an elevated temperature for several hours
26 (usually more than 4 hours, depending on geometry). Zakaria et al.^[65] showed that these low
27 molecular weight compounds greatly influenced the dielectric breakdown strength of dielectric
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1 elastomers. Upon removing residual compounds by post-curing, dielectric breakdown strength
2 increased ~20% despite the sol fraction in the original elastomer constituting less than ~2%.
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4 The most commonly employed hydrosilylation cross-linking system uses f -functional hydride-
5 functional cross-linker molecules and vinyl-terminated PDMS. The functionality, f , of the
6 cross-linker should be ≥ 3 , in order to form a polymer network. The mechanical properties of a
7 silicone network are governed primarily by the molecular weight of the PDMS chains, whereas
8 the functionality of the cross-linker is less significant for cross-linkers with $f > 4$ and no steric
9 hindrance.^[91] When very short polymers are cross-linked, the silicone elastomer becomes glass-
10 like and brittle.^[51] The stoichiometric imbalance (ratio between hydride and vinyl groups) may
11 be used as a mechanical tuning parameter; however, it is important to keep in mind that by
12 lowering the amount of cross-linker, a reduction in the Young's modulus is indeed obtained,
13 though a large fraction of the elastomer will become a sol fraction, which in turn introduces
14 both significant viscous losses and the possibility for significant silicone migration in
15 products.^[92]
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33 Despite many other excellent properties, PDMS elastomers suffer from low tear and tensile
34 strength and are therefore considered intrinsically weak. This is due to the low melting point of
35 PDMS (-40°C), which means that above approximately -30°C the elastomer cannot reinforce
36 itself through strain-induced crystallisation.^[93,94] As a result, almost all applications require
37 reinforcement of the elastomer with particles. The most common and efficient reinforcing filler
38 for silicone elastomers is silica (SiO_2), which is added to elastomer systems in concentrations
39 of 10-60 wt%. Other commonly used fillers for silicone elastomers include titania (TiO_2),
40 zirconia (ZrO_2) and calcium carbonate (CaCO_3). The effectiveness of the reinforcement
41 depends on the available surface area and the interaction between the filler and the base
42 polymer, such as van der Waals forces and hydrogen bonding. The fillers lead to a higher degree
43 of orientation and immobilisation of the polymer chains in the strained elastomer, and therefore
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1 they reinforce the elastomer. Commonly unfilled silicone elastomers can be stretched less than
2 100%, and often significantly less, but when reinforced the extensibility increases dramatically.
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4 Commercial silicone elastomer systems can be divided into two classes, room temperature
5 vulcanising rubber (RTV) and high temperature vulcanising rubber (HTV), based on their
6 curing temperature. Traditionally, an RTV silicone is a condensation cure silicone; however,
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8 RTV silicones can also be addition cure silicones. Examples of RTV addition cure systems
9 include Elastosil RT625, by Wacker Chemie AG, Sylgard 186, from Dow Corning, and Nusil's
10 CF15-2186. As the name indicates, the characteristic of an RTV silicone cure system is that it
11 will cure at room temperature, although the application of heat often decreases reaction time
12 significantly. In order to obtain elastic, reliable elastomers, fast curing is required. This fast
13 reaction 'freezes' in more elasticity (inhomogeneous stress fields are created and maintained)
14 than slow curing, and thus the resulting mechanical properties are different despite reactions
15 proceeding to the same extent. This is due to the presence of various interactions, mainly due
16 to polymer chain entanglements, but particle-polymer and particle-particle interactions may
17 also change, depending on curing conditions.
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HTV can be cured by peroxides, addition cure or by a combination of mechanisms. Addition
cure HTV silicone rubbers are further divided into the subclasses high consistency silicone
rubber (HCR) and liquid silicone rubber (LSR), based on the degree of polymerisation. LSRs
are lower viscosity systems and are ideal for complex moulds due to their flowability.
Frequently used LSRs for DETs include Elastosil LR 3043/30 and 3043/50 from Wacker and
Nusil's CF19-2186. More details on LSRs can be found in the work of Delebecq et al.^[95,96]

It is commonplace for most addition cure systems that they usually come as two-part systems,
namely an A part and a B part, where typically one part contains polymer and a cross-linker
whereas the other part contains polymer and a catalyst. Upon mixing the two parts in ratios
stated by the manufacturer, curing will take place. Furthermore, most commercial silicone

1 elastomers are highly filled (with silica and/or other reinforcing fillers or resins) and contain
2 other additives such as inhibitors.
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7 **2. Commercial silicones for dielectric elastomers**

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10 The initial comparative study of dielectric elastomers, triggering research interest in improving
11 the dielectric permittivity of silicone elastomers, was performed by Pelrine et al.^[62] They
12 compared two types of silicone elastomers with the acrylic elastomer VHB 4910 from 3M and
13 showed how pre-straining was favourable for both silicones and acrylics, where dielectric
14 breakdown strengths were shown to improve by 117% and 215%, respectively, from biaxial
15 pre-straining. A larger study was performed subsequently by the same authors,^[2] in which they
16 conducted a comprehensive study on various types of elastomers, amongst others polyurethane,
17 fluorosilicones, isoprene rubber and various types of silicone elastomers. The addition cure
18 silicone elastomer Nusil CF192-2186, as a representative of RTV silicone elastomers, was
19 shown to be an ideal candidate for dielectric elastomers, as it possessed the highest measured
20 energy density and strain as well as better coupling efficiency, low creep and excellent tolerance
21 to temperature and humidity.^[97] A later study on Nusil CF192-2186 confirmed these results.^[98]
22 Michel et al.^[99] later undertook a comparative study on Dow Corning's silicone elastomer DC
23 3481 and two 3M VHB acrylic elastomers. They concluded that the silicone elastomer
24 possessed superior reproducibility, fast response rates and no frequency-dependent dissipation
25 of work compared to acrylics. However, they also concluded that strains of more than 10%
26 could not be obtained with this type of silicone elastomer, although acrylics could easily be
27 actuated above 10% through a trade-off in relation to slow response, frequency-dependent
28 dissipation and low reproducibility. A similar study was conducted by Molberg et al.,^[52] who
29 compared the commercial silicone elastomer Neukasil RTV-23 with a thermoplastic elastomer
30 from styrene-isoprene block copolymers. Here, the focus was not on the highest achievable
31 strain but rather on the small strain response at low frequencies and establishing how to obtain
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1 frequency-dependent actuation. Again, silicone elastomers outperformed thermoplastic
2 polymers with respect to overall performance. Zhang et al.^[100] investigated the silicone
3 elastomer DC 3481 with various amounts of three types of hardeners. They concluded that for
4 their silicone elastomers optimal actuation was obtained for a pre-strain of 40% despite the
5 elastomers showing strain-hardening behaviour, and the pre-strain therefore led to stiffer films,
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7 albeit an increase in dielectric breakdown strength strongly compensated for this result. An
8
9 actuation response of almost 20% could be obtained at 40 V/ μm for 40% pre-strained films.
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11 Carpi and De Rossi^[101,102] investigated a condensation cure elastomer, namely BJB TC5005.
12 Very soft elastomers with a Young's modulus of 50 kPa and a dielectric permittivity of $\epsilon' = 5$
13 were obtained. The same elastomer was investigated by Galantini et al.^[103] together with a
14 plasticiser in various combinations, which resulted in even softer elastomers.
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16 Jordi et al.^[104] compared three types of dielectric elastomer, namely the corrugated silicone
17 elastomer film from Danfoss PolyPower (Wacker Chemie RT625 with 15 parts per hundred
18 rubber (phr) silicone oil) and two other types of elastomer (VHB and a home-made acrylic
19 interpenetrating polymer network (IPN) - for more details on IPNs see section: Systems with
20 complex network structures – interpenetrating and bimodal networks). The authors concluded
21 that VHB was by far the best material for actuation, but when achievable design cycles, creep
22 behaviour and overall structural efficiency were taken into account, the picture changed and
23 favoured the other two candidates. Taking practical restraints into consideration, the silicone
24 became the favoured elastomer, as there was no need for heavy support structures to maintain
25 the large pre-strains required for the IPN. In a similar study Berardi et al.^[105] investigated the
26 Danfoss PolyPower films^[106–109] and came to the same favourable conclusions for silicones.
27

28 Skov et al.^[110,111] investigated four different LSR elastomers and an RTV silicone elastomer,
29 including the very tough LR 3043/50 which was concluded to be a suitable elastomer for energy
30 generation due to its combined high mechanical and electrical strength as well as suitable
31 flexibility. However, the elastomer reaction mixture was very viscous, which made solvent an
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1 absolute requirement for thin film coating. Another LSR-type elastomer, namely Wacker
2 Silpuran 6000/10 (medical grade), was investigated by Stoyanov et al.,^[112] who reported similar
3 advantages.
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7 A recent study by Akbari et al.^[113] on the effect of pre-straining silicone elastomers, with
8 Sylgard 186 as the investigated elastomer, concluded that for silicone elastomers, large pre-
9 strains were not as favourable as for VHB; rather, intermediate pre-strains should be used to
10 avoid simultaneously the strong effect of strain-hardening as well as electromechanical
11 instability (EMI). The elastomer should simply be coated thinner from the outset, in order to
12 obtain the targeted, pre-strained film thickness. An overview of the discussed studies on
13 commercial silicone elastomers is listed in **Table 1**.
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23 **3. Special home-made silicone formulations for dielectric elastomers**

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28 Only a few studies have focused on tailor-making silicone elastomers for dielectric elastomers.
29 This may be due to the complexity of formulating elastomers, but it may also indicate that
30 current commercial elastomers perform rather well. However, the commonly applied curing
31 reaction, namely hydrosilylation, can be inhibited by the presence of nitrogen- and sulphur-
32 containing substituents, and thus for the further functionalisation of silicone elastomers it may
33 be convenient to change the curing chemistry to, for example, condensation curing^[114] or UV
34 curing.^[115–119]
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45 A common way of designing elastomers with improved mechanical properties for dielectric
46 elastomers is to change the mixing ratio of the two components in the elastomer mixture.
47 Elastomer mixtures are usually designed such that for the stated mixing ratio there is a slight
48 excess of cross-linker, to allow for ideal cross-linking despite steric hindrance.^[91] As described
49 previously, the elastomer usually consists of a premix with PDMS, a catalyst and silica (denoted
50 premix A here) and another premix with PDMS and a cross-linker (denoted premix B). By
51 increasing the mixing ratio of A to B, cross-linker content is reduced. This method can be used
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1 to decrease the Young's modulus, as it scales with the cross-linking density. As a result of
2 stoichiometric imbalance, dangling/pendant chains are formed as well as a significant sol
3 fraction, if the mixing ratio is moved far away from the recommended ratio.^[51,92,120] Dangling
4 chains and sol fractions introduce significant viscous loss and thereby lead to heat generation.
5
6 Furthermore, the sol fraction behaves comparable to silicone oil and therefore acts as a
7 plasticiser. Non-ideal cross-linking leads to soft and – when taken to the extreme – sticky and
8 non-coherent elastomers.
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10 As a summary of the preceding discussions, it is clear that no matter the utilised commercial
11 silicone elastomer, they provide great reliability and are therefore ideal candidates for further
12 elastomer optimisation. However, to exploit fully the potential of silicone-based dielectric
13 elastomers a higher dielectric constant is required. The following sections deal with various
14 methods for improving dielectric permittivity while maintaining the fundamentally favourable
15 properties of the silicone elastomer matrix.
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17 **4. Silicone composites for dielectric elastomers**

18 The traditional choice of fillers for silicones has been silica particles, because they interact well
19 with the PDMS matrix. The fillers can either be blended directly into the elastomer precursor
20 or be incorporated through in-situ condensation reactions during condensation curing.^[121] For
21 application in DETs there is a requirement for increased dielectric permittivity, in order to
22 improve the actuation efficiency of systems. The addition of a filler of high permittivity to the
23 elastomer system is one of the most investigated solutions to this challenge. However, as a
24 result of the often relatively high silica content (30-40%) in most silicone systems, the choice
25 to increase filler content comes at the cost of an inherent increase in the elastic modulus of the
26 elastomer. This is a remarkable disadvantage for actuation, because the electromechanical strain
27 resulting from the electrostatic pressure is inversely proportional to the elastic modulus of the
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1 material.^[122] For the optimal system a balance will have to be found between reinforcement and
2 permittivity increase while not compromising the elastic modulus.
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4 When designing a given formulation there are many considerations that need to be taken into
5 account. In particular the interface between particles and the polymer matrix has been seen to
6 influence greatly the effects of different types of fillers in polymer composites. Here especially,
7 the use of derivatised particles facilitates improved dispersion as well as improved
8 compatibility with the matrix.^[123] In this context both the type of filler particle applied. e.g.
9 SiO₂, TiO₂, BaTiO₃, affects not only the obtained properties, but also the handling of the
10 particles, such as drying to prevent adsorbed moisture, as observed by Böse et al.^[124] as well as
11 Kofod et al.,^[125,126] who recognised the great importance in preventing premature breakdown.
12 In developing new systems, the prediction of properties from mixing rules based on the
13 specifications of a given filler has been sought by applying a range of different models used for
14 the theoretical prediction of dielectric permittivities.^[127] Recently, it appears that examples such
15 as the Yamada^[128] or Bruggeman^[129] models, applied more frequently throughout the literature,
16 have been showing good correlations with experimental data. It is very clear from Table 2 to 6
17 that many different combinations of PDMS based elastomers, different sized nanoparticles and
18 dispersion methods have been tested. The various systems have different advantages and
19 dependencies, although a direct comparison is sometimes difficult, as there are many
20 experimental differences in addition to the abovementioned considerations on filler material
21 and surface derivatisation and compatibilisation. Local availability strongly affects the selection
22 of particles, and it is difficult to conclude anything with respect to these parameters, though it
23 appears to be a general trend that smaller particles provide an improved effect due to a larger
24 surface area and improved distribution in the matrix.
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26 The methods of choice for the mechanical dispersion of particles in silicone generally cover a
27 broad range of methods, such as direct mechanical mixing at various shear strengths and in
28 various laboratory mixers,^[111,127,130–137] in-situ formation of particles,^[121] ultra-sonication (US)

1 in combination with solvents,^[111,138-142] ball milling,^[143,144] three or two roll mills^[145,146] and
2 speedmixing.^[147-149] Often it is noted that a combination of these methods or use of additional
3 dispersion aids in the form of plasticisers or functionalised and/or stabilised particles gives the
4 best results in terms of dispersion. From an industrial point of view many of these processes are
5 only effective on a laboratory scale and would be challenging to implement in full-scale
6 production. However, methods such as roll milling or speedmixing have been implemented and
7 up-scaled for industrial production.

