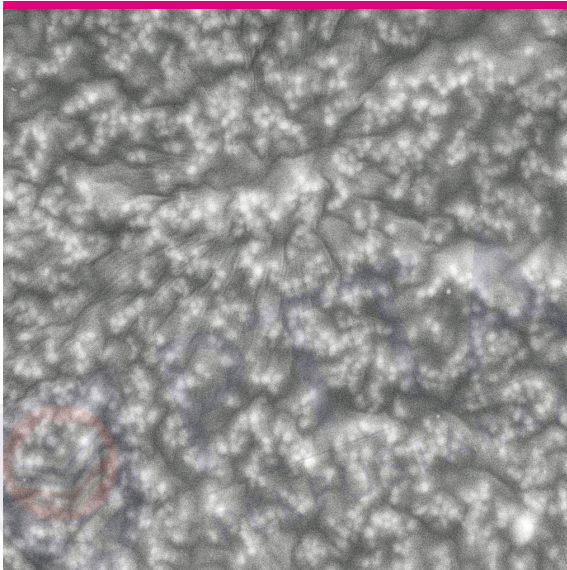


Optimisation of Silicone-based Dielectric Elastomer Transducers by Means of Block Copolymers – Synthesis and Compounding

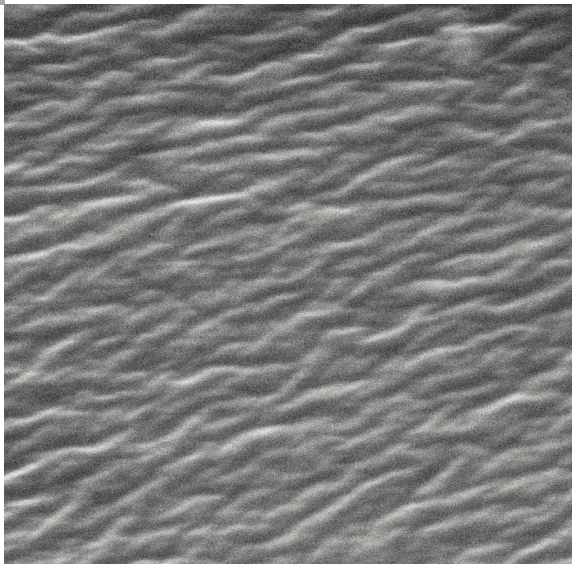


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PhD Thesis

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Ph.D. thesis
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Preface

This thesis is submitted in fulfilment of the requirements of the Danish Doctor of Philosophy (Ph.D.) in chemical engineering. It contains works from December 2013 to December 2016, carried out under the main supervision of Anne Ladegaard Skov and the co-supervision of Peter Szabo. This thesis has been written based on experimental works performed on silicone dielectric elastomers and electrodes by means of block copolymers.

The aim of the thesis is to present novel work on the enhancement of relative permittivity and electrical breakdown strength by incorporating block copolymers. Herein, silicone elastomers with increased relative permittivity and high electrical breakdown strength, as well as a low Young's modulus, were successfully prepared by means of block copolymers via thorough synthesis and compounding. From the synthesised copolymers, a binary system of a copolymer blend consisting of two copolymers was prepared and cross-linked, in order to enhance electro-mechanical properties. Besides preparing silicone elastomers with increased relative permittivity and high electrical breakdown strength, a conductive composite for a stretchable DE electrode was developed from a chain-extended PDMS-based copolymer along with the incorporation of nano-sized conductive fillers.

This thesis contains eight chapters. The introduction, in Chapter 1, provides an overview of dielectric elastomer technology, including silicone elastomers and compliant electrodes. Details of block copolymers are also discussed. Chapter 2 presents the resulting silicone properties from incorporating polydimethylsiloxane-polyethyleneglycol (PDMS-PEG) copolymer in commercial silicone elastomers, and in Chapter 3, the resulting properties of the cross-linked polydimethylsiloxane-polyphenylmethylsiloxane (PDMS-PPMS) copolymer, mainly in terms of electrical breakdown strength, are presented. The synergistic effect of the electro-mechanical properties of binary system of copolymer blend consisting of PDMS-PEG and PDMS-PPMS copolymers is discussed in Chapter 4. Details on compliant electrodes, achieved by incorporating a one-dimensional (1D) conducting network containing multi-walled carbon nanotubes in a PDMS-PEG matrix are described in Chapter 5, while the main conclusion, future works and experimental methods are discussed in Chapters 6, 7 and 8, respectively.

This thesis is based on published/submitted manuscripts, which can be found in the following appendices:

1. A Razak AH, Szabo P, Skov AL (2015) 'Enhancement of dielectric permittivity by incorporating PDMS-PEG multiblock copolymers in silicone elastomers' RSC Adv. 5:53054–53062 – **Appendix I**
2. A Razak AH and Skov AL (2017) 'Silicone elastomers with covalently incorporated aromatic voltage stabilisers' RSC Adv. 7:468-477 – **Appendix II**
3. A Razak AH, Yu L, Skov AL (2017) 'Voltage-stabilised elastomers with increased relative permittivity and high electrical breakdown strength by means of phase

separating binary copolymer blends of silicone elastomers' RSC Adv. 7:17848–17856 – **Appendix III**

4. A Razak AH, Madsen FB, Skov AL (2016) 'Mechanically compliant electrodes and dielectric elastomers from PEG-PDMS copolymers' MRS Adv. 1:3497-3508 – **Appendix IV**



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I would also like to thank the professors and my fellow colleagues at the Danish Polymer Centre (DPC), mainly Liyun Yu for a number of useful suggestions. Also, thank you to Kim Chi Szabo for running my SEC, DSC and TGA samples.

First and foremost, I would like to thank my beloved parents (A Razak and Jamalliah) and siblings (Affiz, Afifah, Afif, Aisyah and Afiqah) for their encouragement and for being good listeners. Thanks also to Jacob Eiland for the proofreading of this thesis, not forgetting to mention Marius N. Mogensen, Sandy L. Mondrup, Roselina and Karsten Mikkelsen, Effa and Steve Daines and my friends for their continuous support and lovely hospitality during my stay in Denmark.

