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Design And Development Of Dielectric Elastomers And Elimination Of Electromechanical Instability Under Equi-Biaxial Loading.

Liang Jiang
Dublin Institute of Technology

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Design and Development of Dielectric Elastomers and Elimination of Electromechanical Instability under Equi-biaxial Loading

by

Liang Jiang, M.Sc.

A thesis submitted to the Dublin Institute of Technology in partial fulfilment of the requirements for the degree of Doctor of Philosophy (Ph.D.)

Supervisors: Prof. Stephen Jerrams, Dr. Anthony Betts and Prof. David Kennedy

School of Mechanical and Design Engineering
Dublin Institute of Technology

April 2016
Abstract
Dielectric elastomers (DEs) possess many useful properties including the capability of achieving large deformation, quietness of operation, high energy density and coupling efficiency. However, DEs generally require very high actuation electric field strength (> 100 V/µm) which can limit their useful lives. A DE with low Young’s modulus, large elongation at break and high dielectric constant has the ability to exhibit high deformation under a relatively low electric field. Much research has been conducted to overcome the need for high actuation electric fields. One popular approach to achieve this goal is to fabricate silicone rubber (SR) based DE composites combined with high dielectric fillers. The primary aim of this work was to design and fabricate DEs which exhibited the capability of large voltage-induced deformations at relatively low electric field strengths whilst eliminating electromechanical instability (EMI) through the application of equi-biaxial pre-stretching.
Barium titanate (BT) possessing a high dielectric constant, was chosen as the filler to enhance the overall dielectric constant of SR based DEs. The morphological features of all materials used in this work were observed using a Scanning Electron Microscope (SEM). The elemental analysis of these particles was carried out using an Energy Dispersive X-Ray Spectrometer (EDS) which was coupled to the SEM and Fourier Transform Infrared Spectroscopy (FTIR). Dielectric measurements of DE films were conducted on a Turnkey broadband dielectric spectrometer. Their equi-biaxial mechanical properties were studied using a bubble inflation test method.
It was found that SR/BT films exhibited large actuated strains of 57% after being subjected to equi-biaxial pre-stretch ratios which coincided with the minimum
secant moduli of the test samples. Using a coating method to modify BT particles with dopamine (DP) not only enhanced the compatibility between the SR and the particles, but also tuned the cross-link density of the SR matrices. One of the resulting DE films of SR/20 wt% DP-BT, possessed a dielectric constant of 7.5, a Young’s modulus of 0.2 MPa and achieved a large voltage induced strain of approximately 80% at a relatively low electric field strength of 53 V/μm when pre-stretched to a ratio of 1.6. Moreover, it was found that the occurrence of EMI in the SR/20 wt% DP-BT composite was eliminated by applying equi-biaxial pre-stretch ratios above 1.6. By comparison, the EMI in a commercial DE, 1 mm thick acrylate film, VHB 4910, was eliminated by equi-biaxially pre-stretching to a ratio above 2.0.

It is recommended that future work should focus on the dynamic performance of an SR/DP-BT DE fabricated in-house when subject to an electric field. Further, fatigue life of the material should be investigated both with and without the application of an electric field. Thereafter, an approach to fabricating DEs having the capability of achieving large voltage-induced strains without the requirement for equi-biaxially pre-stretching is also proposed in order to prolong test sample and component life. Finally, an application for the novel DE material, a rotary motor, is proposed. An in-house designed and fabricated DE with suitably tailored electromechanical properties will be used.
Declaration

I certify that this thesis which I now submit for examination for confirmation of PhD registration is entirely my own work and has not been taken from the work of others, save to the extent that such work has been cited and acknowledged within the text of my own work.

This thesis was prepared according to the regulations for postgraduate study by research of the Dublin Institute of Technology and has not been submitted in whole or in part for another award by any institute.

The work reported on in this thesis conforms to the principles and requirements of the Institute’s guidelines for ethics in research.

The Institute has permission to keep, lend or copy this thesis in whole or in part, on the condition that any such use of the thesis be duly acknowledged.

Signature_____________________  Date_________________________

Candidate
Acknowledgments

This four years PhD study in DIT has become the most significant time in my life. I owe a great appreciation to many people who have helped me in many different ways during my PhD study period and the completion of this thesis.

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### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varphi$</td>
<td>Electric field</td>
<td>V/µm</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Permittivity</td>
<td>F/m</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of vacuum</td>
<td>F/m</td>
</tr>
<tr>
<td>$\varepsilon', \varepsilon_r$</td>
<td>Relative permittivity</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$\varepsilon''$</td>
<td>Dielectric loss</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$\tan \delta$</td>
<td>Dielectric loss factor</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$\varepsilon_1'$</td>
<td>Dielectric constant of isotropic dielectric matrix</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>Volume fraction of isotropic dielectric matrix</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$\varepsilon_2'$</td>
<td>Dielectric constant of dielectric spheroids</td>
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</tr>
<tr>
<td>$\nu_2$</td>
<td>Volume fraction of dielectric spheroids</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Shape-dependent parameter</td>
<td>dimensionless</td>
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<tr>
<td>$\sigma_v$</td>
<td>Maxwell stress</td>
<td>MPa</td>
</tr>
<tr>
<td>$h$</td>
<td>Thickness of DEs</td>
<td>mm</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Applied voltage</td>
<td>kV</td>
</tr>
<tr>
<td>$Y$</td>
<td>Young’s modulus</td>
<td>MPa</td>
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<tr>
<td>$v$</td>
<td>Poisson’s ratio</td>
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<tr>
<td>$s_x$</td>
<td>Strain in x direction</td>
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</tr>
<tr>
<td>$s_y$</td>
<td>Strain in y direction</td>
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<tr>
<td>$s_z$</td>
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<td>$s_{ad}$</td>
<td>Area strain</td>
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<tr>
<td>$A$</td>
<td>Surface area of compliant electrode</td>
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</tr>
<tr>
<td>$C$</td>
<td>Capacitance</td>
<td>F</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Volume of DE</td>
<td>m³</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>$U_S$</td>
<td>Stored elastic energy density</td>
<td>$J/m^3$</td>
</tr>
<tr>
<td>$U_e$</td>
<td>Elastic strain-energy density</td>
<td>$J/m^3$</td>
</tr>
<tr>
<td>$e$</td>
<td>Electromechanical energy density</td>
<td>$J/m^3$</td>
</tr>
<tr>
<td>$K^2$</td>
<td>Electromechanical coupling efficiency</td>
<td>dimensionless</td>
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<tr>
<td>$S_T$</td>
<td>True compressive strain</td>
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<tr>
<td>$\lambda$</td>
<td>Stretch ratio</td>
<td>dimensionless</td>
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<tr>
<td>$\sigma$</td>
<td>Mechanical stress</td>
<td>MPa</td>
</tr>
<tr>
<td>$I_1$</td>
<td>First strain invariant</td>
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<tr>
<td>$I_2$</td>
<td>Second strain invariant</td>
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<tr>
<td>$I_3$</td>
<td>Third strain invariant</td>
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<tr>
<td>$\mu$</td>
<td>Shear modulus</td>
<td>MPa</td>
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<tr>
<td>$P$</td>
<td>Force</td>
<td>N</td>
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<td>$\lambda_{pre}$</td>
<td>Pre-stretch ratio</td>
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</tr>
<tr>
<td>$\sigma_{pre}$</td>
<td>Pre-stretch stress</td>
<td>MPa</td>
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Abbreviations

DE   Dielectric Elastomer
EMI   Electromechanical Instability
PU   Polyurethane
HV   High Voltage
DEAs   DE Actuators
PDMS   Polydimethylsiloxanes
SR   Silicone Rubber
IPN   Interpenetrating Polymer Network
HDDA   Hexandiol Diacrylate
TMPTMA   Trimethylolpropane Trimethacrylate
DBEF   Dibutoxyethoxyethyl Formal
PMN-PT   Lead magnesium Niobate-lead Titanate
FGS   Functional Grapheme Sheet
BT   Barium Titanate
PANI   Polyaniline
PDVB   Poly(divinyl benzene)
AgNPs   Silver Nanoparticles
CPO   Copper-phthalocyanine Oligomer
DOP   Diocetyl Phthalate
OMMT   Organically Modified Montmorillonite
RTV   Room Temperature Vulcanising
HTV   High Temperature Vulcanising
PSS   Poly(styrene sulfonate)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
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<tr>
<td>DBSA</td>
<td>Dodecyl Benzenesulfonic Acid</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>GG</td>
<td>Gelatin and Glycerol</td>
</tr>
<tr>
<td>SEBS</td>
<td>Polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene</td>
</tr>
<tr>
<td>MO</td>
<td>Mineral Oil</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene Fluoride</td>
</tr>
<tr>
<td>HNBR</td>
<td>Hydrogenated Nitrile-butadiene Rubber</td>
</tr>
<tr>
<td>PPO</td>
<td>Poly(propylene oxide)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-Dispersive X-ray Spectrometers</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene Terephthalate</td>
</tr>
<tr>
<td>PBT</td>
<td>Polybutylene Terephthalate</td>
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Chapter 1  Introduction