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17 When considering the use of dispersing agents, plasticisers especially have been investigated
18 in several systems,^[127,133,138,144,150,151] where it has been seen that it is possible to ensure a better
19 dispersion of the filler and a reduction in the Young's modulus of the samples. The addition of
20 free plasticisers into the material introduces a mobile component in the formulation, which
21 could be a problem for long-term stability. Generally, large amounts of mobile additives would
22 be expected to give rise to long-term instabilities and losses in the material, as discussed
23 previously. Therefore, the design of such systems requires a careful balance between the
24 dispersion and stability of the cross-linked system.

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36 In addition to the random orientation of the fillers, anisotropic orientations, in order to imprint
37 specific properties into the material in the actuation direction, have also been investigated in
38 recent years. This has either been obtained by electrical field orientation,^[152] by use of magnetic
39 fields for magnetic particles^[153] or by dielectrophoresis (alignment due to a non-uniform
40 electrical field).^[123]

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One of the most widely studied filler materials used for increasing dielectric permittivity in
silicones is TiO₂, due to its high dielectric permittivity (rutile: $\epsilon' = 114$, anatase: $\epsilon' = 31$). The
first group to report the use of TiO₂ as a dielectric constant-enhancing filler material was Carpi
et al.,^[127] who used mechanical mixing to disperse the TiO₂ in a three-component PDMS
precursor using plasticiser. The approach afforded a cross-linked material with a dielectric
permittivity of $\epsilon' = 8$ at 30 phr of TiO₂. Many systems applying TiO₂ have subsequently been

1 investigated, and it is very often included as a reference material for comparing the properties
2 of new composite candidates in more recent studies.^[110,148] An overview of studies reporting
3 applications of TiO₂ as a filler in silicone for DET applications can be seen in **Table 2**.
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7 In addition to the work on TiO₂, several different inorganic particles with high dielectric
8 permittivity have been investigated for use as fillers in silicones. Titanates of various kinds,
9 such as BaTiO₃ (relative dielectric permittivity of $\epsilon' = 6000$), copper calcium titanate
10 (CuCaTiO₃, CCTO, relative dielectric permittivity of >3000), lead magnesium niobate
11 ((PbMg_{1/3}Nb_{2/3})O₃, PMN, relative dielectric permittivity of $\epsilon' = 4000$), lead magnesium niobate
12 – lead titanate ((PbMg_{1/3}Nb_{2/3})O₃-PbTiO₃, PMN-PT, relative dielectric permittivity of $\epsilon' =$
13 4000) and lead zirconia titanate (PbZrTiO₃, PZT, relative dielectric permittivity of $\epsilon' = 1800$)
14 have been investigated, and a summary of these systems has been compressed into **Table 3**.
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17 Generally speaking, silicones with BaTiO₃ provide similar dielectric permittivities (relative
18 dielectric permittivities of $\epsilon' = 5-8$) compared to the TiO₂ with a lower amount of added filler.
19 However, Zhang et al.^[150] reported the highest relative dielectric permittivity of $\epsilon' = 300$ at 10
20 wt% BaTiO₃ with a dielectric loss of only $\tan \delta = 0.22$. This system, however, did employ 35%
21 plasticiser, which might influence long-term stability. Of the other titanates the highest relative
22 dielectric permittivity was reported by Yang et al.^[146] for PMN with a relative dielectric
23 permittivity of $\epsilon' = 27.5$ at 60 vol% filler. However, they found that for actuating purposes a
24 lower loading of 20 vol%, resulting in a dielectric permittivity of $\epsilon' = 5.2$, was optimal. This
25 resulted in a material with an actuation strain of 7.9% at 53 V/ μm . A number of PZT PDMS
26 composites have been evaluated for use in piezoelectronics, showing highly increased
27 permittivities of $\epsilon' = 28$ with 40 vol% PZT^[154] and $\epsilon' = 160$ with 32.5 vol% PZT.^[155] However,
28 these specific systems have not yet been evaluated for their properties in DET systems with
29 respect to actuation and breakdown properties. Other PMN-PT and PZT PDMS systems have
30 been recently identified as some of the more promising candidates for applications in wave
31 harvesting applications using dielectric elastomers due to their promising overall properties.^[156]
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1 In addition to inorganic fillers, several complexes with various metals in silicone have been
2 investigated for DET applications. As an example, iron, cobalt and titanium complexes were
3 investigated by Cazacu et al.,^[157] who discovered dielectric permittivities of up to $\epsilon' = 4.7$ with
4 3-5 wt% of the respective complexes. Also, copper-phthalocyanine (CPO) complexes have
5 been investigated due to their high dielectric permittivity (>10.000), with Zhang et al.^[100,158]
6 showing a dielectric permittivity of $\epsilon' = 5.85$ at 20 wt% CPO and improved actuation. The
7 dielectric properties of the elastomers were later observed to be strongly influenced by the
8 amount of adsorbed water, as reported by Opris et al.^[159]

9 Based on the assumption that interfacial layers are driving factors behind increasing dielectric
10 permittivity, several groups have used organo-clays incorporated into silicone to increase the
11 respective dielectric permittivities. An overview of the silicone materials reported on the
12 incorporation of clays can be seen in **Table 4**.

13 Generally either pristine clays, surfactant-modified MMT or specially modified clays have been
14 investigated, resulting in dielectric permittivities from $\epsilon' = 3.7$ and up to $\epsilon' = 5.8$ with
15 intermediate losses. In addition, reduced relaxation times were observed in one case by Gharavi
16 et al.^[132] The primary challenge observed has been the dispersion of the clays in the
17 hydrophobic silicone matrix.

18 In an effort to increase permittivity, a range of conductive fillers such as conductive polymers,
19 carbon black, multi-walled carbon nanotubes (MWCNTs) and exfoliated graphite have been
20 investigated. The conductive fillers introduced into silicone for DET applications are
21 summarised in **Table 5**.

22 Generally, the challenge with conductive fillers is preventing percolation and short-circuiting
23 of the electroactive polymers. There are currently two approaches applied in the literature for
24 the use of conductive materials in electroactive polymers. Either the loading of the conductive
25 filler is kept below the percolation threshold or the conductive particles are encapsulated to
26 prevent percolation in the case of higher conductive filler content.

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Fillers loaded at levels below the percolation threshold permit loadings of 1-5 wt% for carbon black, generally up to 0.5 wt% for MWCNT and up to 4 wt% for expanded graphite, depending on the method of dispersion. The advantage of these approaches is the simplicity of adding the filler directly, but substantial loss has been observed in most of these cases which would be expected to give rise to substantial challenges in long-term stability. To circumvent these challenges Goswami et al.^[149] introduced a more advanced mixing scheme to permit in-situ entrapment of MWCNT in silicone while maintaining controlled dispersion. By this approach the content of MWCNT could be increased by up to 1 wt% while still maintaining a non-conductive matrix. However, considerable leakage currents were observed at elevated temperatures and electrical breakdown was reduced to 20 V/ μm at 1 wt% MWCNT.

In the area of conductive polymers both direct mixing and isolation from the matrix have been applied, with the direct blending of conductive polymers (which will be treated in the subsequent section). However, in order to apply these materials for DETs it is necessary to either go below the percolation threshold or to encapsulate the conductive polymer, as illustrated in **Figure 5**.

The encapsulation approach has been investigated by Opris et al. in several publications with divinylbenzene encapsulated polyaniline (PANI) particles (Figure 5 top left and middle). The authors^[52,159] prepared both poly(styrenesulfonic acid)-stabilised PANI nanoparticles as well as poly(divinylbenzene) (PDVB)-encapsulated PANI particles, which after blending into a silicone matrix showed increased dielectric permittivity from $\epsilon' = 2.3$ to almost 5 at low frequencies. Next, 15 vol% PANI in PDVB (13 wt% PANI in 87 wt% PDVB) in a silicone matrix created composites with improved electromechanical responses that reached 12% strain at 50 V/ μm .^[160] In a further development by Opris et al.^[161] the silicone matrix was optimised using different condensation cure cross-linking chemistries to encompass the PDVB-PANI particles better. Using the optimised silicone matrix and 20 wt% PDVB-PANI particles good properties were obtained, such as increased dielectric permittivity, low dielectric loss, large

1 strain at break (>1000 %) and a lateral actuation strain of 12% at 40 V/ μm for a 30% pre-
2 strained film. A summary of the studies conducted on core-shell fillers can be seen in **Table 6**.
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4 As shown in Figure 5 (bottom), Yang et al.^[162] similarly developed a system for encapsulating
5 Ag particles by using a silica core covered with polydopamine, which was in a step-wise fashion
6 covered with Ag particles immobilised on the surface. A subsequent polydopamine layer could
7 be used to control the thickness of the isolating layer, and thereby the permittivity of the system,
8 where an optimum level was found with a dopamine layer of 15 nm and a loading of up to
9 50 vol%, thus providing a dielectric permittivity of up to $\epsilon' = 50$. Recently, Quinsa et al.^[163,164]
10 have also shown how Ag particles covered by a SiO₂ shell could be used to obtain a permittivity
11 of $\epsilon' = 5.9$. As with other conductive fillers they observed a reduced dielectric breakdown
12 strength of 13.4 V/ μm , as also mentioned above for the other conductive fillers.
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15 In addition to the systems mentioned above, there are also reports of the use of inorganic core-
16 shell particles such as SiO₂/TiO₂ by Vudayagiri et al.,^[147] or liquid core-shell particles enabling
17 the use of liquid high-permittivity fillers such as the ionic liquids recently investigated by
18 Mazurek et al.^[165,166] In all cases the use of core-shell particles enables the employment of
19 otherwise inaccessible fillers in dielectric elastomers, and it will be interesting to follow future
20 developments within this area.
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23 However, a very often ignored effect of hard fillers in the silicone elastomer is that the resulting
24 elastomer composites experience severe stress-softening in cyclic experiments (Mullins
25 softening), and they may experience mechanical ageing (fatigue) upon pre-straining,^[65] which
26 subsequently causes loss of tension and strain reversibility in the composites. Young's moduli
27 have been shown to decrease by a factor of approximately two for silicone elastomers with 35
28 phr TiO₂ upon pre-straining at 120% for three months, whereas commercial silicone elastomers
29 do not show the same tendency. Obviously, it is very important when formulating elastomers
30 to maintain elasticity and stability in order to utilise the performance strengths of silicone
31 elastomers, namely fast responses, large and reproducible strains and overall stability.
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1 Commercial elastomers experience negligible ageing, thereby making them ideal candidates for
2 DET products. With the right precautions, i.e. minimising filler content (of course with
3 decreased permittivity as a trade-off) and limiting the amount of oils and solvents used in the
4 preparation process, the favourable properties of commercial elastomers may be transferred
5 successfully to composites.^[65]

5. Silicone/polymer blends for dielectric elastomers

14 Alternatively, a very efficient method to increase effectively the electromechanical response of
15 silicone elastomers involves blending in components such as polymers with high dielectric
16 permittivity. Such polymers simultaneously decrease the Young's modulus and increase
17 dielectric permittivity, thus increasing electromechanical responses significantly. Increasing the
18 electromechanical response of a PDMS elastomer, for example, has been achieved by blending
19 in small amounts (1-6 wt%) of the highly conjugated, un-doped poly(3-hexylthiophene) (PHT)
20 with high values of ϵ' (>2000 at 1 Hz).^[167,168] Blend homogeneity was ensured by initially using
21 liquid phases, PDMS in the pre-polymer stage and PHT as a chloroform solution, after which
22 the silicone matrix was cured. In a blend with 6 wt% PHT low Young's modulus ($Y = 69$ kPa)
23 and high dielectric permittivity ($\epsilon' = 13.8$, at 1 Hz) were obtained. The system, however,
24 suffered from high dielectric losses. A more optimal concentration of 1 wt% is therefore
25 presented in **Table 7**.