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Abstract

Emerging artificial muscle technology has developed from metal-based robotics to soft-type robotics made from soft matter. Research into artificial muscle technology based on soft matter has been conducted mainly in order to mimic soft and robust human muscle. In this regard, dielectric elastomers have been studied. Their actuation occurs when Maxwell stress exceeds elastic stress in the presence of an electrical field, resulting in contraction in thickness and planar expansion in the area. As well as an actuator, dielectric elastomers can be used as generators and sensors. As a dielectric elastomer, silicones have been used extensively in many applications, due to favourable properties such as thermal stability, non-conductivity, high gas permeability and low toxicity. However, silicones have a low dielectric constant and thereby low energy density. In order to enhance actuation performance, it is the aim of this research to develop silicone elastomers with a high dielectric constant and high electrical breakdown strength, as well as a low Young's modulus.

In this Ph.D. thesis, two methods were developed to enhance silicone properties such as the dielectric constant and electrical breakdown strength. The first method was devised to enhance the dielectric constant of silicone elastomers through the use of a polydimethylsiloxane-polyethyleneglycol (PDMS-PEG) copolymer, in order to obtain an elastomer with high electrical energy. PDMS-PEG copolymers were synthesised and blended in commercial silicone and subsequently cross-linked. The relative permittivity of cross-linked silicone with 5 wt% of PDMS-PEG copolymers increased by nearly 50%, without compromising dielectric loss and mechanical properties, compared to the commercial silicone elastomer.

The second investigated method involved enhancing the electrical breakdown strength of silicone by using an aromatic voltage stabiliser. Here, polyphenylmethylsiloxane (PPMS), which contained aromatic voltage stabilisers, was bonded covalently to PDMS through a hydrosilylation reaction obtaining PDMS-PPMS copolymers. The synthesised copolymers were subsequently cross-linked with a vinyl cross-linker. The obtained cross-linked PDMS-PPMS copolymers were inherently soft and robust with increased electrical breakdown strength (21%) compared to the reference elastomer without an aromatic voltage stabiliser.

The conducting polymer was developed through the use of a multi-walled carbon nanotube (MWCNT) in a PDMS-PEG matrix as a compliant electrode of dielectric elastomers. The conductive PDMS-PEG copolymer was incorporated with surface-treated MWCNT, in order to obtain highly conductive elastomer. The prepared sample with 4 parts per hundred rubber (phr) MWCNT was soft and the resulting conductivity of the cross-linked PDMS-PEG copolymer with the addition of MWCNT was high, at $10^{-2} \text{ S cm}^{-1}$, nearly equivalent to a commonly used commercial conducting polymer.

In this thesis, the elastomer and electrode system is referred to as a 'dielectric elastomer transducer.'

Resume På Dansk

I takt med at teknologien indenfor kunstige muskler udvikles, er det forventeligt, at man vil se et skift fra metalbaserede til bløde materialer baseret på elastomerer. Forskning, der har til formål, at efterligne de bløde og robuste menneskelige muskler ved hjælp af elastomerer, forekommer i stigende omfang. I den dielektriske elastomer opnås aktivering, når et elektrisk felt medfører, at Maxwell spændingen overstiger den elastiske spænding. Dette resulterer i en sammentrækning i højderetningen og en udvidelse af overfladearealet. Ud over anvendelse som aktuatorer benyttes dielektriske elastomerer også som generatorer og sensorer. Silikone har som dielektrisk elastomer fundet udbredt anvendelse pga. attraktive egenskaber så som termisk stabilitet, elektrisk isolationsevne, høj gas permeabilitet og lav toksisitet. Silikone er dog kendetegnet ved lav dielektrisk konstant og dermed lav energitæthed. Udviklingen af silikone med høj dielektrisk konstant kombineret med høj elektrisk sammenbrudsstyrke og lavt Youngs modul er afgørende for at kunne forbedre materialets egenskaber som aktuator.

I denne PhD afhandling er der anvendt to forskellige metoder til at forbedre silikones egenskaber såsom dielektrisk konstant og elektrisk sammenbrudsstyrke. Den første metode havde til hensigt at øge den dielektriske konstant for silikone elastomerer ved anvendelsen af polydimethylsiloxane-polyethyleneglycol (PDMS-PEG) copolymer. Formålet med dette var at opnå en elastomer med høj energitæthed. PDMS-PEG copolymer blev syntetiseret og iblandet kommerciel silikone og efterfølgende krydsbundet vha. krydsbindecemolekyler. Sammenlignet med den kommercielle silikone blev den resulterende relative permittivitet af krydsbundet silikone med 5 wt% PDMS-PEG øget med næsten 50%. Dette uden tab af dielektriske og mekaniske egenskaber.

Den anden metode havde til hensigt at øge den elektriske sammenbrudsstyrke af silikone ved at anvende en aromatisk spændingsstabilisator. Polyphenylmethylsiloxane (PPMS) som udgjorde den aromatiske spændingsstabilisator blev covalent bundet til PDMS via en hydrosilylation, hvorved der dannes PDMS-PPMS copolymer. Den syntetiserede copolymer blev efterfølgende krydsbundet med en vinyl krydsbinder. Den fremstillede krydsbundne PDMS-PPMS copolymer var både blød og robust samt udviste øget elektrisk sammenbrudsstyrke (21%) sammenlignet reference materialet uden den aromatiske spændingsstabilisator.

En kompatibel elektrode, i form af en ledende polymer, blev udviklet ved inkorporering af kulstof nanorør (multi-walled carbon nanotubes – MWCNT) i en PDMS-PEG matrix. Overfladebehandlet MWCNT blev inkorporeret i den ledende PDMS-PEG copolymer med henblik på at opnå en elastomer med høj ledningsevne. Det fremstillede materiale indeholdende 4 phr MWCNT var blødt, og den resulterende ledningsevne var høj, $10^{-2} \text{ S cm}^{-1}$, hvilket var tæt på niveauet for kommercielle polymerer.

I denne afhandling er elastomer- og elektrodesystemet refereret til som en 'dielektrisk elastomer transducer'.