1.1 Background

Dielectric Elastomers, (DEs), are materials that can respond to electrical stimuli by changing their shape and belong to the family of smart materials. DEs have attracted increased attention because they offer the advantages of large voltage-induced deformation (> 380%), high energy density (≈ 3.4 MJ/m³) and high electromechanical coupling efficiency (> 85%) [1-7], combined with light weight, low cost and freedom from noise pollution [8-12]. Moreover, they are sometimes referred to as “artificial muscle” materials because they can readily resemble natural muscle under strain, as well as display similar actuation pressures, response speeds, electromechanical energy densities and coupling efficiencies. Consequently they have been proposed for multiple applications in the fields of biomimicry [13-15], artificial intelligence [16-23] and renewable energy [6, 24-27].

Generally, DEs can exhibit several levels of strain (10%–300%), but they require large electric fields (usually around 100 V/μm) to achieve high actuated strains [28]. Furthermore, electromechanical instability (EMI), which is also termed pull-in instability, is highlighted as the most significant failure mode for DEs when they are used as electromechanical actuators [29-31]. This kind of failure occurs when the thickness of a DE falls below a certain threshold and the equivalent Maxwell pressure exceeds the compressive stress of the elastomer film. Its positive feedback leads to an unstable compression of the elastomer material which reduces thickness further and consequently breakdown ensues [32]. Significantly, EMI has been observed to occur when an electric field is applied to
the widely used commercial polyacrylate DE material, VHB 4910, which is manufactured and supplied by 3M (see Fig. 1.1). This has prevented the material from achieving large voltage-induced deformations [32, 33]. In addition, this polyacrylate film has the intrinsic drawbacks of low thermal stability, sensitivity to environmental degradation [34] and high viscoelasticity resulting in a relatively slow response to an electrical signal, thus limiting coupling efficiency [35, 36].

![Fig. 1.1 A photograph of a DE film exhibiting pull-in instability (wrinkled area) [32].](image)

Therefore, in order to ensure the further utilisation of DE materials, it is essential to design and develop new DEs with the capability of overcoming the drawbacks of polyacrylate films. Ideally they should exhibit relatively large deformations under low electric fields and also should operate without the occurrence of EMI.

### 1.2 Research Justification

It was reported that the operating electric field of a DE could be decreased by increasing the DE’s dielectric constant and also through lowering Young’s
modulus [37]. A soft silicone rubber (SR) not only has a low Young’s modulus, but also has the advantages of lower viscoelasticity, good thermal stability and greater biocompatibility when compared with most carbon-based polymers including the commercially available 3M VHB 4910 polyacrylate [34]. However, the dielectric constant of SR is relatively low (≈ 2.9). The conventional method of increasing the dielectric constant of a DE is by incorporating nano/micron sized high-dielectric filler particles into the DE matrix. Barium titanate (BT), with a high dielectric constant (> 1200), has been used as a filler material to improve the dielectric properties of SR-based DEs [38, 39] and its use is explored further in the research described here.

It has also been shown that pre-stretch offers numerous advantages for improving the properties of DEs, such as decreasing the viscoelastic (time-dependent) behaviour of VHB 4910, improving the material’s actuation performance, dielectric strength, response speed and eliminating EMI, when the material is subjected to large voltage-induced deformations. Zhao et al. [40] studied the mechanism of EMI and found that it could be delayed by tuning the stiffness of DEs using mechanical pre-stretch and again this approach is a significant component in the research described in the coming chapters.

Thus, considering the issues and possible solutions discussed in the previous paragraphs, the essential aim of this research was to investigate a method of fabricating new DEs with the potential capability of undergoing large voltage-induced strain under low electric field strength using SR in conjunction with BT particles. Thereafter, a coating method for BT was proposed in order to improve the compatibility between SR and BT and enhance the dielectric constant of the DE composites. An approach of equi-biaxial mechanical pre-stretching to
eliminate EMI in SR-based DEs is also offered. Finally, some discussion in respect of new applications for DEs is provided. This section is included in the thesis to suggest how the enhanced properties of the novel fabricated DE described in this work can best be exploited.

1.3 Research Question

Based on these considerations, the main question posed by this research project was:

Can a DE be fabricated with the capability of achieving large voltage-induced deformation under the operation of a low electric field, whilst minimising or even entirely eliminating EMI?

1.4 Aims and Objectives

Ensuing from the research question, the primary aim of this research was to fabricate a novel DE that could avoid the intrinsic drawbacks of a typical DE material such as those possessed by the commercially available VHB 4910 and at the same time eliminate EMI at higher strains. This was addressed by using a soft silicone matrix and BT with high dielectric constant in order to fabricate DEs capable of large voltage-induced deformation in a low electric field. Furthermore, the mechanism of EMI for SR based DEs was investigated by employing a mechanical model. In order to investigate the EMI of DEs in the presence of large electric fields, equi-biaxial stress-stretch data was obtained by the bubble inflation test method. This was used to fit voltage-stretch curves obtained from an electromechanical test system.
Hence, the main objectives of the project for accomplishing the specified research aim were to:

a. Establish an electromechanical test system to obtain the relation between electric field and actuated strain.

b. Investigate the influence of external factors, such as compliant electrodes and pre-stretch, on the electromechanical properties of VHB 4910.

c. Fabricate DEs with the capability of large voltage-induced deformations at low electric field strengths using BT and SR and thereafter attempt to improve their electromechanical properties.

d. Optimise SR-based DE composites by modifying the surface of BT particles in order to improve the compatibility between the fillers and the matrices and further enhance the dielectric constants of DE composites.

e. Investigate mechanisms of EMI on DEs via theoretical and numerical methods and propose a method to assuage or remove the EMI.

1.5 Research Methodology

This section provides a description of the research methods used in this research. It relates the research objectives to suitable methodologies to achieve the required outcomes. The research includes a literature review from libraries and online repositories, experimental methods and using unique CER developed equipment (i.e. the in-house stretch rig and the equi-biaxial bubble inflation system) and numerical analysis. These methods were used to determine the factors influencing the performance of DEs.
i) A review of existing literature allowed:

- An understanding of the basic concepts and parameters of DEs such as dielectric constant, dielectric loss tangent, Maxwell stress, actuated strain, electromechanical energy density and coupling efficiency.

- A determination and implementation of a method of fabricating compliant electrodes and an approach to apply compliant electrodes to DEs. This allowed the use of appropriate electrodes for the research and an effective method for coating the electrodes onto the surfaces of the DEs made in-house.

- A determination of the influence of pre-stretch on the electromechanical properties of DEs such as dielectric strength, actuated strain, electromechanical energy density and coupling efficiency.

- A review of DE materials reported on in the previous two decades, including the conventional polyacrylate, VHB 4910, SR, polyurethane (PU) and the novel DE matrices and their composites incorporating fillers.

- A review of alternative mechanical models for DEs in order to understand their mechanical behaviour when they undergo large deformations.

- An understanding of the mechanism of EMI and the influence of pre-stretch on EMI in order to provide a method for assuaging the EMI of DEs.

- A consideration of DE applications, such as grippers, renewable energy devices and tactile display devices.
ii) Experimental methods:

- Using an electromechanical test system consisting of a digital camera, a DC high voltage power supply and a stretch rig which was designed in order to characterise the electromechanical properties of DEs.
- Obtaining the relation between equi-biaxial stress and stretch using a hydraulic bubble inflation system.
- Finding the relation between the deformation of DEs and the applied voltage using an electromechanical test system.

iii) A theoretical approach included:

- Investigating the mechanisms of deformation under the condition of equi-biaxial loading of DEs.
- Studying the mechanisms of deformation under an electric field for DEs.
- Evaluating the mechanisms of EMI for DEs.

iv) The numerical approach used was:

- Modelling the curves of stretch related to applied voltage from the data derived from mechanical testing by incorporating a Maxwell stress.