26 Gallone et al.^[169] used a PDMS/polyurethane blend comprised of a commercial three-
27 component PDMS-based formulation (TC-5005 A/B-C by BJB Enterprises Inc.), a moisture-
28 cure system which contains a PDMS-based plasticiser and a two-component polyurethane
29 elastomer (poly 74 from Polytek Development). A blend prepared with 40 vol% polyurethane
30 achieved dielectric permittivity ranging from $\epsilon' = 5.2$ at high frequencies (>1000 Hz) to $\epsilon' =$
31 15.5 at 10 Hz. Thus, permittivity was observed to be even higher than that of pure polyurethane
32 ($\epsilon' = 6.5$ at low frequencies), which was ascribed to the Maxwell-Wagner-Sillars polarisation

1 of the interphases in the blend. An actuation strain of 2.7 % at 5.5 V/ μm was achieved, but
2 dielectric loss was significant and resulted in decreased dielectric breakdown strength.
3

4 In another type of blend two polyethylene glycols, with average molecular weights of 600 g
5 mol⁻¹ (PEG600) and 1500 g mol⁻¹ (PEG1500), were blended with the liquid silicone Silastic
6 DC3481.^[170] In a blend with 5 phr PEG600, a dielectric constant of $\epsilon' = 5.4$, a Young's modulus
7 of 0.85 MPa and an actuation strain of 11.5% at 40 V/ μm were achieved, the latter of which
8 was 64% higher than pure PDMS. In order to overcome the immiscibility of PDMS and PEG,
9 Razak et al.^[171] prepared PEG-PDMS multi-block copolymers which were then blended into a
10 commercial silicone elastomer (MJK 4/13 from Wacker Chemie). On a microscopic scale, such
11 blends with low PEG-PDMS block copolymer concentrations were seen to create completely
12 homogenous films, whereas at high concentrations, spherical domains of PEG were observed
13 in the thin films. Using 5 wt% of the PEG-PDMS block copolymer, dielectric permittivity was
14 found to increase by 60% while dielectric losses remained low and dielectric breakdown
15 strength was maintained at approximately ~ 100 V/ μm .
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18 Risse et al.^[172] prepared a blend of a ~ 2300 g mol⁻¹ cyanopropyl-functional PDMS and a PDMS
19 matrix, where the cyano-functional PDMS acted both as a filler and as a plasticiser, as seen in
20 **Figure 6**. Dielectric permittivity increased significantly (\sim two-fold), but this upturn was
21 accompanied by a 75% decrease in electrical breakdown strength (from 80 V/ μm to 20 V/ μm).
22 Commercial fluorosilicones were investigated early on by Pelrine et al.^[50] but were shown to
23 exhibit high leakage currents.^[47] Later, Böse et al.^[173] prepared a home-made system using
24 trifluoropropyl-functional divinylpolydimethylsiloxane, cross-linked into an elastomer and
25 mixed with fluorinated silicone oil, to create very soft silicone elastomers ($Y = 0.07$ MPa at 45
26 wt% oil) with enhanced dielectric permittivity of up to $\epsilon' = 5.4$. The actuation strain was
27 improved by a factor of five using 40 or 45 wt% fluorinated silicone oil, though the leakage
28 current was not stated.
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In order to overcome the increased dielectric losses that usually arise when attempting to increase dielectric permittivity, Madsen et al.^[174,175] used a chloropropyl-functional silicone oil, namely LMS-152 from Gelest Inc., as an additive to the commercial silicone elastomer LR3043/50, supplied by Wacker Chemie. At a content of up to 30 phr LMS-152 dielectric permittivity increased to $\epsilon' = 4.4$ while the dielectric loss tangent decreased. Furthermore, LMS-152 proved to decrease the dielectric loss of a TiO₂-containing silicone elastomer. Thus, this study proved that it is possible to increase permittivity while not compromising dielectric loss, which is a positive step forward towards low-loss materials. Due to the softening effect of the chloropropyl-functional silicone oil, the Young's modulus of LR3043/50 decreased from 2 MPa to 1.35 MPa. This decrease in the Young's modulus, interestingly, did not decrease dielectric breakdown strength, which in fact increased from 121 V/ μm to 130 V/ μm . Thus, the addition of LMS-152 did not compromise any of the important DET properties, albeit the long-term stability of such materials still needs further investigation.

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Silicone elastomer blends seem like an interesting and simple method for improving the electromechanical response of silicone-based DETs. However, as discussed for the silicone composites, ageing studies are required in order to evaluate the long-term stability and reliability of these blends. Moreover, free species (blended-in species) may migrate and cause changes in the elastomer structure over time.

46 **6. Chemically modified silicones for dielectric elastomers**

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Another approach to silicone elastomers with increased DET performance is to chemically graft organic dipoles to the PDMS elastomer network. Molecules/chemical groups with high dipole moments increase the polarisability of the elastomer and thereby increase dielectric permittivity and energy density. This approach potentially leads to a more controlled network structure, as it does not rely on the efficient and perfect mixing of particles or blends. Furthermore, such

1 covalently grafted systems should provide a more stable elastomer system upon continued
2 activation of the material.^[110] Several interesting systems have been developed in this respect.
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4 Kussmaul et al.^[176,177] and Risse et al.^[178] added the synthesised dipolar molecule *N*-allyl-*N*-
5 methyl-*p*-nitroaniline, together with compensating amounts of a hydride-functional cross-
6 linker, to a PDMS matrix and a commercial silicone elastomer system, respectively, in one-step
7 processes. Two-fold increases in dielectric permittivity were obtained compared to a silicone
8 reference. However, the direct addition resulted in a competitive reaction with the network
9 formation reaction, ultimately resulting in a high risk of network imperfections such as dangling
10 substructures and large sol-fractions, which could be washed out of the network. Therefore, at
11 high nitroaniline concentrations, significantly softer networks were obtained and electrical
12 breakdown strengths were significantly reduced, as seen in **Table 8**.

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26 As an alternative approach Racles et al.^[179] developed a system in which cyanopropyl-groups
27 were distributed along the backbone of PDMS chains. Cyanopropyl-functional hydroxyl-
28 terminated PDMS was prepared through the ring-opening polymerisation of different
29 cyclotetrasiloxanes. Silicone elastomers were then prepared by cross-linking reactions with
30 ethyltriacetoxysilane and a titanium tetra(2-ethylhexoxide) catalyst. Dielectric permittivity was
31 found to increase two-fold, but this increase in permittivity was followed by an increase in
32 conductivity and poorer mechanical properties. Favourable results were obtained when
33 mixtures of the cyanopropyl-functional PDMS and a PDMS pre-polymer were used to form
34 elastomers^[179] (Table 8). In a further development with cyanopropyl-functional
35 materials,^[180,181] (see **Figure 7**) a permittivity of $\epsilon' = 4.5$ and a breakdown strength of 56 V/ μm
36 were achieved, while a 13-times higher actuation strain compared to silicone was also obtained.
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38 In order to distribute functionality in a controlled manner, Madsen et al.^[182-184] developed a
39 new silicone-compatible azido-functional cross-linker that allowed for specific
40 functionalisation with high dipole moment molecules at the cross-linking point of silicone
41 networks. This was achieved by using a copper-catalysed azide-alkyne 1,3-dipolar
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1 cycloaddition (CuAAC), which is orthogonal to the cross-linking reaction, so that functionality
2 could be added without compromising the network-forming addition cure reaction. The
3
4 advantage of this method was highly controlled functionalisation, whereby the dipolar groups
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6 (nitrobenzene and nitroazobenzene) were ensured to be very well distributed throughout the
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8 network, as the cross-linker allowed for only one functional group per cross-linker molecule,
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10 as seen in **Figure 8**. Consequently, the mechanical properties of the functionalised elastomer
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12 could be controlled and maintained easily. Since the functional groups were directly bound to
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14 the cross-linker, this also limited the maximum loading of the dipolar groups, leading to modest
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16 improvements in dielectric permittivity of up to 20%.

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19 In order to increase the possible concentration of functional groups, Madsen et al.^[185,186]
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21 developed a new method distributing the functional groups on the backbone of a copolymer
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23 instead of at the cross-linking points, thereby increasing the amount of functional groups
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25 drastically. Copolymers allowing for addition cure were synthesised through the
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27 tris(pentafluorophenyl)borane-catalysed Piers–Rubinsztajn reaction of 3-
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29 chloropropylmethyldimethoxysilane and hydride-terminated dimethylsiloxane pre-polymers of
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31 different lengths, in order to create copolymers with spatially well-distributed azido groups that
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33 allowed for further functionalisation with, for example, high dipole moment molecules via
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35 CuAAC, as seen in **Scheme 2**. This method allowed for complete control over the concentration
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37 and distribution of functional dipolar groups along the backbone of silicone polymers, and as a
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39 result the mechanical properties could be easily tuned to produce high breakdown strengths.
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41 The system, however, at high functional dipolar nitrobenzene group concentrations, suffered
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43 from high dielectric losses at low frequencies and slightly increased conductivities.

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46 Bele et al.^[187] used an approach similar to that employed by Madsen et al.,^[182] by using
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48 functional cross-linkers to increase the dielectric permittivity of silicone elastomers. The cross-
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50 linkers consisted of commercial R-trialkoxysilanes which were cross-linked with
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52 polydimethylsiloxane- α,ω -diols in condensation cure reactions, using dibutyltin dilaurate as a
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1 catalyst. Although somewhat higher electromechanical actuation was achieved, this method did
2 not increase ϵ' significantly and led to increased moisture sorption values. No conductivity or
3 dielectric breakdown values were presented.
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7 Dünki et al.^[188,189] functionalised a high molecular weight hydroxyl-terminated
8 polymethylvinylsiloxane with 3-mercaptopropionitrile, which were cross-linked using 2,2'-
9 (ethylenedioxy)diethanethiol – a bi-functional thiol. High dielectric permittivity ($\epsilon' = 10$ at
10 1 MHz) and a large actuation strain (20.5% at 10.8 V/ μm) were obtained. However, dielectric
11 losses ($\tan \delta > 1$) and conductivity increased significantly at low frequencies, while dielectric
12 breakdown strength was very low (10.8 V/ μm). A major advantage of this material, nonetheless,
13 was that it experienced self-healing properties upon dielectric breakdown, which is a strongly
14 desired ability for augmenting the lifetime of DETs.
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19 Zhang et al.^[190] created high permittivity silicone elastomers, with a functionalisation approach
20 similar to that used by Kussmaul et al.,^[176] using a dihydroxyl-functional nitroazobenzene
21 dipolar molecule in a condensation reaction with hydroxyl-terminated PDMS, a
22 tetraethylorthosilicate cross-linker and a dibutyltin dilaurate catalyst. However, in this study a
23 *difunctional* dipolar molecule was used in condensation reactions, and therefore it could
24 actively participate in the curing process (as chain extender/additional cross-linking site) and
25 would not just block one of the cross-linking sites (see **Figure 9**). Consequently, the network-
26 forming reaction was not compromised to the same extent as in the work of Kussmaul et al.^[176]
27
28 The dielectric constant was found to increase in line with increasing nitroazobenzene content,
29 reaching $\epsilon' = 4.9$ at 1 KHz. Stress-strain measurements revealed an increasing Young's modulus
30 and elongation at the breaking point in line with increasing nitroazobenzene content, attributed
31 to increased cross-linking density. Dielectric breakdown strength was found to increase to
32 89.4 V/ μm at low concentrations (4 wt% nitroazobenzene), and thereafter it decreased in line
33 with increasing content, reaching 56.7 V/ μm at 13.2 wt%. A maximum actuation strain of 17%
34 at ~ 68 V/ μm was obtained for a sample containing 7.1 wt% nitroazobenzene, which also
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1 showed the highest value of electromechanical sensitivity (ϵ'/Y). Dielectric losses, however,
2 were not presented.
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4 Recently, a very promising and much simpler silicone elastomer system, based on
5 chloropropyl-functional siloxane copolymers, has been developed by Madsen et al.^[174,191]
6
7 These elastomers possessed a low Young's modulus (0.4 – 1 MPa, 75-90% lower than the
8 utilised silicone reference) and high dielectric permittivity ($\epsilon' = 4.7$ at 1 MHz). Dielectric losses,
9 remarkably, remained as low as those of pure PDMS elastomers, and high dielectric breakdown
10 strengths were obtained (94.4 V/ μm), thus increasing the maximum achievable actuation,
11 $\epsilon'/Y \cdot E_B^2$, significantly (between seven and ten times). Furthermore, the gel fractions and viscous
12 losses remained in the same order of magnitude as a PDMS reference elastomer, and so the
13 softness of the system did not compromise material stability.
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26 In summary, chemical modifications made to silicone elastomers, in order to increase dielectric
27 permittivity and/or electromechanical response, frequently lead to a compromise in properties.
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30 At high concentrations of functional groups, high dielectric permittivities are obtained. This,
31 however, is often accompanied by an increase in dielectric loss or a significant decrease in
32 dielectric breakdown strength. In the design of such systems it is therefore very important to
33 keep in mind and investigate these properties, as they all greatly influence the lifetime and
34 stability of the silicone DET. On the other hand, such modified systems will most likely be
35 more stable and reliable over time and less prone to ageing effects than blends or silicones
36 heavily filled with metal oxides.
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49 **7. Systems with complex network structures for dielectric elastomers –** 50 **interpenetrating and bimodal networks** 51

52 A different approach to improving silicone elastomers involves altering the network structure
53 by, for example, creating interpenetrating polymer networks (INPs) or bimodal networks.
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55 An IPN is a network that consists of two or more polymers that are cross-linked in-situ, to
56 produce interlaced networks. IPNs have different and often superior properties compared to the
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respective homo-polymers, which is due to stabilised bulk and surface morphologies created by the interlaced networks. There are two main routes used to prepare IPNs (**Figure 10**): either sequentially or simultaneously. In the sequential method, the IPN is formed in two consecutive steps, where initially a homo-network of polymer(I) is formed through cross-linking. This network is then swollen with monomer or polymer(II), cross-linker and an initiator, and the IPN is formed through in-situ polymerisation or cross-linking. The second method consists of forming two independent networks simultaneously. This is done by either cross-linking two sets of polymers or through polymerisation and cross-linking two monomers through non-interfering orthogonal reactions.^[192,193]

For many years the main focus of IPNs as dielectric elastomer actuators was on highly pre-strained acrylic 3M VHB tape, due to this material's high dielectric breakdown strength and large strains. The VHB IPN is created via a sequential approach by treating the pre-strained acrylic VHB film with a cross-linkable monomer and an initiator and then allowing the monomer and initiator to diffuse into the film. The monomer, upon thermal curing, forms a second polymer network, interlaced with the acrylic network. The formed IPN is allowed to relax to zero stress, which makes the acrylic network contract and the second network compress.^[194-196] The two interpenetrating networks are now in equilibrium, with one network highly stressed and the other highly compressed. The additive network works as a support for the pre-strained acrylic network, thus eliminating external pre-strain supporting structures. These IPNs, however, have poor frequency responses and are very temperature and moisture sensitive, due to their acrylic nature.