1 Introduction

This thesis deals with the inclusion of copolymers into dielectric elastomers and electrodes. Therefore, three main parts are discussed in this chapter, namely elastomers, block copolymers and DE electrodes.

1.1 Dielectric elastomers

Soft elastomers such as silicones, acrylates and polyurethanes have been studied extensively for use in artificial muscle technology [1,2]. Electroactive polymers, known as EAPs, are elastomers that exhibit a change in size or shape when stimulated by an external electrical field [3]. EAPs can be divided into ionic and electronic, with the former requiring low driving voltages and an electrolyte and deforming due to the diffusion of ions in the material in the presence of an electrical field. Electronic EAPs, on the other hand, require high driving voltages and can be operated in the air. Additionally, they possess higher electrical energy than ionic EAPS and come complete with large actuation forces, rapid response times and long lifetimes [1]. Their drawback is that they require high driving voltages, between 500 V to 10 kV, to actuate [2,4]. Polymer electrets [5–7], electro-strictive graft elastomers [8], ionic polymer gels [9] and dielectric elastomers [10–12] are examples of electronic EAPs. Among all of the mentioned electronic EAPs, dielectric elastomers are the most favourable in actuation, due to high actuation speeds, large strains, high work densities and a high degree of electromechanical coupling [1].

1.1.1 Overview of DEs

Dielectric elastomers (DEs) are also known as ‘compliant capacitors,’ with actuation occurring when electrostatic stress exceeds elastic stress [13]. An overall ability to accumulate electrical energy through an elastomeric membrane is denoted as:

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (1.1)$$

where C is the capacitance of the material, ϵ_r and ϵ_0 correspond to the relative permittivity of the measured elastomer and vacuum permittivity ($8.854 \cdot 10^{-12} \text{ F m}^{-1}$), respectively, and A and d are film area and film thickness, respectively.

1.1.2 Modes of application

DEs have been studied extensively with respect to finding both new and better elastomer candidates for novel DE applications [14–17]. Such properties have enabled them to play

a significant role in applications such as actuators, sensors and generators, the working principles for which are described in the following subsections.

1.1.2.1 DE actuators

In general, an actuation is defined as a mechanical motion caused by external forces or applied electrical fields. The operational principle of a dielectric elastomeric actuator (DEA) is presented in Figure 1.1. For a DE film, which is sandwiched between two stretchable electrodes, electrostatic pressure is generated, due to an increase of electrical field, which subsequently induces thinning and planar expansion of the DE [18]. This electrostatic pressure, known as Maxwell pressure (p), is defined as [19]:

$$p = \epsilon_0 \epsilon_r E^2 \quad (1.2)$$

where E is the electrical field.

Assuming a constant Young's modulus during the actuation cycle, the strain (s) of the DE can be determined. At a given voltage (V), the actuation strain of a DE film with a Young's modulus (Y) and thickness (d) is determined from Equation 1.3:

$$s = -\frac{p}{Y} = -\frac{\epsilon_0 \epsilon_r E^2}{Y} = \frac{-\epsilon_0 \epsilon_r}{Y} \left(\frac{V}{d}\right)^2 \quad (1.3)$$

As actuators, DEs are used in various applications such as tuneable lenses [20], miniaturised actuators [21], loud speakers [22], active membrane pumps [23] and artificial muscle rotary motors [24].

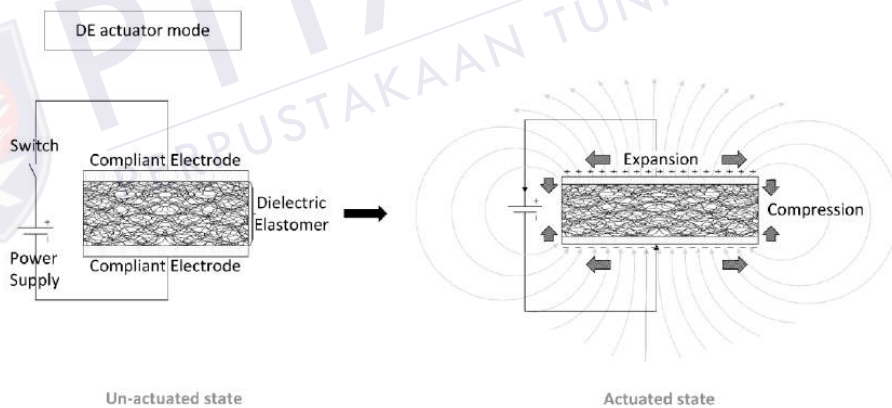


Figure 1.1 Working principle of a DE actuator (DEA).

1.1.2.2 DE generators

A generator is a device which produces electrical energy from potential or kinetic energy. In DE technology, a generator can be developed to harvest energy from ocean waves by utilising DEs, which is well-known as a wave energy harvester [25]. The operational principle of the dielectric elastomeric generator (DEG) is presented in Figure 1.2. In the

initial state, a DE film is supplied with a voltage as a pre-charged film. During oscillation of the mechanical wave, the pre-charged film is stretched, due to the force of the mechanical wave, and the film is released afterwards (relaxed mode), resulting in opposite charges on the two electrodes are pushed apart. Concurrently similar charges are brought closer as the elastomer's area decreases, thereby causing an increase in charge density and thus increasing electrical energy [26].

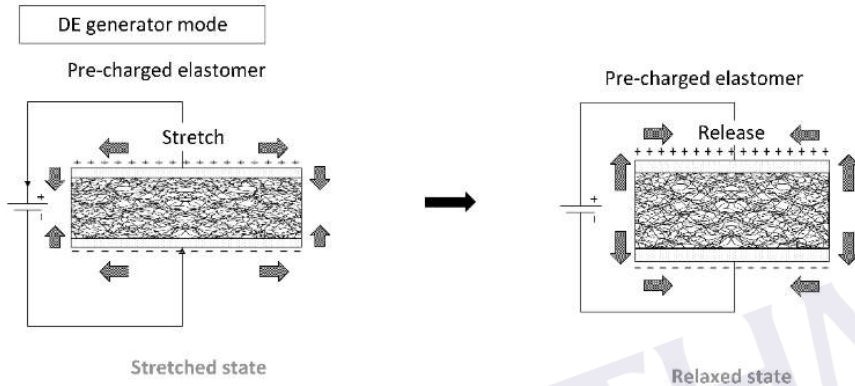


Figure 1.2 Working principle of a DE generator (DEG).