1.6 Thesis Structure

This work includes a literature review, experiment design, methodology and results from experimentation, corresponding discussions on the research findings and some initial conclusions and suggestions for advancing the research. The thesis is divided into eight chapters containing all of the research carried out to date.

Following an introduction to the aim, objectives and methodology in Chapter 1, Chapter 2 undertakes a review of the most significant published literature. This
has been critically reviewed, critiqued and its relevance generally summarised. This chapter begins with the evolution of DEs followed by some basic concepts in DE technology, the essential materials for compliant electrodes, pre-stretch, new DE material fabrication techniques, mechanical models of DEs and potential applications of DEs.

In Chapter 3, the necessary preparation for the experiments undertaken is described and characterisation methods are presented. A description of the mechanical testing used to obtain the stress-stretch behaviour of DEs is given. A dielectric test is used for characterising polarising behaviour of molecular chains, also the dielectric constant was provided in this test for calculating some electromechanical parameters. The electromechanical testing described was essential to establish the experimental relations between electric field and actuated area strain.

In Chapter 4, the investigation into the influence of equi-biaxial pre-stretch on electromechanical properties is described. The DE fabricated in-house and VHB 4910 samples were used in this investigation and those described in later chapters.

In Chapter 5, research into the influence of BT content on the electromechanical properties of SR based DEs is comprehensively discussed. In Chapter 6, in order to get an acceptable level of compatibility between BT and the DE matrix and improve the electromechanical properties of the compound, a coating method is introduced by means of depositing dopamine on BT particles.

Further, the approach to eliminating EMI for SR based DEs is presented in Chapter 7. Some initial conclusions and suggestions for advancing the research are given in Chapter 8. Many unanswered questions are also addressed in this
chapter which outlines the future work plan and the further development of the research programme.

1.7 Summary

Research defining the characteristics of DEs and the fabrication and testing of a novel SR DE containing BT particles is described in this thesis. In this chapter, the background to the research is described and its justification is presented. The central research question is advanced and the project aim that stems from this question and the resulting objectives are specified. Following this, the methodology used in the completion of the proposed objectives is introduced. Finally, the thesis structure, briefly describing the contents of each chapter, is set out.
Chapter 2  Literature Review

2.1  Introduction

This chapter provides an overview of previous research carried out into dielectric elastomers (DEs). It also introduces the framework for the investigations that comprise the main focus of the research described in this thesis. Firstly, in order to understand the context of this research, some basic concepts delineating the properties of DEs are provided. Then, reporting of findings on compliant electrodes and pre-stretch from previous research underpins the design of the experimental methods used in this research. The main purpose of the literature review was to survey previous studies carried out into DEs in respect of the improvement of electromechanical properties and eliminating electromechanical instability (EMI) and understanding the significance of these topics and this is reflected in the quantity of previous work in the literature reviewed. A commentary on research to date into the development of DEs with improved electromechanical properties is also provided. Finally, some potential applications supported by the development of DEs are reviewed at the end of the chapter.

2.2  Concept of DEs

The atoms of all solid materials consist of negatively charged electrons surrounding a central core of positively charged protons and neutrons. Dielectric polarisation occurs when a dipole moment is formed in an insulating material because of an externally applied electric field. When a current interacts with a dielectric (insulating) material, the dielectric material responds with a shift in charge distribution, with the positive charges aligning with the electric field and
the negative charges aligning against it. In a conductor, the charged particles can move over macroscopic distances. By contrast, in a dielectric material, they only move relative to one another over small distances. In dielectric materials, the two processes of deformation and polarisation are inherently coupled. All dielectric materials are electroactive [41].

2.2.1 Dielectric Constant and Loss Factor

Dielectric materials are comprised of small dipoles which are electrically neutral but possess internal charge separation. In the presence of an applied external electric field, the dipoles will rearrange: the positive end points toward lower potential and the negative end points toward higher potential [42]. DE materials are normally structured so that a three-dimensional network is formed by molecular chains cross-linking with each other via covalent bonds [41, 43, 44]. For a single chain, there are a large number of polar monomer units in the chain’s backbone and side-chains. Thus, the crosslinks have a negligible effect on the process of polarisation of these monomers; that is, the elastomer polarises similarly to a polymer melt [45]. As shown in Fig. 2.1, the molecular dipoles will rotate and the re-orientation results in the elastomer deforming during polarisation in the presence of an electric field ($\varphi$) [46]. As a consequence, the electrostatic stress, combined with electrostriction induced by polarisation leads to the deformation of a DE.
The dielectric constant is a unitless measure of the material’s ability to polarise in the presence of an electric field. It is defined as the ratio between the permittivity of the dielectric ($\varepsilon$) and a vacuum ($\varepsilon_0$). In the literature, references are not usually made to the “dielectric constant” of the material, but to “relative permittivity”, $\varepsilon'$ or $\varepsilon_r$ [47, 48], which is synonymous with the dielectric constant. Moreover, the terms “relative dielectric constant” and “relative permittivity” are often substituted for each other. The dielectric constant is both a temperature and a frequency-dependent parameter (Eqn. (2-1)).

$$\varepsilon' = \frac{\varepsilon}{\varepsilon_0}$$

(2-1)

Energy is dissipated and transferred during the polarisation of dipoles. This is referred to as dielectric loss ($\varepsilon''$). The energy loss inevitably occurs, because, on the one hand, the thermal motion affects dielectric polarisability by distortion of aligned dipoles and on the other hand, the dielectric relaxation is caused by the applied electric field frequency [49]. In this case, part of the energy is dissipated and transferred. The dielectric constant $\varepsilon'$ represents the energy stored in a cycle. The dielectric loss factor ($\tan \delta$) is described as the ratio of dielectric loss to dielectric constant (Eqn. (2-2)):
\[ \tan \delta = \varepsilon'' / \varepsilon' \]  

(2-2)

It demonstrates the quantity of lost energy in a cycle compared with the stored energy. Therefore, actual permittivity of the material is a complex parameter given by Eqn. (2-3)

\[ \varepsilon = \varepsilon' - i\varepsilon'' \]  

(2-3)

The dielectric constant of materials depends on both their chemical composition and structure, while loss factor is also influenced by the peculiarities of molecular motion and purity of the polymer [50].

In order to improve understanding of the dielectric behaviour of DEs, several mixing rules [51-55] have been proposed for estimating the dielectric constant \( \varepsilon' \) of polymer composites which comprise the isotropic dielectric matrix (dielectric constant \( \varepsilon_i' \), volume fraction \( \upsilon_i \)), filled with dielectric spheroids (dielectric constant \( \varepsilon_2' \), volume fraction \( \upsilon_2 = 1 - \upsilon_i \)). The following equations are used to express the relations between the dielectric constant of DEs and the volume fraction of spherical fillers in DEs:

a) The Maxwell-Wagner formula [53] (Eqn. (2-4)) describes the change of dielectric properties of a diluted suspension with spherical conducting particles. It is derived under the assumption that particles are dispersed in a continuous matrix phase in such a low concentration that there is no interaction between particles.

\[
\varepsilon' = \varepsilon_i' \left[ 2\varepsilon_i' + \varepsilon_2' + 2\upsilon_i \left( \varepsilon_2' - \varepsilon_i' \right) \right] / \left[ 2\varepsilon_i' + \varepsilon_2' - \upsilon_i \left( \varepsilon_2' - \varepsilon_i' \right) \right] 
\]  

(2-4)

b) When the particle volume concentration is high, the assumption is invalid. In order to overcome this disadvantage, Eqn. (2-5) was proposed by Böttcher [56]:
\[ 3\varepsilon' (\varepsilon' - \varepsilon_1' ) = \nu_2 (\varepsilon_2' - \varepsilon_1' ) \left( 2\varepsilon' + \varepsilon_2' \right) \]  

(2-5)

c) In accordance with Maxwell’s equation, Looyenga [57] developed an equation by assuming that the variable particle volume concentration was a function of \( \varepsilon' \) and \( \Delta \varepsilon \) provided that

\[ \varepsilon_1' = \varepsilon' - \Delta \varepsilon \]  and \( \varepsilon_2' = \varepsilon' + \Delta \varepsilon \).