In order to exploit some of the advantageous properties of silicones, such as their broad temperature operating range, low moisture absorption and lower tensile modulus, Mathew et al.^[197] combined VHB acrylic elastomers with a silicone-based elastomer. The silicone chains were swollen with a co-solvent into the acrylic film and subsequently cross-linked. The resultant IPN material was shown to possess properties between the properties of the homo-

1 networks, thus improving some important properties of the acrylic elastomer. This included
2 greater tensile strength, which was believed to be due to the reinforcing silicone network which
3 represented constraining points during the deformation of the acrylic network, and a Maxwell
4 stress higher than that obtained by pure acrylic elastomer at similar voltage levels.
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9 Limited literature has been published regarding the use of non-acrylic-based IPNs as dielectric
10 elastomers; however, Brochu et al.^[63] prepared an all-silicone-based IPN using a soft room
11 temperature vulcanising (RTV) (Dow Corning HSIII) silicone, which served as a host elastomer
12 matrix, and a rigid high temperature vulcanising (HTV) (Elastosil LR3003/70) silicone, which
13 was used to preserve pre-straining in the host elastomer. The IPN was prepared by mixing the
14 two liquid silicones in a co-solvent and drop-casting the mixture on a poly(styrene sulfonate)-
15 treated glass. The RTV Dow Corning HSIII silicone, based on silanol-terminated PDMS, a
16 tetrapropyl orthosilicate cross-linker and a dimethyl tin di-neodecyl ester catalyst were then
17 allowed to cure at RT, and the resulting film was then peeled from the substrate and pre-strained
18 bi-axially. The HTV Elastosil LR3003/70 silicone, based on addition cure components, was
19 then cured at 180°C. The prepared materials showed increasing stiffness in line with increasing
20 HTV Elastosil silicone concentration, and therefore it also showed increased dielectric
21 breakdown strength in line with increasing content. Furthermore, the prepared materials had
22 higher achievable actuation strains of 25% at 55 V/ μm , which was 100% more than the homo-
23 polymer alone. An additional advantage of the method was that the electrode materials could
24 be bonded strongly to the surface layer of the silicone by applying the electrode material before
25 curing the HTV silicone.
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50 Building on the procedure set out by Brochu et al.,^[63] Tugui et al.^[198] also used an
51 interpenetrating silicone system of addition and moisture cure components to lock-in pre-strain.
52 The difference in this work was the molecular weight of the chosen components, giving the
53 network bimodality. The vinyl-cure polymer ($\bar{M}_n = 34,500 \text{ g mol}^{-1}$) had a molecular weight ten
54 times lower than that of the moisture cure polymer ($\bar{M}_n = 370,000 \text{ g mol}^{-1}$). The resulting IPNs
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1 had increased breakdown strength compared to their un-stretched IPN counterparts, and similar
2 to the findings of Brochu et al.,^[63] breakdown strength increased in line with increasing content
3 of the addition cure network. The study, however, found that while the actuation strain increases
4 in line with increasing content of the addition cure network, it decreases when pre-straining of
5 one of the networks is applied. The authors concluded that bimodality seems to be more
6 significant for the actuation strain than the pre-straining facilitated by the IPN structure. The
7 data presented in **Table 9** are therefore for an IPN prepared with no pre-straining.

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17 IPNs composed of ionic networks with very high dielectric permittivities^[199,200] and
18 conventional silicone elastomers in various ratios constitute a novel class of dielectric
19 elastomer. In the most recent development, cross-linked ammonium carboxylates were
20 prepared by blending carboxydecyl-terminated PDMS (DMS-B15 or DMS-B25 from Gelest
21 Inc.) and aminopropylmethylsiloxane dimethylsiloxane copolymer with, on average, four
22 amino groups per chain (AMS-162).^[201,202] Blends of these ionic networks and commercial
23 silicone elastomers, such as Elastosil RT625 (RTV), Powersil XLR630 (LSR) and Elastosil
24 LR3043/30 (LSR), created a range of high-energy density interpenetrating networks. Good
25 overall properties stemmed from the softening effect and very high permittivity of ionic
26 networks – as high as $\epsilon' = 7500$ at 0.1 Hz – while the silicone elastomer part of the IPN provided
27 mechanical integrity as well as relatively high breakdown strength (around 90 V/ μm). When all
28 of these parameters were compared to a commercial silicone elastomer in figure of merit
29 calculations for both actuator and generator applications, the IPNs prepared particularly with
30 LR3043/30 performed exceedingly better than the silicone reference at the lowest frequencies,
31 albeit with moderately better behaviour at the high frequencies only. Another interesting feature
32 of these IPNs was their self-healing properties, which allow broken materials that have suffered
33 dielectric breakdown to be repaired after moderate heating for a few hours.^[201,202]

1 Bimodal networks, which consist of a mixture of very short and relatively long chemically
2 identical polymer chains, can be used as a tool to improve the mechanical properties of silicone
3 networks.^[203,204] Several studies have investigated the unexpected high tear and ultimate
4 strength of bimodal networks.^[205–207] The elastic modulus of these bimodal networks increases
5 significantly at high elongations, and consequently the ultimate strength of these silicone
6 networks is very high. Improvements in ultimate strength stem from the limited extensibility of
7 the short chains, which gives the networks toughness.^[208,209] Furthermore, these relatively long
8 chains retard the rupture process and are responsible for the extensibility of the network.^[207]
9 Therefore, bimodal networks exhibit both significant ultimate stress and major ultimate
10 strain.^[204] Bimodal networks can be created with a random distribution of short polymer chains
11 within the long chains (homogeneous bimodal networks)^[204,210–212] or as heavily cross-linked
12 short chain clusters joined to the long chain network (heterogeneous bimodal networks).^[213–215]
13 Bejenariu et al.^[215,216] prepared both homogenous and heterogeneous bimodal networks and
14 evaluated them as candidates for dielectric elastomers. The heterogeneous bimodal networks
15 exhibited improved mechanical properties for DETs, such as a lower elastic modulus, which
16 made them very soft and extensible, without compromising other properties such as network
17 stability and viscous loss – something that is very difficult to obtain by using traditional
18 monomodal networks. Madsen et al.^[217] developed a novel visualisation tool which allowed the
19 small-chain domains in heterogeneous bimodal networks to be characterised according to their
20 size and distribution, and then they correlated this to their mechanical properties. This led to a
21 multi-domain theory which suggested that effective cross-linking density is lower around the
22 small-chain domains than in the bulk network, as seen in **Figure 11**. Small-chain domains
23 therefore create a local softening effect in bimodal silicone networks, while the networks are
24 still perfectly cross-linked due to a high number of reactive groups on the surface of the small-
25 chain domains. These networks will consequently be softer and have a lower elastic modulus
26 and lower viscous loss than mono-modal networks despite higher average cross-linking density.
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1 This theory could possibly explain the interesting and non-contrary relationship between
2 modulus and viscous loss exhibited by heterogeneous bimodal networks.
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4 Goswami et al.^[115,149] used heterogeneous bimodal networks as a means of incorporating
5 percolative amounts of multi-walled carbon nanotubes (MWCNT) into thiolene-cured silicone
6 elastomers. The elastomer composites were designed to contain amounts of MWCNT above
7 the percolation threshold, without becoming conductive. This was done by adding the
8 MWCNTs inside the small chain domains, which thus acted as macromolecular insulating
9 shells around MWCNT clusters, as seen in **Figure 12**. Dielectric spectroscopy measurements
10 showed an increase in dielectric permittivity in line with increasing MWCNT content, reaching
11 $\epsilon' = 4.7$ at 1 wt% MWCNT, as well as the desired frequency-dependent conductivity for all
12 samples. Furthermore, dielectric losses remained low. The composites showed moderate
13 dielectric breakdown strength of 48 V/ μm at 0.33 wt% MWCNT, which decreased to 20 V/ μm
14 at 1 wt%. This decreasing breakdown strength was explained by increased conductivity at
15 elevated temperatures, due to sample heating at high MWCNT loading.
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33 Since the emergence of synthetic elastomers, the structure-property relationship has been
34 heavily investigated. Silicone elastomers from hydrosilylation reactions have been denoted as
35 a so-called 'model elastomer system', as side reactions are limited and the reaction can be
36 controlled easily by both temperature and inhibitors.^[218] An understanding of cross-linking
37 density, combined with various interactions arising when the silicone elastomer is filled with
38 silica, is crucial for designing elastomers with specific mechanical properties. The filler
39 addition is – as discussed earlier – vital for strength and elongation, as silicone elastomers with
40 no fillers are usually too brittle or too soft to provide stable mechanical properties (depending
41 on polymer chain length). However, altering the structure of the elastomer, such as by creating
42 bimodal elastomers, may render fillers obsolete and open up the way for very soft, elastic
43 elastomers with reliable elastomer properties. Further research into this notion may lead to
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1 increased actuation, as softness can be introduced without increased viscous and dielectric
2 losses.^[217]
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4 Also very recently, Goff et al.^[219] presented work on a hetero-bifunctional chain extender
5 leading to infinitely long PDMS chains with superior elasticity and without the waxy
6 consistency of traditional high-molecular weight silicone. Yet another recent publication also
7 proves that the effect of entanglements could be avoided by grafting side chains to the PDMS
8 backbone.^[220] These findings open up the opportunity to rethink the design of silicone
9 elastomers, as both methods produce stable silicone elastomers with very low elastic moduli.

10 Additionally, the field of IPN is still relatively unexplored in relation to elastomers for dielectric
11 elastomers, where the main focus up to now has been on utilising IPNs to lock in pre-strain.
12 Further exploration into this type of elastomer may also lead to the discovery of better
13 elastomers with favourable features, such as the possibility of locking in pre-strain in a
14 commercially feasible way and adding self-healing properties to the elastomer.
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31 **8. Summary and conclusion**

32 Silicone elastomers provide the basis for fast and reliable actuation. Commercially available
33 elastomers that have been tested as DETs have shown great promise, with respect to both
34 actuation and reliability, but they still suffer from being designed originally for other
35 applications. In particular, the dielectric permittivities of commercial silicone elastomers still
36 remain too low for most practical DET applications, due to high driving voltages. The simplest
37 approach to increase dielectric permittivity is to add high dielectric permittivity fillers. The
38 advantage of this approach is in particular the easy preparation as well as the large variety of
39 fillers available from a large number of suppliers. Highly efficient mixing methods are essential
40 tools in obtaining high-quality elastomers. Moreover, methods such as roll-milling or
41 speedmixing seem to be the most promising approaches for an industrial application to be
42 implemented and up-scaled for industrial production. For filled systems it is essential to strike
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1 a balance between increases in permittivity, only a limited increase in Young's moduli, good
2 film-forming properties, tear strength, process ability as well as long-term stability. In
3 particular, stability needs to be tested fully for the most promising composite systems, in order
4 to determine the optimal level of loading. Alternatively, other reinforcing approaches should be
5 considered, thereby enabling a higher level of fillers, as seen in heterogeneous bimodal systems,
6 for instance.

7 The formation of blends constitutes yet another facile method for improving the
8 electromechanical response of DETs. The advantage of this method includes ease of fabrication,
9 which could make the method directly applicable in the large-scale manufacture of dielectric
10 elastomers. The obvious disadvantages of blending in components in silicone matrices include
11 potential poor compatibility between the silicone matrix and the polymer filler, which can lead
12 to unwanted phase-separation. If a silicone-like polymer filler is used, compatibility issues may
13 be overcome, but long-term material stability due to migration might still be a major issue, since
14 mechanical and/or dielectric properties are likely to change drastically over time. Therefore,
15 ageing studies on such blends are of the utmost importance.

16 To ensure long-term stability, chemically modified silicones, such as grafted silicone
17 elastomers with high dielectric permittivity, should be considered. Such systems have long-
18 term stability due to a lesser tendency to exhibit Mullins effects as well as improved mechanical
19 properties such as a lower Young's modulus and increased stress at breaking compared to
20 composite systems. Chemically modified systems, however, often suffer from increased
21 dielectric losses due to dipole relaxation mechanisms and Maxwell-Wagner-Sillars
22 polarisation. This may in turn lead to reduced dielectric breakdown strengths, and therefore care
23 must be taken to keep dielectric losses to reasonable levels. Furthermore, some types of
24 chemical groups may inhibit cross-linking (whether addition or condensation cure), and so
25 proper cross-linking of the elastomer must be ensured via an investigation of either sol fractions,
26 through extraction experiments, or by measuring viscous losses.

1 In all of the above approaches focusing on improved dielectric permittivity, it is essential to
2 consider the systems holistically and ensure network integrity and stability. The network
3 structure can be used as a means of improved actuation through a controlled Young's modulus
4 as well as to maintain low viscous losses. Bimodal networks can be used if soft and stretchable
5 elastomers are desired, whereas IPNs make it possible to create free-standing films with pre-
6 strain within the elastomer, without the need for support structures. The major disadvantage of
7 these systems is their complexity, since their curing reactions are expanded to several steps.
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10 11 12 13 14 15 16 17 18 19 **9. Perspective** 20

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23 Even though several challenges still exist on the road toward commercialising DETs, they
24 nevertheless hold great promise for future applications due to their unique properties, such as
25 being lightweight, capable of large strains and of relatively low cost compared to similar
26 technologies. Due to the complexity of dielectric elastomers there may be many paths toward
27 improved materials. Both tuning the stress-strain response of the elastomers and increasing
28 energy density via dielectric permittivity, or through combinations of the techniques discussed
29 herein, may be suitable approaches. Too strong a focus on increasing dielectric permittivity or
30 actuation strain, however, may not be the most optimal way to proceed forward, since there
31 needs to be a greater emphasis on DETs as a whole because the lifetime of silicone elastomers
32 with high permittivity or increased actuation strain may still be very poor. Therefore, a complete
33 standardised characterisation of materials is essential for the proper evaluation of new elastomer
34 candidates for DETs, following for example the standards recently proposed by the European
35 Scientific Network for Artificial Muscles (ESNAM).^[221] Lifetime is a key aspect in the further
36 improvement of DETs, and it is vital for the potential commercialisation of the technology. A
37 potential way to obtain higher lifetimes is by introducing self-healing capabilities into both
38 elastomers^[188,201] and electrodes,^[222] as seen recently. It will be interesting to follow the
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developments of self-healing materials for DETs and how this will affect materials research
and especially future DET products.