1.1.2.3 DE sensors

A sensor is a device which measures input from the physical environment, e.g. pressure and stretching, and sends the output in a form of a human-readable display for further analysis. For a pre-charged DE film, any external forces that deform the DE, such as pressing, stretching and touching, change the capacitance of the elastomer. The signal can be measured from the capacitance change, which is proportional to the square of the strain ratio between the final strain and the initial strain [27]. The operational principle of a dielectric elastomeric sensor (DES) is presented in Figure 1.3. DE-based sensors have been used for purposes of military, physiotherapeutic and haptic devices [27,28].

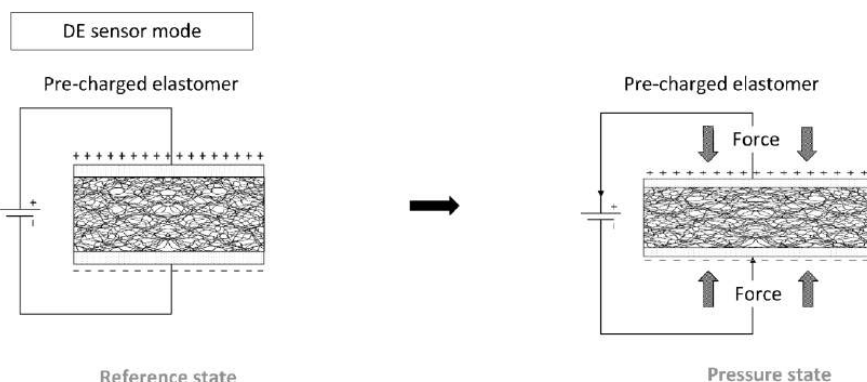


Figure 1.3 Working principle of a DE sensor (DES).

1.1.3 Performance strategies for dielectric elastomers (DEs)

1.1.3.1 Performance of a DE actuator

The actuation performance of a DE actuator at a given voltage (V) can be improved by enhancing its relative permittivity (ϵ_r) or by reducing the Young's modulus (Y). These handles are obvious from the actuation equation derived by Pelrine et al. [19], which relates actuation strain (s) to the mentioned parameters via:

$$s = \frac{-\epsilon_0 \epsilon_r}{Y} \left(\frac{V}{d} \right)^2 \quad (1.4)$$

where $\epsilon_0 = 8.85 \cdot 10^{-12} \text{ F m}^{-1}$ is the permittivity of free space.

The largest achievable electrical field over the dielectric elastomer before electrical failure (E_{BD}) is denoted as 'electrical breakdown strength.' In this electrical field the maximum theoretical actuation strain (s_{max}) is achieved under the assumption that the elastomer is highly extensible and does not break down mechanically prior to electrical breakdown:

$$s_{max} = \frac{-\epsilon_0 \epsilon_r}{Y} E_{BD}^2 \quad (1.5)$$

1.1.3.2 Performance of a DE generator

When converting the electromechanical energy of DEs, electrostatic potential energy (U_e) occurs between maximum strain upon stretching (s_{max}) and minimum strain upon relaxing (s_{min}). The electrical field generated while harvesting wave-mechanical energy can be presented in three cycles: constant-charge, constant-voltage and constant-field, where the conversion of electromechanical energy is the most efficient in the constant-field cycle compared to the other cycles, because mechanical/electrical energy is stored temporarily in the other cycles. The electrostatic potential energy of the DE generator is constant for a constant-electrical field and is given by [29]:

$$U_e = \frac{1}{2} \epsilon_r \epsilon_0 V E_{BD}^2 \quad (1.6)$$

where V denotes total active elastomer volume.

The potential energy of the DE generator can be optimised by utilising dielectric elastomers with a high dielectric constant, high electrical breakdown strength and large sample density.

1.1.3.3 Performance of a DE sensor

A change in the capacitance of a DE is related to different modes of operation, such as pressure, stretch, touch, shear and proximity. In a sensor, the capacitance of the DE with the effect of parasitic capacitance ($C_{parasitic}$) is shown as:

$$C = \epsilon_r \epsilon_0 \frac{A}{d} + C_{parasitic} \quad (1.7)$$

The increased capacitance of a DE sensor depends on the mode of operation, because when one is stretched or pressurised, or applied with a shear force, capacitance increases due to an increase in the sample area to film thickness ratio. In touch mode, capacitance increases due to increased parasitic capacitance, which is defined as unavoidable capacitance occurring between parts of an electronic component. In proximity mode, the capacitance of the DE sensor increases due to the increased relative permittivity of the DE. Proximity mode occurs due to electromagnetic radiations.

1.1.3.4 Common strategies for enhancing the performance of DEs

1.1.3.4.1 Enhancement of relative permittivity

Several works have been performed on elastomers for enhancing relative permittivity by adding highly polarisable ceramic and conductive fillers from metal oxides, e.g. titanium (IV) dioxide (TiO_2) [30], barium titanate (BaTiO_3) [31–34] and calcium copper titanate – CCTO ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) [35]. Besides metal oxides fillers, different alternatives to obtaining elastomers with high relative permittivity have been explored, such as chemical functionalisation through the covalent grafting of dipoles such as trifluoropropyl [36], p-nitroaniline [37] or azide groups [38] to the silicone backbone. Besides from the addition of metal oxides and chemical functionalisation, the incorporation of encapsulated high-permittivity fillers, such as polyaniline (PANI) [39], silver nanoparticles [40] and water [41], and ionic liquids, such as glycerol [42], into silicone elastomers has been reported to improve relative permittivity.

1.1.3.4.2 Strain-hardening of elastomer

Another approach to improving actuation performance for DEs is by strain-hardening the elastomer, which can be achieved by either pre-straining externally, by stretching films onto a stiff supporting structure [43], or pre-straining internally, achieved through an interpenetrating polymer network (IPN) [44,45] or by creating bimodal networks [46]. Out of all the stretching methods, stretching films using a supporting structure is the most commonly used in DE technology.