The resulting equation is expressed as:

\[ \varepsilon' = \left[ (1 - \nu_2)\varepsilon_1' (1/3) + \nu_2 \varepsilon_2' (1/3) \right]^3 \]  

(2-6)

d) The modified Rother-Lichtenecker model [52, 58] based on the Rother-Lichtenecker equation is a representation of a logarithmic law of mixing for a chaotic or statistical mixture, as shown in Eqn. (2-7):

\[ \ln \varepsilon' = \ln \varepsilon_1' + \nu_2 (1 - \kappa) (\ln \varepsilon_2' - \ln \varepsilon_1') \]  

(2-7)

where \( \kappa \) is a shape-dependent parameter. It was reported that \( \kappa \) had a value around 0.1–0.3 for most well-dispersed polymer-ceramic composites [59]. For example, a \( \kappa \) of 0.1 was reported for a DE compound consisting of a form of lead-free perovskite ceramic particle (\( \text{CaTiO}_3 \)) in a polyvinylidene fluoride (PVDF) [60].

e) Jayasundere and Smith derived Eqn. (2-8) for permittivity as a randomly connected state in a binary piezoelectric 0–3 composite by modifying the well-known Kerner equation [61] including interactions between neighbouring spheres.

\[ \varepsilon' = \frac{\varepsilon_1' (1 - \nu_2) + \varepsilon_2' \nu_2 \left[ 3\varepsilon_1' / \left( 2\varepsilon_1' + \varepsilon_2' \right) \right]}{(1 - \nu_2) + \nu_2 \left[ 3\varepsilon_1' / \left( 2\varepsilon_1' + \varepsilon_2' \right) \right]} \left[ 1 + 3\nu_2 \left( \varepsilon_2' - \varepsilon_1' \right) \left( 2\varepsilon_1' + \varepsilon_2' \right) \right] \]  

(2-8)
2.2.2 Maxwell Stress

Pelrine [62] initially found that the dielectric properties of DEs can be used to induce high actuated strains through the application of an electrical field [51]. In his experiments, area strains of up to 30%, corresponding to actuation pressures of up to 1.9 MPa and high specific energy densities up to 0.1 J/g were obtained. The working principle of DEs is illustrated in Fig. 2.2. When a high voltage is applied to the compliant electrodes which are coated on the surfaces of a DE, the DE can quickly change its shape; when the electric stimulus is removed, it can recover its original shape [63-69]. The Maxwell stress \( \sigma_v \) produced by the attraction of negative and positive charges on parallel surfaces compresses the film to transform the electrical energy into mechanical energy.

\[
\sigma_v = \varepsilon' \varepsilon_0 \left( \Phi / h \right)^2 = \varepsilon' \varepsilon_0 \phi^2
\]  

(2-9)

Where \( h \) is the thickness of the DE, \( \varepsilon' \) is the dielectric constant of the DE material, \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} \, \text{F/m}) \), \( \phi \) is the electric field which

Fig. 2.2 Schematic representation of a DE’s working principle: (a) A DE does not change its shape in the absence of a high voltage (HV); (b) The DE is compressed in thickness and expanded in area under a HV [63].
is equal to the applied high voltage ($\Phi$) divided by the thickness of the DE ($h$). As shown here, $\sigma_v$ can be increased by either increasing the dielectric constant or the applied electric field.

### 2.2.3 Actuated Strain

For low strains, (e.g. < 20%), the actuated strain is closely related to Maxwell stress and Young’s modulus ($Y$) [63, 72]. The thickness strain ($s_z$) can be approximately calculated using Eqn. (2-10) on the basis of Hooke’s law (Poisson’s ratio $\nu \approx 0.5$) [20].

$$s_z = -\sigma_v / Y = -\varepsilon\varepsilon_0 \Phi^2 / Y$$

(2-10)

However, Hooke’s law is not applicable for large strains beyond 20%. Due to the isochoric behaviour of a DE (whether or not a high voltage is imposed), volume remains virtually constant. Thus the strains for the different directions of $x$, $y$ and $z$ can be related to each other using Eqn. (2-11):

$$(1 + s_x)(1 + s_y)(1 + s_z) = 1$$

(2-11)

where $s_x$, $s_y$ and $s_z$ are the strains in the $x$, $y$ and $z$ directions respectively; meanwhile the relation of area strain $s_a$ in the plane normal to thickness strain $s_z$ can be easily obtained using Eqn. (2-12) and the relationship between $s_a$ and $s_z$ is represented by:

$$(1 + s_a)(1 + s_z) = 1$$

(2-12)
2.2.4 Electromechanical Energy Density and Electromechanical Coupling Efficiency

For actuator materials, energy density and coupling efficiency are two important factors for characterising the performance of DEs. In order to generate high elastic energy density, high electric fields are required. The stored elastic energy density \( U_S \) is specified by Eqn. (2-13), where \( C = \varepsilon_0 \varepsilon' A / h \) is the capacitance, \( A \) is the surface area of the compliant electrode coated on the DE, \( v \) is the volume of the DE and \( \phi = Q / \varepsilon_0 \varepsilon' A \):

\[
U_S = 0.5Q^2 / C = 0.5Q^2 / \varepsilon' \varepsilon_0 A = 0.5\varepsilon_0 \varepsilon' \varepsilon_0 \phi^2
\]

Therefore, the input energy density increases with increases in the dielectric constant of a polymer. So a large dielectric constant is also necessary if feasible effective actuated strains (and corresponding stresses) are to be achieved. The strain energy density of a DE is defined as the amount of work generated in one actuation cycle per unit volume of actuator, exclusive of overhead peripherals, such as electrolytes, counter electrodes and packaging. The strain energy density can be calculated directly from experimentally measured quantities including the Maxwell stress and transverse strain discussed in the previous sections. If the DE materials produce small strains below 10% under a relatively low electric field, the elastic strain energy density \( U_e \) can be obtained from \(-\sigma_s s_z / 2\) on a unit volume basis. Thus, combined with Eqn. (2-10), the relationship between \( U_e \) and \( s_z \) can also be expressed as

\[
U_e = \frac{Ys_z^2}{2}
\]

For large actuation strains, a more useful measure of performance is the electromechanical energy density \( \varepsilon \) [63]. It is related to the transverse strain and the Maxwell stress and can be derived from the following equation [51]:

17
\[
e = -\int \sigma_v \left[ 1/(1 + s_z) \right] ds_z = -\sigma_v \ln(1 + s_z)
\] (2-15)

As well as energy density, another often used parameter for characterising a DE’s performance is the electromechanical coupling efficiency \( (K^2) \) [34], which is the electrical energy converted into mechanical work per cycle relative to the electrical energy applied per cycle (or, alternatively, the proportion of stored mechanical energy to input electrical energy). Presuming that the elastomeric materials are operating under isochoric conditions, the change in electrical energy upon actuation is approximately equal to the work output, in which case \( K^2 \) can be calculated using Eqn. (2-16):

\[
K^2 = -2s_z - s_z^2
\] (2-16)

### 2.3 Compliant Electrodes

DE actuators can produce large deformations induced by high electric fields with compliant electrodes directly coated onto their surfaces. Thus, the compliant electrodes are required to have good conductivity in order to avoid voltage drop along the conductive tracks. Furthermore, the electrodes should be compatible with the DE material and not impede its large deformation. Such electrodes are patternable (capable of conforming to different shapes when applied to the DE outer surfaces) and can be made thin relative to the polymer thickness [62]. Different kinds of compliant electrodes used in conjunction with DE actuators have been reported extensively in the literature [73-75]. Graphite and carbon black powders along with their compounds mixed with grease or with elastomers are the most popular and widely used compliant electrodes for DE actuators (DEAs) [76]. They have the advantages of low stiffness and the ability to remain conductive at large strains. This kind of carbon based electrode applied with a
paintbrush, has limitations in respect of patternability, scalability for large volume production, compatibility with clean-room processes, reliability, lifetime and ease of application [75].

To overcome these drawbacks, new types of electrodes have emerged during the past few years. Metallic thin-films [77], although not intrinsically stretchable beyond a few percent, can be patterned in-plane or made to ripple out of plane. The major obstacles for their future application as electrodes on DEs are the high Young’s moduli of metals (several orders of magnitude higher than those of DEs) which can restrain a DE’s deformation and low elasticity and so can lead to the electrode cracking and islands forming separated by the non-conductive polymer [78].