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Abbreviations and symbols

1		
2	CCTO	CuCaTiO ₃ , copper calcium titanate
3	CPO	copper-phthalocyanine
4	CuAAC	copper(I)-catalysed azide-alkyne cycloaddition
5	<i>d</i>	thickness of elastomer
6	DC	direct current
7	DET	dielectric elastomer transducer
8	ε'	dielectric permittivity
9	ε''	dielectric loss
10	ε_r	relative dielectric permittivity
11	ε_0	vacuum permittivity
12	EAP	electroactive polymer
13	E_B	dielectric breakdown strength
14	EMI	electromechanical instability
15	<i>f</i>	cross-linker functionality
16	<i>F</i>	frequency
17	F_c	critical frequency
18	F_{om}	figure of merit
19	φ	strain energy function
20	G^*	complex shear modulus
21	G'	storage modulus
22	G''	loss modulus
23	HCR	high consistency silicone rubber
24	HMDS	hexamethyldisilazane
25	HTV	high temperature vulcanising
26	IPN	interpenetrating polymer network
27	λ	strain
28	LR	liquid rubber
29	LSR	liquid silicone rubber
30	ν	Poisson's ratio
31	MMT	montmorillonite
32	\bar{M}_w	weight average molecular weight
33	MWCNT	multi walled carbon nanotube
34	μ	dipole moment
35	ω	frequency
36	ω_c	critical frequency
37	PANI	polyaniline
38	PDA	polydopamine
39	PDMS	polydimethylsiloxane
40	PDVB	polydivinyl benzene
41	P_{el}	electrostatic pressure
42	PEG	polyethylene glycol
43	phr	parts per hundred rubber
44	PHT	poly(3-hexylthiophene)
45	PMN	(PbMg _{1/3} Nb _{2/3})O ₃ , lead magnesium niobate
46	PMN-PT	(PbMg _{1/3} Nb _{2/3})O ₃ – PbTiO ₃ , lead magnesium niobate – lead titanate
47	PU	polyurethane
48	PZT	PbZrTiO ₃ , lead zirconia titanate
49	<i>r</i>	stoichiometric imbalance/ratio
50	r_c	stoichiometric imbalance/ratio for critical gelation
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RT	room temperature
RTV	room temperature vulcanising
σ	conductivity
s	thickness strain
SC	space charge
SDBS	sodium dodecyl benzene sulfonate
SEM	scanning electron microscopy
Tan δ	loss tangent
THF	tetrahydrofuran
U	voltage
US	ultra-sonication
wt%	weight percent
Y	Young's modulus

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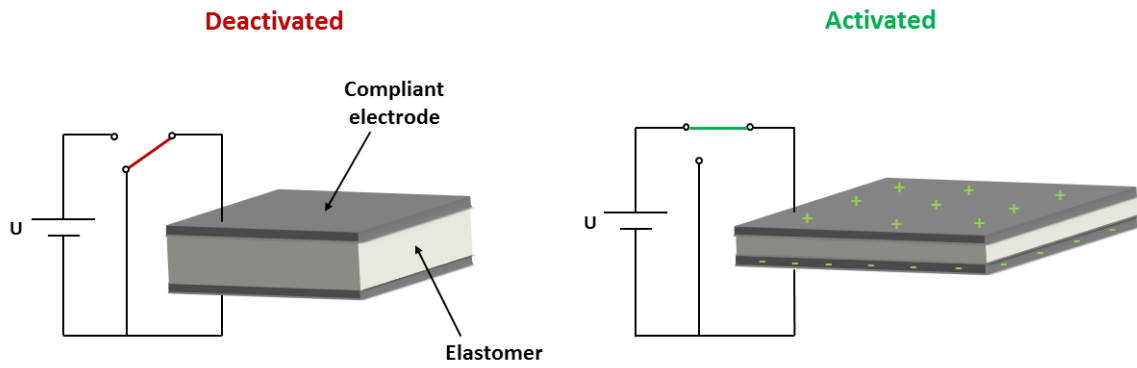
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Figure 1. Schematic illustration of the transduction principle of DET.

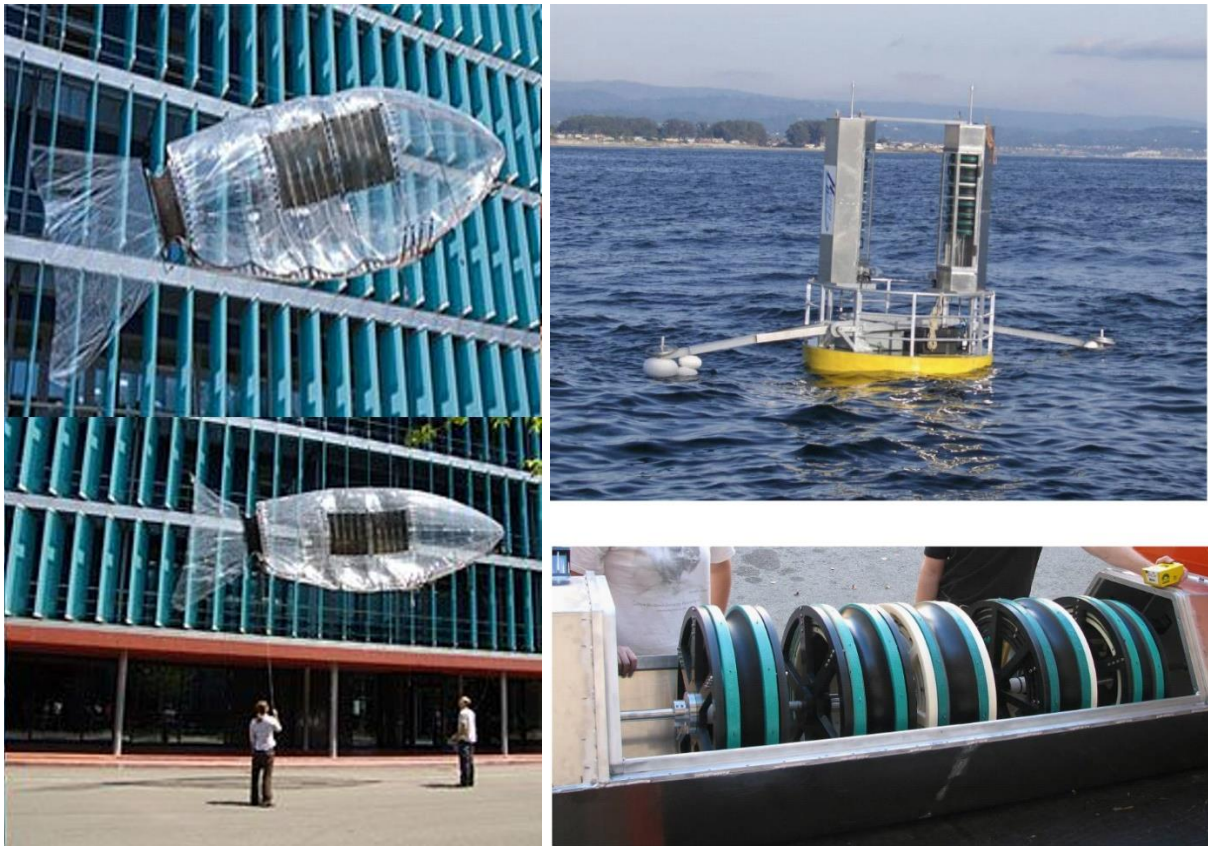
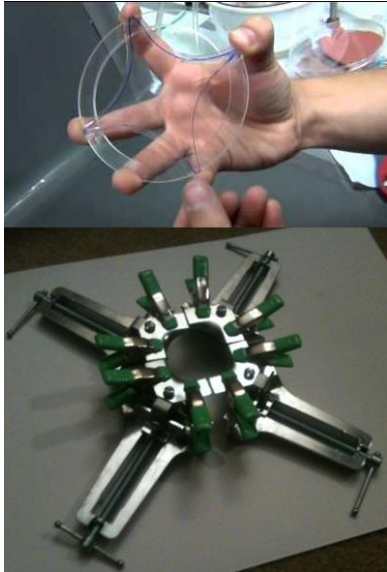


Figure 2. Examples of extraordinary DET applications. Left: Flying fish blimp by EMPA.^[40]
Right: Dielectric elastomer ocean wave power generator by SRI International.^[41]



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19 *Figure 3.* Pre-straining devices. The top picture illustrates a simple frame which is applicable
20 when the dielectric elastomer is adhesive.^[223] The bottom picture illustrates a mechanical
21 solution to homogeneous stretching.^[224]
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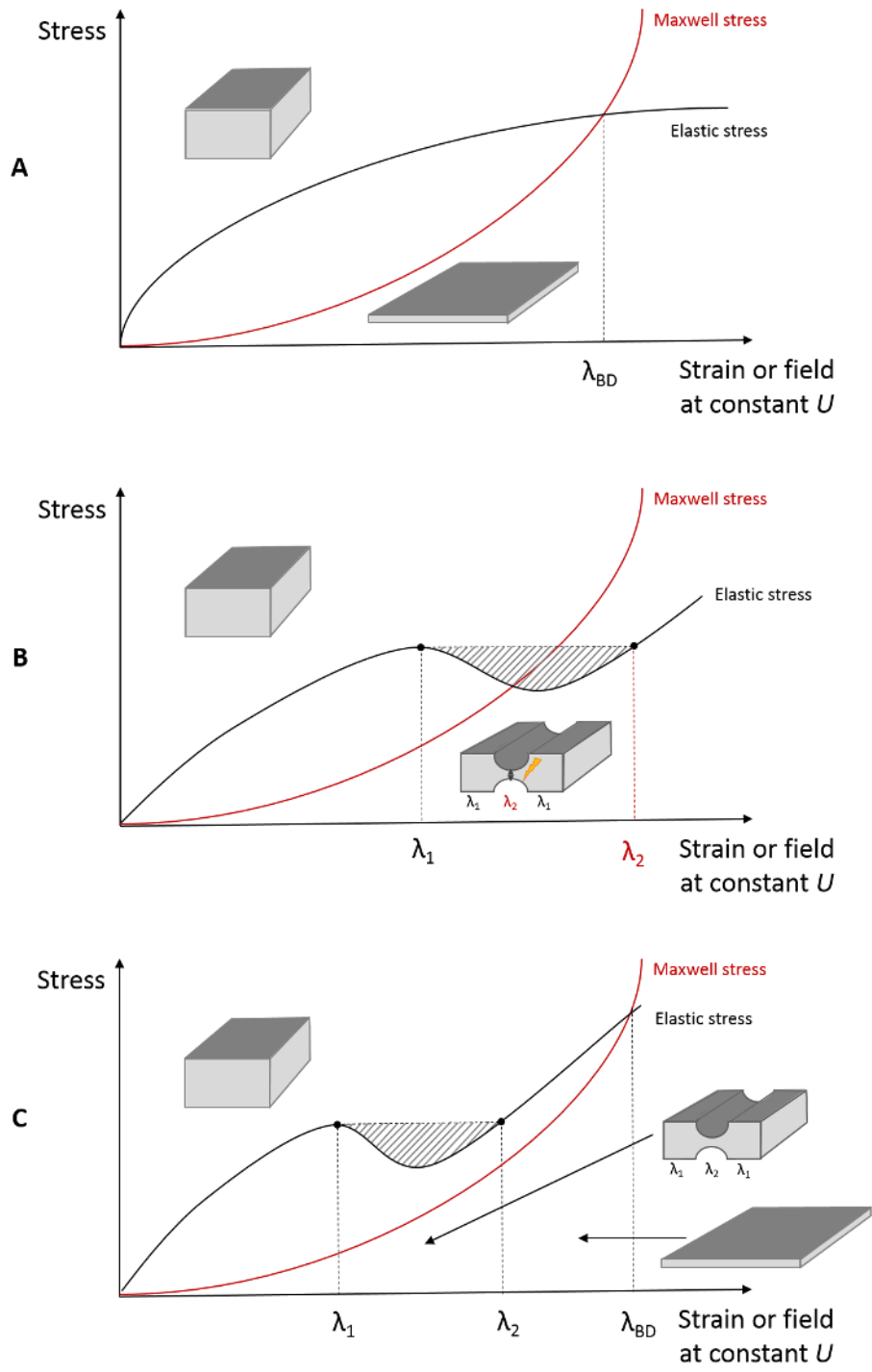


Figure 4. Illustration of stress-strain diagrams of elastomers with various behaviours with respect to electromechanical instability (EMI). A) Elastomer with no EMI. Ideally, the elastomer fails at the strain that corresponds to the intrinsic breakdown strength of the elastomer. B) Elastomer with snap-through and EMI. The elastomer will break down at $\lambda=\lambda_1$ as the snap-through facilitates dielectric breakdown as the Maxwell stress exceeds the elastic stress before reaching $\lambda=\lambda_2$. C) Elastomer with snap-through but no EMI due to pre-straining. The snap-through will proceed without breakdown and will, as for the elastomer in A), ideally break down at the intrinsic breakdown strength of the elastomer.

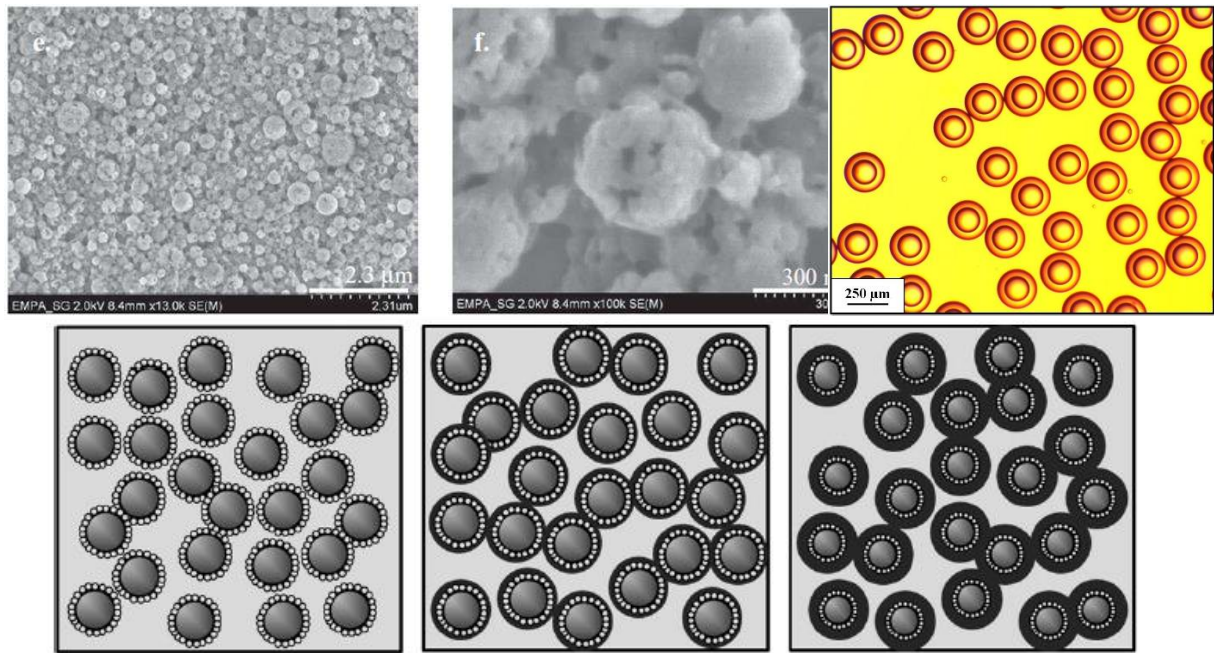


Figure 5. Examples of core-shell or encapsulated fillers for DET applications. Top left and middle: Encapsulated PANI (SEM micrographs).^[160] Top right: Liquid core-shell particles for liquid high permittivity fillers (microscopy)^[166] Reproduced with permission.^[166] 2015, The Royal Society of Chemistry. Bottom: Dopamine-covered Ag/SiO₂ core-shell particles. Reproduced with permission.^[162] 2015, Elsevier.