1.1.3.4.3 Enhancement of electrical breakdown strength

The effect of electrode configuration on the electrical breakdown strength of pre-stretched DEs has been studied by Tröls et al. [47] and Zakaria et al. [48]. As the electrode size increases, the sample volume also increases and the increased sample volume needs to be considered when determining electrical breakdown strength. In the work performed by Tröls et al., compliant and rigid electrodes were used for the measurement of pre-stretched elastomer electrical breakdown, and the effects of both electrodes were compared. The resulting electrical breakdown strengths depended on the electrode configuration, where the electrical breakdown strength was lower when measured using compliant electrodes than when using rigid electrodes. The drawback in the work performed by Tröls et al. is that the volume of pre-stretched samples was not conserved such that the sample volume was reduced significantly by pre-stretching. Therefore,

constant volumes of tested samples are necessary to obtain comparable data. The electrical breakdown study of a pre-stretched sample with constant volume was reported by Zakaria et al [48]. Two experimental configurations, with and without constant sample volume, were used to determine the stretch dependence of the electrical breakdown strength of PDMS elastomers. Breakdown strength was determined for samples with and without volume conservation and was found to depend strongly on the stretch ratio and the thickness of the samples.

Several film fabrication processes have been used to make DE films, including direct hot-pressing, centrifuging and drop-casting. These different types of processing method create different mechanical properties for the obtained elastomers, as reported by Kollosche et al. [49]. Among all the mentioned processing methods, films prepared via the centrifuging and drop-casting methods were softer, i.e. a decreased Young's modulus, than hot-pressed films. An elastomer with a low Young's modulus (Y) possesses decreased electrical breakdown strength compared to one with high Y [30,49,50]. Therefore, increased electrical breakdown strength can be obtained from DE films prepared by drop-casting.

A highly pre-stretched DE film results in large actuation strain. Pre-stretching enhances the actuation performance of DE film, due to the favourable realignment of material imperfections such as voids and micro-cracks. In addition, pre-stretching reduces the film thickness of the DE and lowers the driving voltage, which subsequently increases electrical breakdown strength, as reported by Zakaria et al. [51] and Huang et al. [50].

The effect of different types and amounts of filler on the electrical breakdown strength of DEs has been investigated. Several types of fillers, such as an anatase titanium(IV) oxide (TiO_2), a core-shell of titanium dioxide-silica ($\text{TiO}_2\text{-SiO}_2$) and a calcium copper titanate (CCTO- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$), were incorporated into liquid and room-temperature vulcanisable silicone elastomers [30]. Among these fillers, a silicone elastomer containing $\text{TiO}_2\text{-SiO}_2$ filler possesses very high electrical breakdown strength, as reported by Vudayagiri et al. [30]. Aside from having high electrical breakdown strength, the resulting Young's modulus of the silicone- $\text{TiO}_2\text{-SiO}_2$ composite was high. A DE with an increased Young's modulus delays the rapid thinning process, due to electromechanical instability (EMI), and thereby increases electrical breakdown strength [52].

1.1.4 Dielectric silicone elastomers

Polydimethylsiloxanes (PDMS) or silicones are semi-inorganic polymers that are composed of a siloxane (Si-O) backbone. Silicones possess a very low glass transition temperature (T_g), as low as -120°C , and they are usually thermally stable up to more than 300°C [53]. Other good qualities of silicones include good oxidation and UV resistance, high gas permeability, excellent electrical properties and are biocompatible. Without cross-linking, PDMS is a liquid. When making an elastomer, functional PDMS can be cross-linked with a cross-linker. For film preparation, the formulation containing PDMS, a cross-linker and a catalyst is cast on a substrate before cross-linking. Finally, the DE film is cured either at room or elevated temperatures, or in the presence of UV light.

Hydrosilylation is a commonly used reaction to produce silicone elastomers and is defined as the vinyl addition cure between a silyl hydride and a vinyl group catalysed by a platinum complex [54,55]. The formation of elastomer with a high degree of network control can be obtained through a hydrosilylation reaction. Another advantage of hydrosilylation is that no by-product is formed; however, it is sensitive to sulphur and amine moieties, which can poison the platinum catalyst and subsequently stop hydrosilylation altogether.

Silicone polymers can be cured using a room-temperature vulcanising (RTV) moisture system via a condensation reaction. At room temperature, a cross-linker which is exposed to ambient humidity is hydrolysed producing a silanol group. Subsequently, the silanol cross-linker condenses further with silanol-functionalised silicones or another silanol cross-linker, and the condensation reaction proceeds until a cured system is obtained. With the addition of a titanium 2-ethylhexoxide catalyst, the condensation reaction occurs quite quickly and thereby reduces the time taken for film formation.

Different mechanical properties of silicone elastomer can be obtained from different cross-linking densities, while non-cross-linked silicone polymers can be obtained commercially at molecular weights between 0.2 and 100 kg mol⁻¹. Silicone elastomers with low cross-linking density result in soft silicone elastomers, such that they can be actuated at a lower voltage compared to stiffer elastomers, which possess high cross-linking density; however, they suffer from poor mechanical robustness. To enhance mechanical robustness, fillers such as surface-treated silica nanoparticles are often incorporated into silicone elastomers.

Preparing a silicone elastomer film from a high-molecular weight PDMS can be difficult, due to a high viscosity mixture. Usually a film coating containing viscous PDMS reduces the quality of thin films prior to cross-linking. As a solution to reducing the viscosity of the silicone mixture, common organic solvents, such as tetrahydrofuran (THF) and toluene, or methylsiloxane fluids are used for a smooth film coating, thereby improving the quality of the film. Nevertheless, the use of solvents may trap air in the films, even for carefully prepared samples.

1.2 Block copolymers

Block copolymers are macromolecules that consist of two or more repeating polymer units. Macromolecules are obtained by combining two or more chemically immiscible polymer blocks that are thermodynamically incompatible. All block copolymers belong to soft matter and are often characterised by a fluid-like disorder on the molecular scale and a high degree of order at longer lengths [56]. In order to minimise Gibbs free energy, the blocks in a copolymer undergo self-assembly and organise themselves into well-defined and periodic nanostructures. Due to these well-defined nanostructures, block copolymers have been explored for providing many useful and desirable properties in products such as lubricant, asphalt, adhesive material and dielectric elastomer.