![Fig. 2.3 Schematic representation of a low energy filtered cathodic vacuum arc (FCVA) implanter. An HV pulse on the trigger electrode initiates the main arc between the source (cathode) and the anode. The electrons, ions and macroparticles produced by the arc enter the filter which traps the macroparticles. The substrate holder is negatively biased to accelerate the positive ions through the plasma sheath [79].](image)
In order to address the shortcomings of carbon-based electrodes and metallic thin film electrodes, more and more novel technologies are being used to fabricate compliant electrodes. Metal ion implanted electrodes were reported as good candidates thus attracting considerable attention. Samuel et al. [79] reported a method to form nanometer-scale metallic clusters (ie. Au, Ti, Pd···) up to 50 nm below the surface of polydimethylsiloxanes (PDMS) with the capability of sustaining up to 175% strain while remaining conductive yet having only a minimal impact on the DE’s mechanical properties (see Fig. 2.3). However, the requirement for equipment to implant the metal ions in DEs was regarded as the main disadvantage in limiting the widespread use of this technology [80].

Furthermore, in order to improve the lives of DEs, self-clearing electrodes have been proposed by other researchers [74, 81, 82]. Generally, an electrical short can be formed through the film when an electrical breakdown occurs. Using this method, the electrical short can be self-cleared via the decomposition of the electrode material surrounding the breakdown area so that the breakdown site is isolated and the actuator can resume its function [74]. Even though the DE membrane can survive the electric field, it will inevitably suffer mechanical damage due to the low tear-strength of the material. The main advantages and disadvantages of different types of compliant electrodes used for DEAs are summarised in Table 2-1.
Table 2-1 Main advantages and disadvantages of the principal types of compliant electrodes used for DEAs.

<table>
<thead>
<tr>
<th>Electrode Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon electrodes</td>
<td>• Low impact on stiffness</td>
<td>o High resistivity</td>
</tr>
<tr>
<td></td>
<td>• Cheap and rapidly made</td>
<td>o Easily damaged</td>
</tr>
<tr>
<td>Metallic electrodes</td>
<td>• High conductivity</td>
<td>o High impact on stiffness</td>
</tr>
<tr>
<td></td>
<td>• Patternability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Easily adapted to large scale production</td>
<td>o Low elasticity</td>
</tr>
<tr>
<td>Metal ion implanted electrodes</td>
<td>• Low impact on stiffness</td>
<td>o Complex process</td>
</tr>
<tr>
<td></td>
<td>• High conductivity</td>
<td>o Expensive</td>
</tr>
<tr>
<td></td>
<td>• Patternability</td>
<td></td>
</tr>
<tr>
<td>Self-clearing electrodes</td>
<td>• Low impact on stiffness</td>
<td>o Still suffering</td>
</tr>
<tr>
<td></td>
<td>• High conductivity</td>
<td>mechanical damage</td>
</tr>
<tr>
<td></td>
<td>• The ability to improve the life of a DEA</td>
<td>from electrical breakdown at the site</td>
</tr>
</tbody>
</table>

2.4 Pre-stretch

Pre-stretch has been employed as an effective and significant approach in order to obtain excellent actuation performance of a DE when applying an electric field. Some researchers reported that larger actuated strains can be achieved at smaller voltages and electric fields and this can be explained in terms of a thermodynamic stability criterion [83]. Pelrine et al. first demonstrated that a DE could achieve actuation strains above 100% by uniaxially or biaxially pre-stretching DEs such as polyacrylate and silicone rubber [63]. It has also been proven that pre-stretch can increase dielectric strength [1]. However, the mechanism of this effect is still not completely understood. In addition, the relation between the increase in actuated strain and dielectric strength need further study, because pre-stretch can cause
strain induced stiffening which may prevent the DE film deforming further. Furthermore, pre-stretch can not only increase the response speed to the application of an electric field but also eliminate EMI which significantly impedes the deformation of the VHB 4910 acrylate film [84]. The ability to suppress EMI by using pre-stretch is mainly due to the property of strain stiffening [40]. In Suo’s work, a very large voltage-induced deformation of 1692% was achieved by means of pre-stretching acrylate film without EMI occurring [85]. Section 2.7 in this chapter gives a detailed explanation of the occurrence of EMI in DEs and the influence of pre-stretch on the properties of DEs. However, it has been reported that pre-stretch has led to the device structures becoming complicated, limited applications and lowered lifetimes of DEAs due to stress relaxation and fatigue in the pre-stretched materials [1]. Also, stress concentrations have been induced along the rigid frames that are required to support the pre-stretch.

2.5 DE Materials

The performance of elastomer actuators can be tailored, with ease and versatility in most cases, by choosing different types of elastomers, changing the cross-linking of polymer chains, adding functional entities and improving fabrication techniques. However, DEs should have a favourable combination of high dielectric breakdown strength, high elongation and relatively low mechanical and electrical losses [9]. As can be observed in Table 2-2, many types of polymers are used for DE matrices including silicone rubber (SR) [71, 86-89], polyacrylate [90-93] and polyurethane (PU) [94-97].
Table 2-2 Comparison of DE material properties [1, 98].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Pre-strain (%)</th>
<th>Thickness Strain&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Area Strain&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Young's Modulus (MPa)</th>
<th>Electric Field&lt;sup&gt;b&lt;/sup&gt; (V/μm)</th>
<th>ε*&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
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<td>−</td>
<td>32</td>
<td>−</td>
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<td>3.5</td>
<td>0.29</td>
<td>56</td>
<td>3.1</td>
</tr>
<tr>
<td>Polymer</td>
<td>Pre-strain (%)</td>
<td>Thickness Strain$^a$ (%)</td>
<td>Area Strain$^a$ (%)</td>
<td>Young's Modulus (MPa)</td>
<td>Electric Field$^b$ (V/μm)</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>----------------</td>
<td>-------------------------</td>
<td>-------------------</td>
<td>----------------------</td>
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<td>--------------</td>
</tr>
<tr>
<td>Silicone (Wacker Elastosil RT 625)</td>
<td>(0,10)</td>
<td>12</td>
<td>–</td>
<td>0.303</td>
<td>75</td>
<td>3.2</td>
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<td>0.5</td>
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<td>8</td>
<td>–</td>
<td>2.5</td>
<td>32</td>
<td>12.7</td>
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<tr>
<td>PU (Decerfield PT6100S) and</td>
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<td>11</td>
<td>–</td>
<td>17</td>
<td>160</td>
<td>7</td>
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<tr>
<td>PU (Polytek Poly74-20)</td>
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<td>–</td>
<td>0.292</td>
<td>–</td>
<td>7.6</td>
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<tr>
<td>HNBR (Zetpol 3310, ACN content 25%)</td>
<td>–</td>
<td>–</td>
<td>5.8</td>
<td>1.6</td>
<td>30</td>
<td>12.4</td>
</tr>
<tr>
<td>NBR</td>
<td>–</td>
<td>–</td>
<td>2.2</td>
<td>1.3</td>
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<td>9.71</td>
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<tr>
<td>Acrylic (3M VHB 4910)</td>
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<td>61</td>
<td>158</td>
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<tr>
<td>Acrylic (3M VHB 4910)</td>
<td>(15,15)</td>
<td>29</td>
<td>40</td>
<td>–</td>
<td>55</td>
<td>4.8</td>
</tr>
<tr>
<td>Acrylic (3M VHB 4910)</td>
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<td>68</td>
<td>215</td>
<td>–</td>
<td>239</td>
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<tr>
<td>SEBS 75 (GLS Corp)</td>
<td>(300,300)</td>
<td>62–22</td>
<td>180–30</td>
<td>0.007–0.163</td>
<td>32–133</td>
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</tr>
<tr>
<td>SEBS 161 (GLS Corp)</td>
<td>Nominal</td>
<td>14</td>
<td>16.5</td>
<td>1.3</td>
<td>27</td>
<td>–</td>
</tr>
<tr>
<td>Polymer</td>
<td>Pre-strain (%)</td>
<td>Thickness Strain (a) (%)</td>
<td>Area Strain (a) (%)</td>
<td>Young's Modulus (MPa)</td>
<td>Electric Field (V/μm)</td>
<td>εc</td>
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<tr>
<td>---------------------------------------------</td>
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<td>--------------------------</td>
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<tr>
<td>SEBS 217 (GLS Corp)</td>
<td>(300,300)</td>
<td>71-31</td>
<td>245–47</td>
<td>0.002–0.133</td>
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<td>1.8–2.2</td>
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<tr>
<td>SEBS 217 (GLS Corp)</td>
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<td>16</td>
<td>18.8</td>
<td>1.1</td>
<td>29</td>
<td>–</td>
</tr>
<tr>
<td>SEBS (Elastoteknik AB Dryflex 500040)</td>
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<td>12</td>
<td>–</td>
<td>0.25</td>
<td>58</td>
<td>2.3</td>
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<tr>
<td>SEBS-g-MA(Kraton)</td>
<td>–</td>
<td>0.4</td>
<td>–</td>
<td>2.144</td>
<td>136</td>
<td>2.0</td>
</tr>
<tr>
<td>IPN (VHB 4910-HDDA)</td>
<td>(0,0)</td>
<td>70</td>
<td>233</td>
<td>2.5</td>
<td>300</td>
<td>–</td>
</tr>
<tr>
<td>IPN (VHB 4905-TMPTMA)</td>
<td>(0,0)</td>
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<td>146</td>
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<tr>
<td>IPN (VHB 4910-TMPTMA)</td>
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<td>74.97</td>
<td>300</td>
<td>4.15</td>
<td>418</td>
<td>3.27</td>
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<tr>
<td>PTBA</td>
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<td>77</td>
<td>335</td>
<td>0.42</td>
<td>260</td>
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</table>