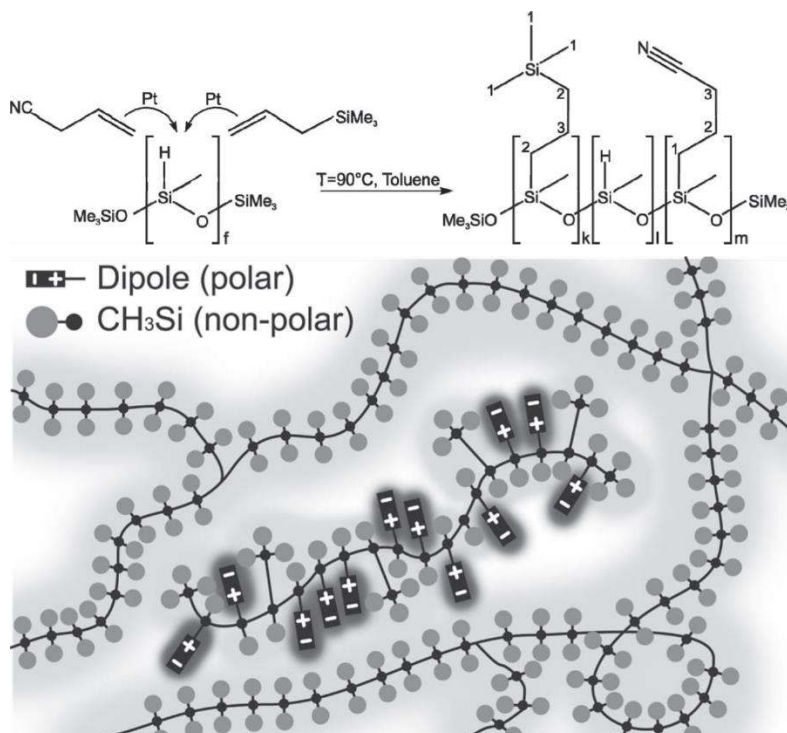


Figure 6. Cyano-functionalised siloxane acting both as a high permittivity filler and a plasticiser in the silicone matrix.^[172]

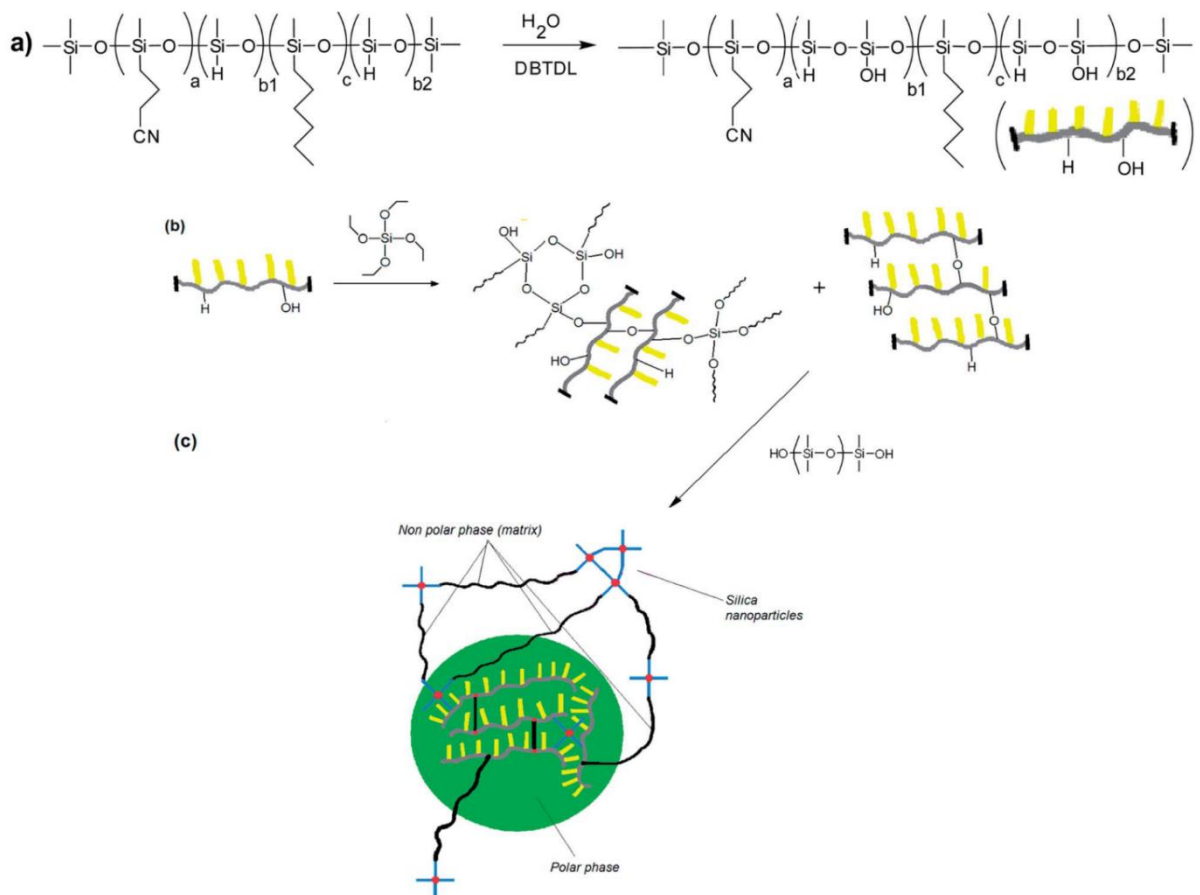
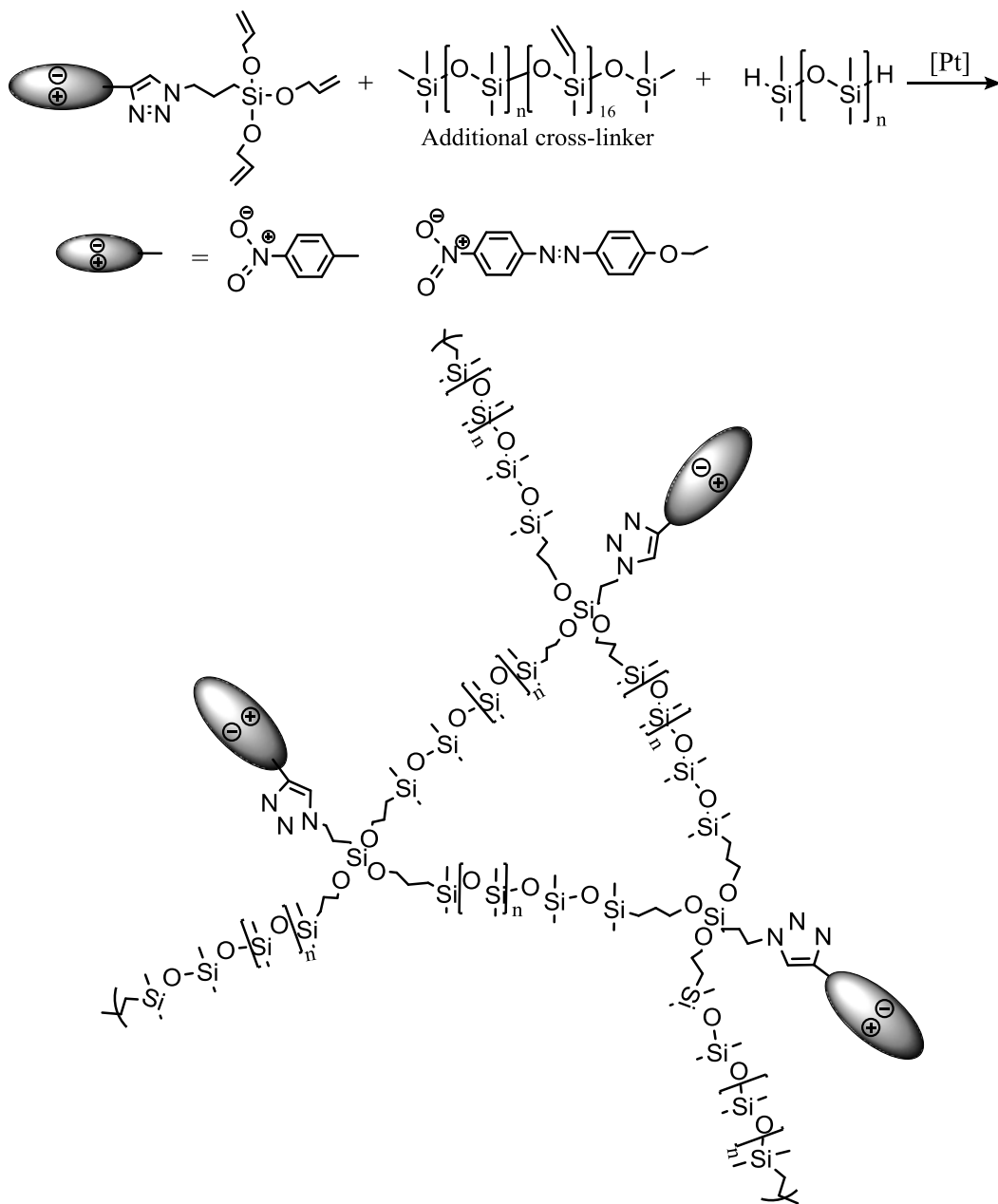
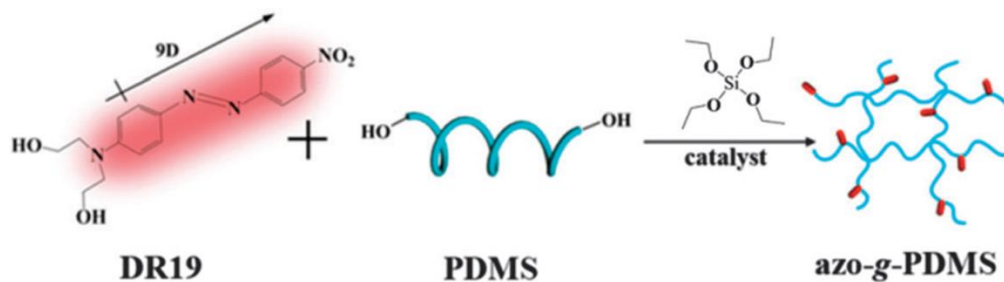


Figure 7. Schematic illustration of the route to improved cyanopropyl-functional PDMS networks. Reproduced with permission.^[181] 2015, The Royal Society of Chemistry.

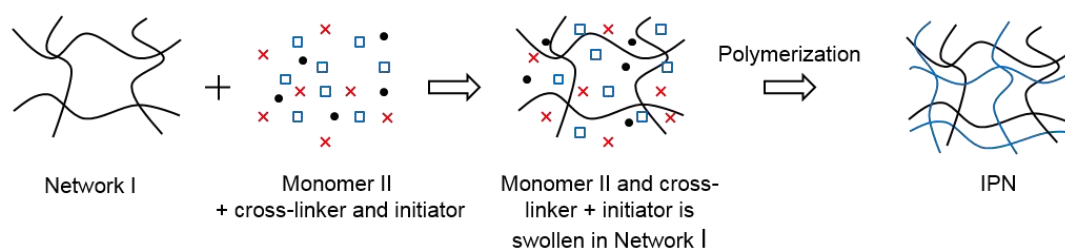


43 *Figure 8.* Cross-linking reaction between nitrobenzene and azonitrobenzene-functional cross-
 44 linkers and PDMS. Reproduced with permission.^[183] 2013, IOPscience.
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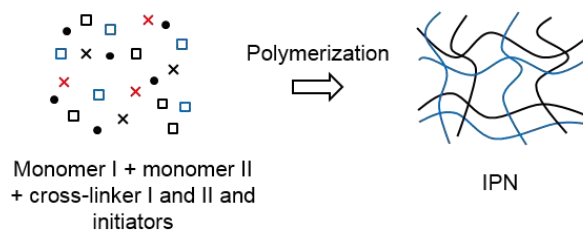


10 *Figure 9.* The synthetic approach to the nitroazobenzene-grafted PDMS network using a
 11 condensation cure reaction. Reproduced with permission.^[190] 2015, The Royal Society of
 12 Chemistry.

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16 **a) Sequential IPN formation**



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28 **b) Simultaneous IPN formation**



38 *Figure 10.* Schematic illustration of sequential (a) and simultaneous (b) IPN formation.