1.2.1 Morphologies of block copolymers

Due to the minimisation of free energy, diblock copolymers phase separately and subsequently assemble into different morphologies such as spheres (S), cylinders (C), gyroids (G) and lamellars (L), as shown in Figure 1.4 [56–60]. These architectures are achieved when two immiscible polymers, which are covalently bonded, segregate to form well-defined structures [61]. The different morphologies can be obtained by varying the volume fraction of one constituent in the diblock copolymer. The self-assembly of copolymer depends on the incompatibility degree (χN , where χ is the Flory-Huggins interaction parameter and N is the degree of polymerisation) and volume fraction of one constituent in the block copolymer (f) [56,62].

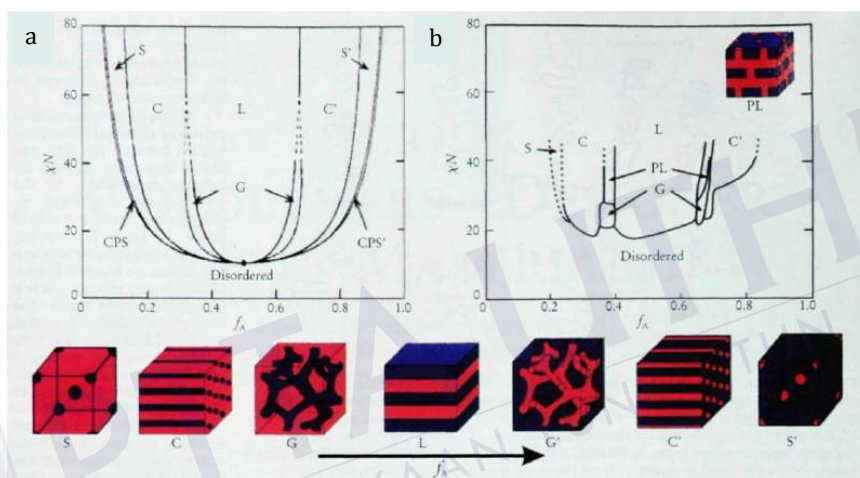


Figure 1.4 Two phase diagrams of linear AB diblock copolymers a: Prediction of four equilibrium morphologies from self-consistent mean-field theory [56], b: Phase diagram of poly(isoprene-styrene) diblock copolymers [57], reproduced from [Bates FS, Fredrickson GH (1999) Block copolymers—Designer soft materials. *Phys Today* 52:32–38], with the permission of the American Institute of Physics.

1.2.2 Miscibility of copolymers

Copolymer blocks are expected to phase-separate, due to the minimisation of Gibbs free energy and the miscibility of two copolymers' blocks, subsequently forming well-defined morphologies which may give the most favourable electro-mechanical properties of DEs. However, preparing an elastomer by means of a block copolymer can be rather challenging, as the phase separation may occur on the macroscale, resulting in an inhomogeneous elastomer. When utilising the block copolymer, phase separation occurring on the micro- and nanoscales is favoured, in order to obtain a homogeneous elastomer with enhanced electrical and mechanical properties.

In order to optimise a silicone dielectric elastomer, a polymer/copolymer, which is conductive or possesses a high dielectric constant, can be incorporated into the silicone elastomer by means of either a binary polymer blend or copolymerisation. In a binary

system of polymer blends consisting of a conducting polymer/copolymer and a non-conducting PDMS, an elastomer is prepared from phase separation, whereby the desired morphology of the continuous non-conducting PDMS phase and conducting polymer/copolymer discontinuous phase is created in the blends. However, the phase separation of binary polymer blends is macroscopic rather than microscopic or nanoscopic, and consequently it compromises the homogeneity of the two components in the elastomeric matrix. Preventing macroscopic phase separation when preparing the DE is significant for long DE lifetimes.

As a solution to the macroscopic phase-separated binary polymer blend, a conducting polymer, which is immiscible in PDMS, is copolymerised with PDMS as a block copolymer. The covalent-bonded copolymers' blocks, containing conducting and non-conducting polymers, phase separate and form the more favourable micro- or nanoscopic phase separation, which ascribes to the desired electro-mechanical properties of the DE. The favourable morphology of a copolymer results from phase separation between the rich domain of a non-conducting block (continuous phase) and the small domain of a conducting block (discontinuous phase). Therefore, the optimised silicone elastomer, prepared from a phase-separating system by means of copolymerisation, results in phase separation on the micro- or nanoscale, indicating that the elastomer is homogeneous.

1.2.3 Voltage-stabilised elastomer by means of a block copolymer

When optimising dielectric elastomers (DEs) a conflict exists, namely that for large, achievable actuation strains softness is required, although with increased softness electrical breakdown strength decreases. A strategy for enhanced electrical breakdown strength in DEs can be achieved by voltage stabilisation, due to electron-trapping effects, which have been investigated previously by including minute concentrations of aromatic voltage stabilisers in polymers, mainly polyethylene (PE), with the purpose of reducing power loss for high-voltage insulation cables [63–65]. Aromatic voltage stabilisers, which have delocalised π -electrons, trap energetic electrons and create radicals, as they interrupt the distribution of the π -electron cloud [66]. In high-voltage insulation cables, the electrical breakdown strength of PE increases by utilising aromatic azo-compounds, which have six different side groups with electron-acceptors (NO_2 , CN) or electron-donors (NH_2 , CH_3 , OH), as reported by Yamano et al. [63]. A PE composite containing an azo-compound with $(\text{OH})_2$ and NO_2 side groups in remarkably low concentrations has the highest electrical breakdown strength, improving by 48% compared to the PE without an additive. This indicates that both electron-donating (OH) and -accepting (NO_2) groups efficiently increase electrical breakdown strength, due to the increased polarity in the aromatic group, and thus lower excitation energies. Yamano [64] enhanced further electrical breakdown strength in PE by employing acene compounds (naphthalene, anthracene, tetracene and pentacene) as aromatic voltage stabilisers.