(a) Deformation at electric field breakdown or maximum deformation reported
(b) Electric field at breakdown or maximum electric field reported
(c) Measured at 1 kHz
2.5.1 Polyacrylate Film

To date, the polyacrylate film, VHB4910, is the most widely used DE material because of its ability to deliver large voltage-induced strains (> 100%) and high energy densities (> 3 MJ/m³) when combined with pre-stretching [63]. However, the support frame which is required to maintain the pre-stretch on the film significantly increases the weight of any DE based application. Some researchers endeavored to improve the polyacrylate film in respect of achieving large actuation strains by inducing free pre-stretch [99].

The approach to fulfill this goal was to form a second interpenetrating polymer network (IPN) (see Fig. 2.4) to maintain the pre-stretch needed to obtain excellent electromechanical performance [99-101]. Furthermore, it has been proven that this approach reduced the viscoelasticity of DEs and mitigated EMI [102]. These IPN films were fabricated by spraying thermally curable multifunctional additives and initiators onto the pre-stretched polyacrylate film [1, 101, 103, 104]. The additives were diffused into the film and cured. Thus, the treated polyacrylate film was then formed into a second rigid polymer network [104]. Upon releasing the film from its support, the additive network will resist the contraction of the VHB host, preventing it from returning to its un-stretched state.
The modified VHB 4910 films without pre-stretch have the ability of achieving large voltage-induced deformations similar to the conventionally pre-stretched VHB 4910 films. Ha et al. [105] obtained the IPNs incorporating bi-functional 1, 6-hexandiol diacrylate (HDDA) and tri-functional trimethylolpropane trimethacrylate (TMPTMA) monomers. The IPN films demonstrated high elastic strain energy densities ($\approx 3.5$ MJ/m$^3$) and high electromechanical coupling efficiencies ($\approx 97\%$) without pre-stretch.
However, the intrinsic drawbacks of the polyacrylate based materials have inevitably impeded their applications. These drawbacks include:

i) low thermal stability

ii) great variation in modulus with temperature change

iii) sensitivity to environmental degradation [34] and

iv) viscoelasticity; the deformation is time-dependent (strain rate-dependent) which results in a relatively slow response to an electrical signal and limits coupling efficiency [35, 36, 106]. To obviate these problems, other researchers proposed using plasticiser to broaden the operating temperature range, lower the elastic modulus and decrease the losses due to viscoelasticity. Zhang et al. [107] reported that a DE containing 40 wt% of an effective plasticising agent exhibited a large deformation of 215% when a voltage of 6.5 kV was applied. The plasticiser used was dibutoxyethoxyethyl formal (DBEF) mixed into the IPN films. Though it was suggested that the dielectric constant of the films increased with plasticiser concentration [108], dielectric loss tangent at low frequencies also increased with plasticiser concentration, leading to decreased efficiency and breakdown strength [108].

2.5.2 SR Based DEs

SR cannot only overcome the shortcomings of the polyacrylate materials, but also has a greater biocompatibility than most carbon based polymers [34]. SR can achieve large voltage-induced deformations of above 30%, large energy densities and rapid responses to electrical signals. However, because of the low dielectric constant, it requires a high electric field in order to be actuated. Reductions in voltage can be realised by decreasing the thickness of SR films or increasing the
dielectric constant. Reducing the film thickness has the advantage of maintaining
dielectric strength and dielectric loss. However, the SR film suffers from a
decrease in output force and can be susceptible to an increase in inhomogeneity in
the film which can lead to breakdown occurring [1]. Much work has been
undertaken in order to increase the dielectric constants of SR based DEs.
The most popular approach to increasing the dielectric constant is based on the
use of high permittivity ceramic fillers, typically in the form of powder. Examples
of the fillers used are titanium dioxide (TiO$_2$) [54, 109-111], lead magnesium
niobate-lead titanate (PMN-PT) [53, 112], barium titanate (BT) [38, 113] and
functional graphene sheet (FGS) [114]. However, it is thought that disadvantages
such as high dielectric loss, the increase in elastic modulus and poor compatibility
of fillers with SR, limit their further application [47]. In order to solve these
problems, endeavours in encapsulating the filler particles with an organic group
have been made including modifying BT with phosphonic acid [115],
encapsulating conductive polyaniline (PANI) particles into poly(divinyl benzene)
(PDVB) [116], coating spherical silver nanoparticles (AgNPs) with thin silica
shells [48] and modifying BT with $\gamma$-methacryloxypropyl trimethoxy silane
(KH570) [47].
Conductive inorganic fillers such as carbon black [117] and organic systems such
as copper-phthalocyanine oligomer (CPO) [118], dioctyl phthalate (DOP) [119]
and organically modified montmorillonite (OMMT) nano-clay [120] have been
tested too. Also, the method of blending with other polymers has been used to
increase the dielectric constant of the SR based DE materials. Carpi et al. [70, 121]
studied the electromechanical performance of SR mixed with the undoped poly-
hexyl-thiophene. It was found that very low percentages (1–6 wt%) of poly-hexyl-
thiophene yielded both an increase of the dielectric constant and an expected reduction of the tensile elastic modulus. The SR with 1 wt% content of the conjugated polymer achieved an actuated strain of about 8%.

Moreover, modification of SR molecular chains was introduced in order to improve electromechanical properties. Racles et al. [122] obtained a new DE by blending PDMS with cyanopropyl-modified silicone. The blend had a permittivity of 3.5 and attained a 10% actuation strain at 40 V/µm which is a factor of 3.8 larger than the matrix material alone (2.6% actuation strain at the same voltage). However, the blend had a higher modulus of elasticity than the matrix. Generally, all the SR based DE composites discussed in the test allowed actuated area strains of 15%–35% to be achieved.

In order to eliminate the effect of pre-stretch on the electromechanical performance of SR based DEs, IPN was also introduced by using a soft SR as the matrix material and a rigid SR as an additive [102, 123, 124]. Brochu et al. [102] designed a novel all-silicone pre-strain-locked IPN DE. The elastomer was fabricated using a combination of two silicones: a soft room temperature vulcanising (RTV) silicone that served as the host elastomer matrix and a more rigid high temperature vulcanising (HTV) silicone that acted to preserve the pre-strain in the host network.

The process for preparing the IPN DE is shown in Fig. 2.5. The pre-stretch-locked IPN films were fabricated by mixing the RTV silicone with HTV silicone at various concentrations in an isoparafinic solvent (ExxonMobil Chemical Isopar G). The solution was drop cast on a poly(styrene sulfonate) (PSS) treated glass and left for two days to allow the excess solvent to evaporate and for the RTV silicone to cure. The resulting films were peeled from the glass substrate and pre-
strained equi-biaxially to a stretch ratio of 2 in each perpendicular plane. The films were then heated in an oven at 180°C for 20–30 min to cure the HTV silicone. After the heat treatment, the films were released from the support structure and allowed to fully relax. The amount of preserved pre-strain was calculated from the final dimensions after relaxation with respect to the sample size before pre-strain was applied. Thus, the quoted preserved pre-strain values represent the actual pre-strain of the RTV host elastomer.