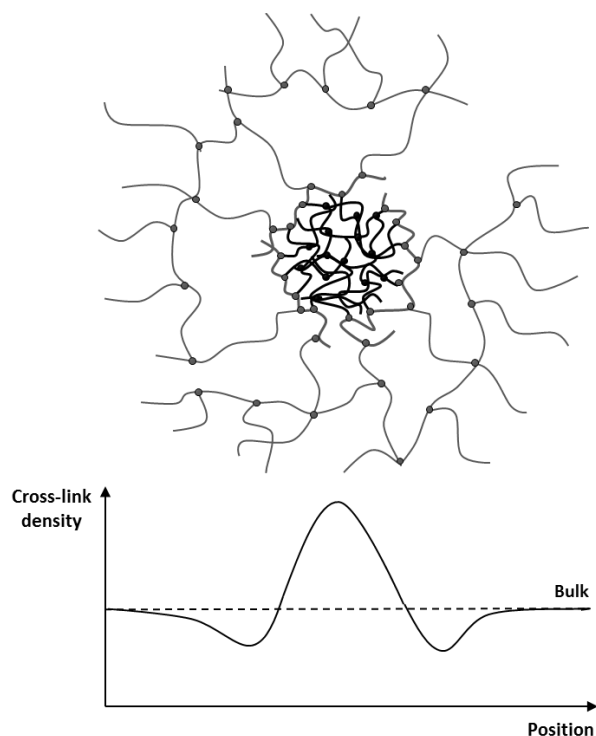


Figure 11. Schematic illustration of efficient cross-linking density in a heterogeneous bimodal network. Reproduced with permission.^[217] 2014, The Royal Society of Chemistry.

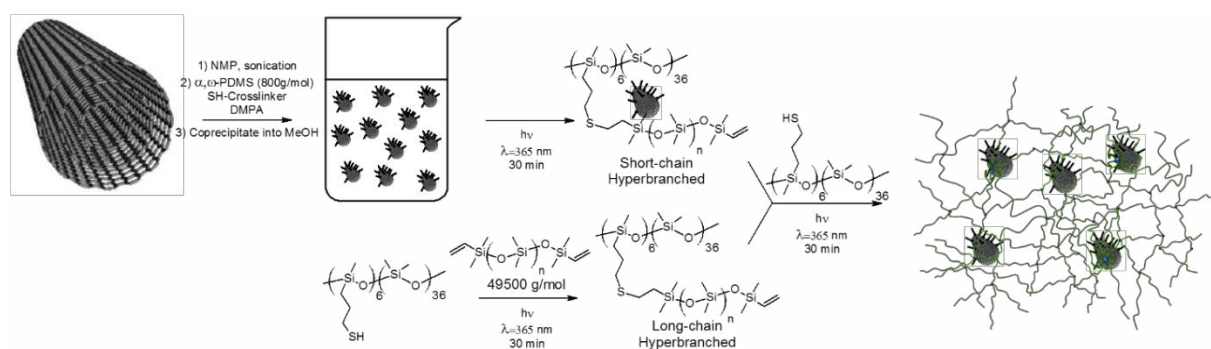
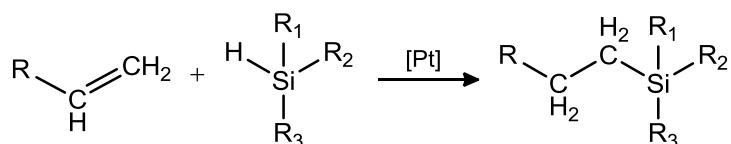
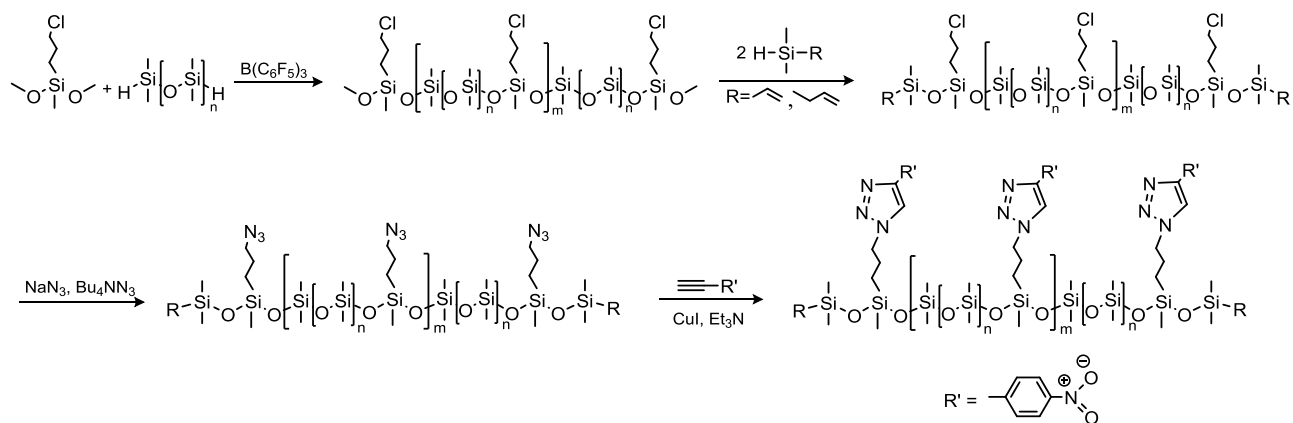


Figure 12. Preparation procedure for MWCNT-filled, thiolene-cured heterogeneous bimodal silicone networks. Reproduced with permission.^[149] 2015, The Royal Society of Chemistry.



Scheme 1. Hydrosilylation reaction, where R, R₁, R₂ and R₃ can be various groups such as CH₃, phenyl-groups or polymer chains.



Scheme 2. Synthetic route to azido- and CuAAC-functionalised copolymers. Reproduced with permission.^[185] 2014, The Royal Society of Chemistry.

Table 1. Properties of commercial silicone elastomers for DETs.

Base elastomer	ε' @0.1 Hz	ε' @1 MHz	$\tan \delta$ @0.1 Hz	Y [MPa]	Maximum strain [%]	Thickness of film for E_B [μm]	E_B [V/ μm]	Maximum thickness actuation strain [%]	Ref.
BJB TC5005 with Plasticiser (40 phr stated)	5.2 ^{a)}	4.2	0.7/5.2 ^{a)}	0.050	300	1000 pre-strained to ~500	10 ^{b)}	11 @ 10V/ μm	[103]
Silastic LC-20-2004 with self-clearing electrodes	n.a.	n.a.	n.a.	n.a.	700 ^{e)}	100 pre-strained to ~25	250 (pre-strained)	50 @ 230V/ μm	[222]
Neukasil RTV-23	2.5	2.5	n.a.	0.4 (when pre-strained 50%)	n.a.	n.a.	n.a.	1 in cyclic experiment	[52]
HS3 Dow Corning (centrifuged) ^{d)}	2.8	2.8	0.005 ^{e)}	0.1	2.8	225 pre-strained to ~80	110 (pre-strained 68% in both directions)	48 @ 110 V/ μm	[62]
Nusil CF19-2186	2.8	2.8	0.005 ^{e)}	1.0 ^{c)}	600 ^{e)}	50 pre-strained to ~24	350 (pre-strained 45% in both directions)	39 ^{f)}	[3,62]
Sylgard 186	n.a.	n.a.	n.a.	n.a.	n.a.	31 pre-strained to ~6	na	70 @ 3.7 kV	[113]
Sylgard 186	2.8	n.a.	n.a.	0.7	n.a.	n.a.	144 ^{b)}	32 @ 144 V/ μm	[2]

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Fluorosilicone Dow Corning 730 (centrifuged to remove particles)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	80 ^{b)}	28 @ 80 V/ μm	[2]
Danfoss PolyPower film	2.6 (pre- strained)	n.a.	n.a.	n.a.	n.a.	100 pre-strained to 71	50	7 @ 3kV	[104]
Silastic LC-50- 2004	2.8	n.a.	n.a.	0.9	n.a.	60-100	105	n.a.	[110,111]
LR 3005/50	3.0	n.a.	n.a.	0.8	n.a.	60-100	115	n.a.	[110,111]
LR3043/30	2.8	n.a.	n.a.	0.8	n.a.	60-100	118	n.a.	[110,111]
LR3043/50	2.8	n.a.	n.a.	1.5	n.a.	60-100	130	n.a.	[110,111]
Wacker Silpuran 6000/10	n.a.	n.a.	n.a.	0.22 – 0.32	n.a.	10,000 pre- strained to 2,000	120 (pre- strained)	n.a.	[112]

^{a)} @ 1 Hz; ^{b)} The breakdown strength is determined from the actuation plot; ^{c)} Data from data sheet supplied by supplier; ^{d)} Elastomer no longer available from Dow Corning; ^{e)} @ 1 kHz; ^{f)} Field not available.

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Table 2. TiO₂-filled PDMS elastomers.

Base elastomer	Filler/plasticiser	Method of dispersion	Content	ϵ'	$\tan \delta$ @0.1 Hz	Y [MPa]	Maximum strain [%]	Thickness of film for E_B [μm]	E_B [V/ μm]	Maximum actuation strain [%]	Ref.
Sineskin A/B/C 50% silicone)	TiO ₂ (Rutile, 10 μm) + plasticizer (C)	Mech. mix.	30 wt %	7.5 @10 Hz	0.08	0.016	400	1000	10 ^{d)}	11 @10 V/ μm	[127]
HO-PDMS-OH , condens. cure	TiO ₂ (50 nm), 100 phr PDMS oil	US + THF, magn. mix.	30 phr	3.5 @5 kHz	n.a.	0.1	n.a.	100	35 ^{d)}	17 @35 V/ μm^a	[138]
v-PDMS, addition cure	TiO ₂ (25 nm), PEG-PDMS	Ball milling	5 wt%	3.9 @100 Hz	n.a.	0.57	n.a.	n.a.	n.a.	b)	[143,144]
Silastic 3481	TiO ₂ (Rutile, 3 μm)	US + THF, solvent casting	30 phr	6 @10 Hz	0.06 @10 Hz	0.669	6	n.a.	n.a.	18 @50 V/ μm^c	[139]
PDMS w. 28 phr SiO ₂ , condens. cure	TiO ₂ and SiO ₂	Yanke-Kunkel lab.mix.	50 phr TiO ₂	5 @1 Hz	0.02 @1Hz	1.02	635	n.a.	n.a.	0.5 @0.51 V/ μm	[136]
Sylgard 184	TiO ₂ (200 nm)	Mech. mix, electrical	11 vol % ^{d)}	5.5 @1 kHz	0.006 @1 kHz	2.2 ^{e)}	150	n.a.	n.a.	n.a.	[130,25]

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Silpuran 6000/10	TiO ₂ (Rutile, 20 nm) functionalized with short PDMS chains	Mixed in isopar, US	5 wt%	20% inc. comp. to PDMS ^{f)}	n.a.	1.5	n.a.	n.a.	80 ^{g)}	30 @80 V/ μ m	[140]	
Powersil XLR630	TiO ₂ T805 Evonik (21 nm) HMDS treated	Speedmix.	9 wt%	3.32 @0.1 Hz	0.008 @1 kHz	0.549	n.a.	30-90	107	n.a.	[147,148]	
LR 3005/50	TiO ₂ T805 Evonik (21 nm), HMDS treated	Speedmix.	9 wt%	3.18 @0.1 Hz	n.a.	0.224	n.a.	30-90	136	n.a.	[147]	

a) Areal strain

b) Reduced driving voltage from 250V to 230 V and reduced response time from 9 μ s to 6 μ s

c) @ 5 % pre-strain

d) Dielectrophoretically oriented sample

e) @ 50% strain

f) Calculated from the blocking force.

g) From the actuation plot

Table 3. Various titanate-filled PDMS systems.

Base elastomer	Filler/plasticizer	Method of dispersion	Content	ϵ'	$\tan \delta$	Y [MPa]	Max. strain [%]	Thickness of film for E_B [μm]	E_B [V/ μm]	Maximum actuation strain [%]	Ref
PDMS	BaTiO ₃ (100nm) + 100 phr silicone oil	Mech. mix.	100 phr BaTiO ₃	5 @1 kHz-1 MHz	n.a.	0.15	n.a.	n.a.	n.a.	13.5 @35 V/ μm^a	[133]
Shinetsu KE103	BaTiO ₃ (100-500 nm)	Electrical field orient.	44 wt%	5.8 @1 kHz	0.03	0.312	n.a.	n.a.	n.a.	b)	[226]
Elastosil 601	BaTiO ₃	Pebble mill w. toluene	30 wt%	4 @1Hz	n.a.	2.0	n.a.	150	25	0.4 @25 V/ μm	[227]
TC5005–A/B-C	BaTiO ₃ , 35% plasticizer	Mech. blender	10 wt% BaTiO ₃	300 ^{c)}	0.0008	n.a.	140	50	103	28 @8.5 V/ μm	[150]
TC5005–A/B-C	BaTiO ₃ , 30% plasticiser	High velocity agitator	10 wt% BaTiO ₃	8 ^{c)}	0.016	n.a.	250	n.a.	n.a.	n.a.	[151]
RT625	BaTiO ₃ , (<3 μm)	High speed mixer	20 vol%	7.5 @1 kHz	0.0067	0.2	450	250	40	8 @22 V/ μm	[124]
Elastosil P7670	BaTiO ₃ (50-70 nm)	Sonication, mech. mix	1.6 vol%	4.2 ^{c)}	n.a.	0.125	n.a.	4-100	27	n.a.	[228]
v-PDMS, peroxide cure	BaTiO ₃ (<3 μm), 5 phr Pluoronic L-31	Mech. mix., CHCl ₃	5 wt%	4.17 @10 Hz	0.11	0.27	n.a.	500-1000	13	n.a.	[229]
v-PDMS w. 10 wt% SiO ₂ , peroxide cure	BaTiO ₃ hydrophob. (<3 μm)	Yanke-Kunkel laboratory mixer	5 wt% BaTiO ₃	3.67 @10 Hz	0.0027	0.81	5.4	n.a.	n.a.	e)	[230]

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Rhodorsil MF620U	CCTO (5 μm)	Roll milling	20 wt%	5.3 @0.1 Hz	0.05	n.a.	n.a.	n.a.	n.a.	6.0 @25 V/ μm	[145]
LR3005/50	CCTO	Speedmixing	6 wt%	4.09 @1 MHz	0.002	0.183	n.a.	30-90	123	n.a.	[147]
RTV3483	CCTO (300 nm)	THF, US	2 wt%	4.37 @50 Hz	0.013	0.29	n.a.	500	10 ^{f)}	14.3 @10 V/ μm	[231]
TC5005 A/B-C 45% C, silicone)	PMN-PT	Mech. mix.	10 vol%	10.2 @1 kHz	0.08	0.1	575	n.a.	n.a.	n.a.	[232]
PDMS, peroxide cure	PMN (1.5 μm). Silicone oil	Two roll mill	20 vol%	5.2 @1 kHz	n.a.	1.0	n.a.	n.a.	53 ^{f)}	7.9 @53 V/ μm	[146]
APH-20, peroxide cure	Vinylsilane-PZT (<500 nm)	Brabender mixer and two roll mill	10 wt%	3.7 @1 kHz	0.08	2.21 ^{g)}	n.a.	n.a.	n.a.	Increased actuation strain was observed	[233]
v-PDMS	PZT	Speedmix.	40 vol%	28	0.022	4.8	30	n.a.	n.a.	n.a.	[154]

a) Areal strain, 350% increased actuation strain; b) Piezoelectric response increased with loading; c) Frequency not reported; d) 100% improved actuation strain at 20 V/ μm ; e) Energy harvesting potential was evaluated, showing 157 V/mm in output voltage for the given sample; f) From the actuation plot; g) Taken at 25% strain

Table 4. Clays used as fillers in DET applications.