The homogeneity of elastomer is affected by phase separation of the mixture. With proper sample preparation, phase separation can be achieved on the nanoscale, while the nanoscopic phase-separating system has influenced the enhanced electrical and mechanical properties of DEs.

Utilising aromatic voltage stabilisers of any kind as a silicone additive will unavoidably cause phase separation of the mixture. Preventing this on both the macro- and the microscale during preparation, as well as during actuation, is a key requirement for long DE lifetimes [65]. PPMS possesses voltage stabilisation capabilities but is immiscible in PDMS, and thus the copolymerisation of the two components is necessary for homogeneity. The effect of electron-trapping by phenyl groups, so-called ‘homo-aromatics’, in a silicone elastomer is illustrated in Figure 1.5. Electrons in the presence of an electrical field accumulate initially at the interfacial boundary between the film and the electrode, as shown in Figure 1.5(b). The electrons then migrate and are trapped in the phenyl groups, as seen in Figure 1.5(c). When electrons migrate and collide with the homo-aromatic group, they disturb the cloud of π -electrons in the aromatic group, and this results in the formation of electron-accepting radicals, as shown in Figure 1.5(d). The depth of the electron trap is highly influenced by the type of radical [66], where the depth of the aromatic group with the radical of an electron-accepting type is greater than that of the aromatic group without a radical [64,66]. The trapped electrons act as negative space charges in the elastomer, causing a decrease in electrical field strength on the cathode [64]. This decreased electrical field strength then reduces electron migration from the cathode. The trapped electrons remain in the film bulk and therefore delay electrical breakdown; thus, increased electrical breakdown strength is achieved.

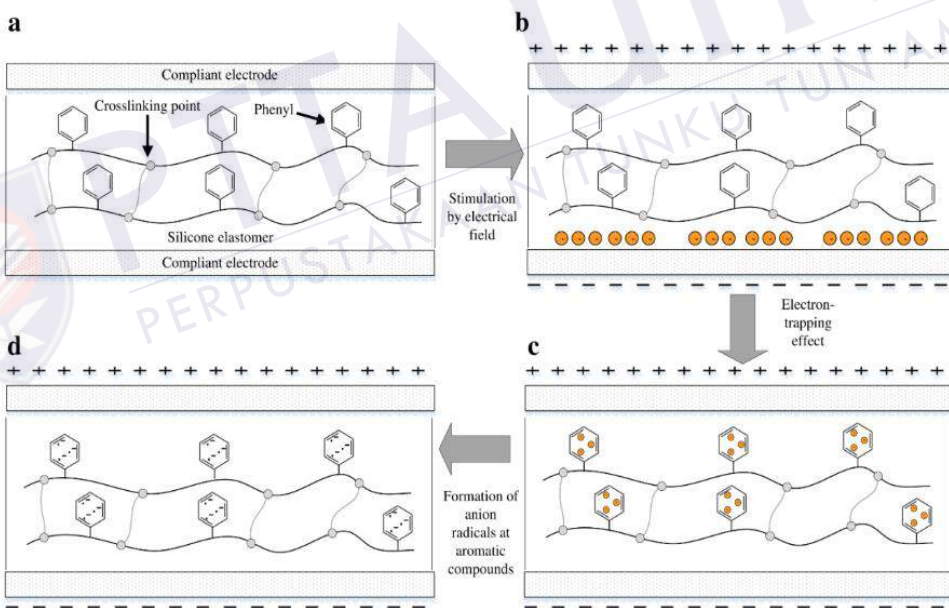


Figure 1.5 The enhancement of electrical breakdown strength, due to electron-trapping: a) A silicone elastomer with an aromatic group grafted to the silicone backbone and a coating of compliant electrodes on the top and bottom surfaces. b) The existence of electrons at the interfaces between the elastomer and the compliant electrode in the presence of an electrical field. c) The electron-trapping effect as a consequence of a collision between electrons and the phenyl group. d) The formation of anion radicals resulting from the disturbance of the cloud of phenyl group π -electrons.

1.3 Elastomer parameters

For the optimisation of elastomer, the cross-linked copolymer is further characterised for electrical and mechanical properties, and often a conflict exists between the optimised parameter and other parameters, e.g. relative permittivity versus electrical breakdown strength and mechanical properties. As a result, it is necessary to consider the compromised parameter during the optimisation of DEs.

1.3.1 Permittivity

Permittivity measures the level of electrical energy stored in the form of charge separation caused by polarisation. Relative permittivity is the ratio of the storage permittivity of an elastomer (ϵ') to the storage permittivity of a vacuum ($\epsilon_0 = 8.854 \cdot 10^{-12}$ F/m). In this thesis, frequency-dependent storage permittivity (ϵ') is referred to as 'relative permittivity', in line with DE standards. DEs with increased relative permittivity have been studied extensively for the optimisation of DEs [38,53,67–70]. An elastomer with high relative permittivity, such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF) with $\epsilon_r = \sim 12$, indicates that PVDF possesses high electrical energy [69]. An elastomer with high electrical energy is important for better performance in DE applications. $\tan \delta$ is the ratio of loss permittivity (ϵ'') to storage permittivity (ϵ').

An un-actuated DE consists of dipolar molecules (Si-O, Si-CH₃) randomly aligned in an elastomeric matrix (see

Figure 1.6). When the DE is polarised, the dipolar molecules realign such that the positive charges of the dipoles orient toward the negative charges on the electrode (refer to Figure 1.7).