Fig. 2.5 Process for preparing IPN films; (a) solution is drop cast onto treated glass, (b) solvent is allowed to evaporate and the RTV silicone cured at room temperature, (c) film is peeled off the glass substrate, (d) film is stretched biaxially by 100 × 100%, (e) HTV silicone is cured at 180°C for 30 min and (f) film is relaxed and some pre-strain is preserved [102].
The DE films obtained achieved a large elongation of above 400%. Furthermore, a peak actuated area stain of 45% was achieved by the IPN film containing 15 wt% HTV without pre-strain, which was 276% larger than that of the original matrix. Due to the low dielectric constant of SR, the resultant film was considered to possess a low electromechanical energy density.

2.5.3 Polyurethane (PU) Based DEs
PU has been regarded as another DE material with good electromechanical performance due to the large force output and high dielectric constant which, in film form, allowed the DE to be actuated at low electric fields. Putson et al. [95] reported on a PU based DEs filled with PANI. For this material, it was found that the dielectric constant increased when the concentration of PANI increased and a maximum dielectric constant of about 45 was obtained by adding 5 wt% PANI to the matrix. Moreover, the glass transition temperature ($T_g$) of the polymer composites also increased with increasing PANI fillers indicating a strong interaction between the matrices and the fillers. Chiou et al. [125] studied the dielectric properties of a DE which was fabricated by incorporating copper coated phospholipid microtubules into a PU-PDMS interpenetrating polymer network. The tubule concentration ranged from 8 to 16 vol%, whereas the PDMS concentration ranged from 0 to 75 wt%. For the DEs at a specific tubule concentration, the permittivity increased for higher PDMS concentrations. Chwang et al. [126] developed a polyurethane based DE blended with polyaniline-dodecyl benzenesulfonic acid (PANI-DBSA). The dielectric constant of the blend increased with the content of PANI and rose drastically as PANI-DBSA content exceeded 15 wt%. The DE composite with 17 wt% PANI gave a
dielectric constant of about 1120 at a frequency of 1 kHz. Huang et al. [127] obtained a PU based DE with high-dielectric copper phthalocyanine oligomer (PolyCuPc) and PANI. The three-component dielectric-percolative composite showed a high dielectric constant of 800 and achieved an electromechanical strain of 9.3% and elastic energy density of 0.4 J/cm$^3$ under an electric field of 20 V/µm. Liu et al. [128] investigated the dielectric properties of PU based DEs with polyvinylpyrrolidone (PVP) coated silver (Ag) particles. The PU with 40 wt% PVP coated Ag particles showed a maximum dielectric constant of 860 with a higher dielectric loss tangent of above 10 at 0.1 Hz. Tian et al. [129] reported the fabrication of a DE by mixing gelatin and glycerol (GG) with PU. The resulting DE exhibited good mechanical strength and 5.5% actuation strain at a very low electric field of 0.5 kV/mm. However, these PU based films were limited in their ability to generate large strains because of their high Young’s moduli [130, 131].

2.5.4 Other DE Materials

In order to overcome the drawbacks of conventional DEs, a series of novel DE materials with low elastic moduli, large elongation and high dielectric constant, have been designed and fabricated [48, 104, 132]. Shankar et al. [133] designed a new DE material that differed from conventional DEs. The material was derived from a polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene (SEBS) triblock copolymer swollen with a midblock-selective solvent—aliphatic mineral oil (MO). This kind of material exhibited a low dielectric constant of below 2.15, a large compressive modulus of above 1.8 MPa and large deformations of about 250% as a result of being biaxially pre-strained to 300%. However the requirement to apply low loads to the polymer whilst achieving large
deformations was limited by a high block stress which is required to return a fully energised actuator to the original size in plane direction [34] and electrical breakdown field [1].

Lin et al. [134] reported a PVDF based DE filled with a dopamine coated BT. It was found that the compatibility between the filler and the matrix was improved. Furthermore, the resultant nanocomposite showed a high dielectric constant of 56.8 with a low dielectric loss. Fang et al. [135] studied the dielectric properties of DE composites composed of graphene and PVDF. In research, a high dielectric constant of more than 340 at 100 Hz was obtained within the vicinity of the percolation threshold when the graphene volume fraction was 0.00177.

Yang et al. [136] reported a new polyester DE exhibiting a large actuated strain for a low electric field. The sample with the lowest crosslink density of 3.28×10^{-5} mol/cm^3 showed a high actuated strain of 11.9% at a low electric field strength of 15.6 kV/mm without any pre-stretch. Moreover, they studied the electromechanical properties of TiO_2/polyester composites. In this work it was found that the dielectric constant of the composites increased with increasing filler content. However, the actuated strain was not improved [51]. In another project, dopamine coated BT was incorporated into hydrogenated nitrile-butadiene rubber (HNBR). The HNBR based DE with a 50 phr filler loading presented a maximum dielectric constant of about 16 and a low dielectric loss tangent of below 0.007 at 1 kHz and achieved a maximum actuated strain of 20% at 45 kV/mm which was 54% larger than that of the elastomer without filler [72].

Goswami et al. [137] developed a novel soft elastomeric material — poly(propylene oxide) (PPO). It was found that the dielectric constant of PPO was 5.6 at 1 kHz and incorporation of silica particles improved the stability of the
mechanically weak pure PPO network. Among the PPO composites studied, a PPO with the addition of 5 phr treated fumed silica showed a maximum actuation strain of about 3% at a relatively low electric field of below 20 V/µm.

2.6 Mechanical Models

DEs are smart materials and belong to the electroactive polymer group. In order to study incompressible elastomers with linear [138] or nonlinear mechanical properties [41, 139], a linear elastic model, a power-law model and some hyperelastic models were reviewed and are described in this section.

2.6.1 Linear Elasticity

Linear elasticity is the mathematical description of the physical behaviour of a material considered to conform to Hooke’s law which assumes strain is directly proportional to stress, as long as the strain imparted to the elastic material is relatively small. For an elastomer assumed to be in the linear elastic range, the mechanical stress in compression is given by $\sigma = Y S_T$, where $Y$ is the Young’s modulus (modulus of elasticity) and $S_T = \ln (\lambda) = \ln \left(\frac{h}{H}\right)$ is the true compressive strain, where $\lambda$ is the compression ratio (refer to Fig. 2.6). Therefore, mechanical stress can be expressed as [140]:

$$\sigma = -Y \ln \lambda = Y \ln \left(\frac{H}{h}\right)$$

(2-17)
Fig. 2.6 Compression of a linear elastic elastomer; the thickness changes from \( H \) to \( h \).

2.6.2 A Power-law Model

Semicrystalline elastomers with high elasticity such as PVDF are widely used as dielectrics in cables, capacitors and actuators. When the polymer is subject to a uniaxial compressive stress \( \sigma \), the true strain in the thickness direction is \( S_T = \ln (\lambda) = \ln (h/H) \) and the compressive stress is related to the compressive ratio \( \lambda \) by [29]:

\[
\sigma = \kappa(-\ln \lambda)^N = \kappa(\ln \frac{H}{h})^N
\]  

(2-18)

2.6.3 Hyperelastic Models

Incompressible or nearly incompressible isotropic materials, such as rubber and muscle fibre etc., are capable of undergoing large reversible elastic deformations and are often characterised by a strain energy function per unit volume denoted by \( W \) [141, 142]. One type of function is obtained from symmetry, thermodynamics and energy considerations and depends upon the three simplest even powered strain invariants \( (I_1, I_2, I_3) \) for the material [143]. Hence:

\[
W = W(I_1, I_2, I_3)
\]  

(2-19)

The strain energy function of Eqn. (2-19) can be replaced by means of Lagrange multiplier [144] to give:

\[
W(I_1, I_2, I_3) = W(I_1, I_2) - \frac{P}{2}(I_3 - 1)
\]  

(2-20)
where

\[ I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \]  
\[ I_2 = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \]  
\[ I_3 = \lambda_1^2 \lambda_2^2 \lambda_3^2 = 1 \]

As the strain invariants depend on principal stretches \((\lambda_1, \lambda_2, \lambda_3)\), the expression for strain-energy may alternatively appear as a function of stretches:

\[ W(I_1, I_2) = W(\lambda_1, \lambda_2, \lambda_3) \]  