Base elastomer	Filler	Method of dispersion	Content	ε'	$\tan \delta$ @0.1 Hz	Y [MPa]	Max. strain [%]	Ref
APH-20 peroxide cure	MMT cloisite 15A	High shear mix. brabender and roll mill	5 wt%	3.7 @1 kHz	0.07	0.347 ^{c)}	854	[131]
Silastic 3481	MMT cloisite 15A	Low shear solvent mixing	5 wt%	4.2 @1 kHz	0.1	0.76 ^{c)}	93	[131]
v-PDMS, addition cure	Pristine MMT	Mech. mix., US in heptane	2 wt%	5.8 @1 Hz	0.001	0.166	n.a.	[111]
v-PDMS, addition cure	Mod. ^{a)} MMT	Three roll mill	30 phr	10 @0.1 MHz	0.008	n.a.	106	[234]
Silastic 3481 ^{b)}	MMT cloisite 15A	Low shear solvent mixing	5 wt%	4.2 @1 kHz	0.1	0.76	93	[132]

^{a)} γ -glycidoxypropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, stearic acid isopropyl trioleic titanate; ^{b)} Actuation stress 5.8 kPa @ 23 kV/mm for films of 450 μ m thickness. Reduced relaxation time was observed for composites compared to pristine PDMS; ^{c)} At 25 % elongation.

Table 5. Conductive fillers.

Base elastomer	Filler	Method of dispersion	Content	ϵ'	$\tan \delta$	Y [MPa]	Max. strain [%]	Thickness of film for E_B [μm]	E_B [V/ μm]	Maximum actuation strain [%]	Ref.
v-PDMS	BaTiO ₃ (100nm) and carbon black (50 nm) ^{a)}	THF, mech. mix.	3 wt% C. black, 40 vol% BaTiO ₃	40 @1 kHz	n.a.	100	n.a.	n.a.	n.a.	n.a.	[235]
Silastic 3481	Expanded graphite	THF, US, SDBS	1.6 wt%	18.3 @1 kHz	0.008	1.2	n.a.	n.a.	n.a.	2.5 @15 V/ μm	[236]
v-PDMS, addition cure	MWCNT (d=10-20 nm, length 20 μm) ^{b)}	Xylene, US	0.05 wt%	3.56 @100 kHz	0.00014	0.22-0.4	250	n.a.	n.a.	0.5 @28 V/ μm	[141]
v-PDMS, UV cure by thiol-ene	MWCNT (d=10 nm, length 1.5 μm)	Speedmix. ^{c)}	1 wt%	4.5 @1 kHz	0.006	0.05	n.a.	105-150	20	n.a.	[149]
v-PDMS, addition cure	Expanded graphite	Speedmix.	2 wt%	4.5 @1 kHz	0.09	0.002	n.a.	120-150	50	3.8 @42.5 V/ μm	[237]
Rhodorsil MF620U	Functionalized graphene	Two-roll mixer	1 wt%	4.5 @10 Hz	0.03	n.a.	644	n.a.	n.a.	n.a.	[238]

^{a)} Carbon black and BaTiO₃ was modified with silane coupling agent KH550; ^{b)} Covalently functionalized with PDMS; ^{c)} Entrapped in a PDMS bimodal network

Table 6. Core-shell fillers used for DET applications.

Base elastomer	Filler	Method of dispersion	Content	ϵ'	$\tan \delta$ @0.1 Hz	Y [MPa]	Max. strain [%]	Thick ness of film for E_B [μm]	E_B [V/ μm]	Maximum actuation strain [%]	Ref
OH-PDMS, condens. cure	PANI in PDVB shell	Three roll mill, toluene	15 vol%	3.3 @100 Hz	0.036 ^{c)}	0.39 ^{d)}	755	n.a.	50.9	12 @50 V/ μm	[160]
OH-PDMS, condens. cure	PANI in PDVB shell	Three roll mill, toluene	20 wt%	3.4 @100 Hz	0.05 ^{c)}	2.32	>1000	100	43.4	15.5 % @43 V/ μm	[161]
XLR630	TiO ₂ /SiO ₂ Aeroxide (STX801)	Speedmix.	6 wt%	3.88 @1 MHz	0.005	0.187	n.a.	30-90	173	n.a.	[147]
v-PDMS, peroxide cure	SiO ₂ /PDA/Ag/PDA ^{a)}	Two roll mill	52 vol%	48 @1 kHz	0.004	n.a.	n.a.	n.a.	n.a.	n.a.	[162]
PDMS, condens. cure	Ag/SiO ₂ core shell particles 68 nm HMDS treated	Sonication, mechanical mixing	20 vol%	5.9 @1 kHz	0.0078	1.44 ^{b)}	805	58	13.4	805	[163, 164]

^{a)} PDA: Polydopamine. By use of the PDA layer it is possible to prevent percolation by control of shell thickness. Data given for 15 nm shell; ^{b)} Reported at 10% strain; ^{c)} @100 Hz; ^{d)} @10% strain.

Table 7. Properties of materials prepared as blends.

Base elastomer	Additive	Content	ϵ' @0.1 Hz	ϵ' @1 MHz	$\tan \delta$ @0.1 Hz	Y	Maximum strain	Thickness of film for E_B	E_B	Maximum actuation strain	Ref.
						[MPa]	[%]	[μm]	[V/ μm]	[%]	
TC-5005 A/B-C	Poly(3-hexylthiophene)	1 wt%	5.5 ^{a)}	3.8	0.14 ^{a)}	0.03	300	1000	8.5	7.6 @8 V/ μm	[167]
TC-5005 A/B-C (moisture cure)	PU	40 vol%	15.5 ^{a)}	5.2	0.6 ^{d)}	n.a.	n.a.	1000	5.5	2.7 % @5.5 V/ μm	[169]
SILASTIC 3481	PEG (600 g mol ⁻¹)	5 phr	5.4 ^{b)}	4.75 ^{c)}	0.03 ^{b)}	0.47 ^{f)}	n.a.	350	40	11.5 @40 V/ μm	[170]
MJK 4/13	PEG-PDMS block copolymer	5 wt%	4.7	4.4	0.12	0.123 ^{g)}	n.a.	<100	103	n.a.	[171]
PDMS (DMS-V41)	Cyanopropyl-functional copolymer	38.9 wt%	17	6	0.25	0.25 ^{e)}	n.a.	n.a.	25	0.75 @8 V/ μm	[172]
Trifluoropropyl-divinylpolydimethylsiloxane	Fluorinated silicone oil	45 wt%	5.9	5.4	0.9	0.07 ^{e)}	270	250	22	4.2 @10 V/ μm	[173]

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LR3043/50	Chloropro pyl- functional silicone oil (LMS- 152)	30 phr	4.4	4.4	0.004	1.35 ^{f)}	780	80	129.9	n.a.	[174]
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a) @ 10 Hz; b) @ 100 Hz; c) @ 0.4 MHz; d) @ 1000 Hz; e) @ 10% strain; f) @ 5% strain; g) Calculated from storage modulus, G' , where $Y = 3G'$.

Table 8. Properties of chemically modified silicone dielectric elastomers.

Base elastomer	Additive	Content	ϵ' @0.1 Hz	ϵ' @1 MHz	$\tan \delta$ @0.1 Hz	Y [MPa]	Maximum strain [%]	Thickness of film for E_B [μm]	E_B [V/ μm]	Maximum actuation strain [%]	Ref.
PDMS (DMS-V31) + HMS-301 cross-linker	<i>N</i> -allyl- <i>N</i> -methyl- <i>p</i> -nitroaniline	13.4 wt%	19	5.9	2	0.41 ^{b)}	n.a.	80	39	1.25 @15.5 V/ μm	[176]
PDMS (DMS-V41) + HMS-301 cross-linker	<i>N</i> -allyl- <i>N</i> -methyl- <i>p</i> -nitroaniline	13.4 wt%	14	5	1	0.25 ^{c)}	680	n.a.	25	0.5 @7 V/ μm	[177]
Sylgard 184	<i>N</i> -allyl- <i>N</i> -methyl- <i>p</i> -nitroaniline	10.7 wt%	10.1	6.2	0.4	0.85 ^{c)}	350	n.a.	61	3 @28 V/ μm	[178]
Elastosil RT625	<i>N</i> -allyl- <i>N</i> -methyl- <i>p</i> -nitroaniline	10.7 wt%	8	5.6	1	0.142 ^{c)}	170	n.a.	31	2 @10 V/ μm	[178]
OH-PDMS	OH-Cyanopropyl-functional siloxane copolymer	28 wt%	n.a.	3.5	n.a.	0.71 ^{c)}	228	150	42	10 @40 V/ μm	[179]
OH-PDMS	OH-Cyanopropyl-functional	27 wt%	12 ^{d)}	4.5	5 ^{a)}	0.8 ^{c)}	170	n.a.	56	8 @56 V/ μm	[181]

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PDMS (DMS-H21)	siloxane copolymer Nitrobenzene and azonitrobenzene synthesized cross-linker	0.5 wt%	3.3	3.3	0.0006	0.167 ^e	n.a.	150	92	n.a.	[182]
Synthesized azido-functional siloxane copolymers	Nitrobenzene	5.6 wt%	14.2	5.0	6.5	0.08 ^{f)}	n.a.	75	69.2	n.a.	[239]
OH-PDMS	R-trialkoxysilanes as functional cross-linkers	15 wt%	3.2 ^{a)}	3.15	3.45 ^{a)}	0.723 ^{c)}	180	600	0.63	3 @0.63 V/ μ m	[187]
OH-polymethylvinylsiloxane	3-mercaptopropionitrile	48 wt%	10.1	40	10	0.15 ^{c)}	260	~1200	10.8	20.5 @10.8 V/ μ m	[188]
OH-PDMS	Dihydroxynitroazobenzene	7.1 wt%	n.a.	4.64	n.a.	0.325 ^{f)}	375	170	70.0	17 @68 V/ μ m	[190]
Synthesized copolysiloxanes	Chloropropyl-groups	10 wt%	4.9	4.7	0.02	1 ^{g)}	125	80	94.4	n.a.	[191]

^{a)} @ 1 Hz; ^{b)} @ small strains and calculated from the elastic modulus, M_{Act} , where $Y = M_{act} * 4/3$; ^{c)} @ 10% strain; ^{d)} @ 10 Hz

^{e)} Calculated from stated storage modulus, G' , where $Y = 3G'$; ^{f)} @ small strains; ^{g)} @ 5% strain.

Table 9. Properties of interpenetrating and bimodal networks.

Type	Base elastomer	Additive	Content	ϵ' @0.1 Hz	ϵ' @1 MHz	$\tan \delta$ @0.1 Hz	Y [MPa]	Maximum strain [%]	Thickness of film for E_B [μm]	E_B [V/ μm]	Maximum actuation strain [%]	Ref.
IPN	VHB-4910 film	Sylgard-184 (addition cure)	50 wt%	n.a.	n.a.	n.a.	0.25	850	n.a.	n.a.	120 @72 V/ μm^{d}	[197]
IPN	VHB-4910 film	Elastosil E-43 (moisture cure)	50 wt%	n.a.	n.a.	n.a.	0.25	n.a.	n.a.	n.a.	100 @72 V/ μm^{d}	[197]
IPN	Dow Corning HSIII (moisture cure)	Elastosil LR 3003/70 (addition cure)	15 wt%	n.a.	n.a.	n.a.	0.54	500	n.a.	55	25 @55 V/ μm	[63]
IPN/bimodal	OH-PDMS	Vinyl-PDMS	50 wt%	3.2 ^{a)}	3.0	5.8 ^{a)}	0.35 ^{c)}	433	210	48	7.9 @40 V/ μm	[198]
IPN	Elastosil LR3043/30	Amino-functional PDMS (AMS-162)+ carboxydecyl-terminated PDMS (DMS-B12)	90 wt%	2100	4.1	2.3	0.035 ^{b)}	n.a.	40-100	87	n.a.	[201]
Bimodal	DMS-V35	DMS-V05	10 wt%	n.a.	n.a.	n.a.	0.06 ^{b)}	n.a.	n.a.	n.a.	n.a.	[215]
Bimodal	DMS-V35, DMS-V05 and (mercaptopropyl) methylsiloxane-dimethylsiloxane copolymer (GP)	Multi-walled carbon nanotubes (MWCNT)	1 wt%	4.7	4.5	0.025	0.165 ^{b)}	n.a.	105–150	20	n.a.	[149]

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367) as cross-
linker

a) @ 1 Hz; b) Calculated from stated storage modulus, G' , where $Y = 3G'$; c) @ 10% strain; d) Determined from stress-strain curves coupled with actuation data.



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1 **Silicone elastomers are favourable materials for dielectric elastomer transducers (DETs),**
2 but for the field to progress, a leap in material development is required and it is essential that
3 all aspects of the elastomer are taken into account. In this review the current state of silicone
4 elastomers for DETs is summarised and critically discussed.

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8 **The current state of silicone-based dielectric elastomer transducers**
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