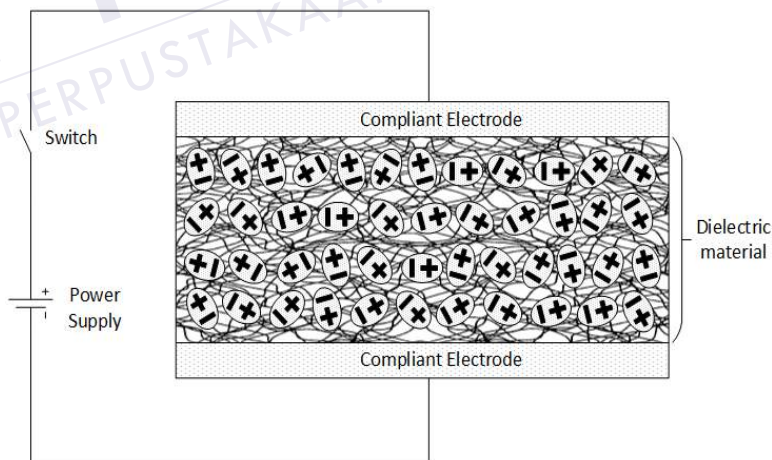


Figure 1.6 Unpolarised dipoles randomly aligned in the elastomeric matrix.

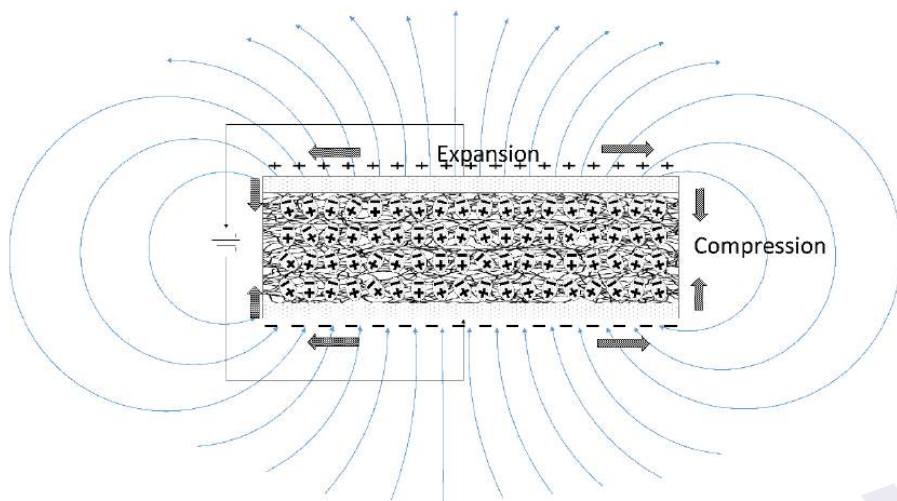


Figure 1.7 Re-orientation of polarised dipoles in the elastomeric matrix.

1.3.2 Electrical breakdown strength

The elastomer can withstand a maximum electrical field, but above the maximum electrical field the DE will short-circuit and form a pinhole, defined as the electrical breakdown strength of DEs [71]. The optimisation of electrical breakdown strength and the mechanism behind the electrical breakdown of DEs have been studied recently.

In the next subsections, several mechanisms that lead to electrical breakdown in DEs namely electromechanical breakdown, electrothermal breakdown and partial discharge, will be discussed.

1.3.2.1 Electromechanical breakdown

Another form of electrical breakdown in DEs is electromechanical breakdown, which occurs during actuation when attractive forces between the two electrodes become dominant and locally exceed a certain threshold value that cannot be balanced by the elastomer's resistance to compression [72,73]. For DEs, electromechanical breakdown is also known as 'electromechanical instability', or 'EMI'. Electrical stress in the local regions of a DE may give rise to localised thinning, known as the 'Stark and Garton' thinning process [74], which causes an increase in the electrical field, due to a decrease in film thickness, and subsequently results in an increase in electrostatic forces such as positive-feedback effect. These local regions, which are subjected to a higher electrical field, possess high shear stresses and subsequently form indentations [75], which in turn result in inhomogeneous fields where these indentations create sharp notches and caused the elastomer to push away radially by a certain degree, depending on the DE's Young's modulus. Above the critical voltage, the DE will short-circuit, due to void formation. Electromechanical breakdown can be eliminated by pre-stretching the elastomer, since

pre-stretching has a combined effect of improving the alignment of film imperfection, decreasing film thickness and increasing electrical breakdown strength [48,76].

1.3.2.2 Electrothermal breakdown

During DE electrical breakdown, heat generated inside the film, which cannot be balanced by heat lost to the surrounding area, is defined as ‘electrothermal breakdown’ [77]. When a voltage is applied to a DE, electrical power is dissipated, causing increased temperature, which then creates local heating and results in increased electrical power dissipation and subsequently a further increase in temperature [78]. This process is known as ‘thermal runaway’. Above a critical temperature, electrothermal breakdown will occur. The electrothermal breakdown in silicone DEs has been studied by Zakaria et al. [51], who used a model based on numerical analysis with quasi-steady state approximation to estimate the thermal runaway in silicone DEs. The outcomes from the modelling were compared to experimental data on the temperature effects of silicone elastomers. Studies have proven theoretically and experimentally that electrothermal breakdown is not the main cause of the electrical breakdown of thin silicone elastomer, due to the very low electrical field required to initiate the thermal runaway.

1.3.2.3 Partial discharge

In a DE film, a partial discharge is commonly associated with voids. Whilst preparing the elastomer, the formation of small voids is unavoidable, even in the most carefully executed preparation technique. Trapped gas in the voids results in decreased relative permittivity and low electrical breakdown strength of the DE, caused by a rise in the electrical field, and subsequently these voids break down electrically before the elastomer [77,79]. In DEs, several conditions lead to partial discharges, namely gas pressure, void shape and void size [77]. For a very thin DE, partial discharge may lead rapidly to failure.

1.3.3 Young’s Modulus

The Young’s modulus (Y) can be estimated from a molecular theory on the viscoelastic behaviour of incompressible cross-linked polymer. In Chapter 2, Young’s moduli of the prepared elastomers were calculated from this molecular theory and then used to determine the figure of merit (F_{OM}) for the DE actuator.

The elastomer is stretched uniaxially in the z -direction. Assuming the elastomer is incompressible, $l_0^3 = l_x l_y l_z$, where l_0 is the initial length of the cube and l_x , l_y and l_z are the dimensions after deformations in the x -, y - and z -directions, respectively. Based on Helmholtz free energy per volume and incompressibility, isotropic stress (σ_{ii}) for a chemical cross-linked elastomer is given by:

$$\sigma_{ii} = nk_B T \lambda_i^2 - P \quad (1.8)$$

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