Generally, for an incompressible material under uniaxial elongation, \(\lambda_1 = \lambda\) and \(\lambda_2 = \lambda_3 = \lambda^{-0.5}\). This allows the three simplest even powered strain invariants to be expressed as:

\[ I_1 = \lambda^2 + \frac{2}{\lambda} \]  
\[ I_2 = 2\lambda + \frac{1}{\lambda^2} \]  
\[ I_3 = 1 \]

whereas for equi-biaxial tension, the principal stretches are \(\lambda_1 = \lambda_2 = \lambda\) and \(\lambda_3 = \lambda^{-2}\), so:

\[ I_1 = 2\lambda^2 + \frac{1}{\lambda^4} \]  
\[ I_2 = \lambda^4 + \frac{2}{\lambda^2} \]  
\[ I_3 = 1 \]

Meanwhile the true stress-strain relationship \(\sigma(\lambda)\) for elastomers can be derived from a strain energy density function [145] as shown in Eqn. (2-31).

\[ \sigma(\lambda) = \lambda \frac{\partial W(\lambda)}{\partial \lambda} \]
Numerous models have been proposed so far. Some of the most commonly used strain energy density functions in computational mechanics for describing deformation in incompressible and isotropic elastomers are mentioned here. They are classified in two categories of formulation, depending on the approach of developing the strain energy function. One kind of category which is termed phenomenological is derived from mathematical developments of strain energy functions and the category includes the Mooney-Rivlin [146, 147], Odgen [148-150], Yeoh [151], Gent [85] and modified Gent models. For these models, material parameters can be difficult to determine. Furthermore, they lead to error when they are used outside the test range and loading mode for which the material constants are determined. The other kinds of models belong to the mechanistic category of models. They are developed from physical motivations. Such models are based on both the physics of polymer chain networks and statistical methods [152, 153]. They lead to different strain energy functions that are dependent on taking microscopic phenomena into account. Most of their mathematical formulations are quite complicated.

Hyperelastic models are discussed here.

1) The Mooney Rivlin model is derived from the assumption that the rubber response is linear under simple shear loading conditions. The model is well known and exhibits high accuracy in predicting the nonlinear behaviour of isotropic rubber-like materials when deformation remains moderate (lower than 200%) (Eqn. (2-32)) [153].

\[ W = C_1 (I_1 - 3) + C_2 (I_2 - 3) \]  

(2-32)

where \( C_1 \) and \( C_2 \) are material dependent constants (MPa) derived from physical testing.
2) The neo-Hookean model is the simplest physically based constitutive equation for rubbers. It matches the Mooney-Rivlin model for the case that \( C_2 = 0 \). However, this model was based on a consideration of molecular chain statistics. This approach depends on the assumption that rubber materials are considered to be three-dimensional networks of long chain molecules connected at a few points [148]. The elasticity of the network is mainly due to entropic changes during deformation and the entropy of the material is defined by the number of possible conformations of macromolecular chains. The strain energy function was deduced using a Gaussian statistical distribution. This model, given by Eqn. (2-33), was revealed to be in good agreement with tensile, simple shear and biaxial tests for deformations lower than 50% [153].

\[
W = C_1 (I_1 - 3) \tag{2-33}
\]

3) The Arruda-Boyce model is derived from a chain model with a distribution of chains following eight directions corresponding to the vertices of a cube inscribed in a unit sphere. This model is governed by the stretch of the diagonal of the cube, \( \hat{\lambda} = \sqrt{I_1 / 3} \). It offers close agreement with experimental data for equi-biaxial extension.

\[
W = \mu \sum_{i=1}^{N} \frac{C_i}{\hat{\lambda}_L^{2i-2}} (I_1^i - 3^i) \tag{2-34}
\]

4) The Yeoh hyperelastic model [145] is another phenomenological model for the deformation of nearly incompressible nonlinear elastic materials such as rubber. The Yeoh model for incompressible rubber is a function of \( I_1 \) only [148] (Eqn. (2-35)). Due to the absence of the influence of \( I_2 \) which
is more pronounced at high strains, it has not been widely adopted in hyperelastic modelling [154].

\[ W = \sum_{i=1}^{3} C_i (I_1 - 3)^i \]  
(2-35)

5) Odgen proposed a stretch ratio based model. This means that strain energy density is a function of principal stretches rather than the invariants of the strain tensor. This was a sensible approach, since there was no physical justification for the first three even powered strain invariants to be originally chosen. The Ogden model proposed a strain energy function based on principal stretches \((\lambda_1, \lambda_2, \lambda_3)\) as shown in Eqn. (2-36). The principal stretches are directly measurable quantities and this is an obvious advantage of using them [155]. The number of coefficients \((c_1, c_2, c_3 \ldots)\) and \((b_1, b_2, b_3 \ldots)\) required to fit the stress-strain curve depend on the level of accuracy desired by the user. Generally it is observed that three sets of coefficients \((N = 3)\) are of sufficient accuracy to fit the data for most types of rubbers under uniaxial, pure shear and equi-biaxial loading [153].

\[ W = \sum_{i=1}^{3} \sum_{j=1}^{m} \left( \frac{c_i}{b_j} (\lambda_{ij}^{b_j} - 1) \right) \]  
(2-36)

6) The Gent hyperelastic material model belongs to the category of phenomenological models of rubber elasticity and is based on the concept of limited chain extensibility. The strain energy function is given as [156]

\[ W = -\frac{\mu J_m}{2} \ln \left( 1 - \frac{I_1 - \frac{3}{J_m}}{J_m} \right) \]  
(2-37)

This model (Eqn. (2-37)) represents the stiffening of the material at large strains with acceptable accuracy. It has the advantage of mathematical
simplicity and allows detailed analysis and explicit solutions of particular boundary-value problems.

7) The Pucci-Saccomandi model is a modification of the Gent model with the addition of a logarithmic term. This model gives the simplest rational approximation for reduced tensile force associated with uniaxial extension that satisfies the common basic assumptions of continuum mechanics [157] (refer to Eqn. (2-38)).

\[ W = -\frac{\mu J}{2} \ln \left(1 - \frac{I_1 - 3}{J_m}\right) + c_2 \ln \left(\frac{I_2}{3}\right) \]  

(2-38)

where \( \mu \) is the shear modulus, \( C_2 \) is a material constant and \( J_m \) is the constant limiting value for \( I_1 - 3 \), accounting for finite chain extensibility. \( I_1 \) and \( I_2 \) are the first and second even powered strain invariants respectively.

2.7 Electromechanical Instability

Under high deformations most DEs suffer from EMI, which is also termed pull-in instability [40, 41, 158]. In fact, electromechanical instability is a well-known phenomenon, occurring not only in DE materials but also in magnetostatic actuators and micro/nano-electromechanical systems (MEMS/NEMS) [159]. The EMI occurs when the film thickness falls below a certain threshold and the equivalent Maxwell pressure becomes greater than the compressive stress in the DE film [32]. This positive feedback leads to a drastic localised reduction in thickness and normally results in breakdown. Here, six physical states for a DE subjected to a high voltage are considered based on Suo’s theory [139] in respect of EMI. These states include consideration of two other common failure modes: electrical breakdown and fracture under tensile load.
According to the theory, the applied voltage \( \Phi \) is a function of stretch \( \lambda \) which can be obtained from Eqn. (2-39) [84].

\[
\sigma_{\text{pre}} + \sigma_v = \sigma(\lambda) \tag{2-39}
\]

where the membrane is subjected to a fixed force \( P \) and is mechanically pre-stretched to a ratio \( \lambda_{\text{pre}} \) corresponding to a stress \( \sigma_{\text{pre}} = P/h\lambda_{\text{pre}} \); \( \sigma(\lambda) \) is the true stress related to stretch. Combined with Eqn. (2-9), \( \Phi(\lambda) \) can be determined using the expression:

\[
\Phi(\lambda) = H\lambda^{-2}\sqrt{\left(\sigma(\lambda) - \sigma_{\text{pre}}\right)/\varepsilon'\varepsilon_0} \tag{2-40}
\]

Consequently, the voltage-stretch curve is not monotonic and the electric breakdown voltage \( \Phi_B \) equals \( \varphi_B H/\lambda^2 \) [44]. For an ideal DE, the dielectric constant and breakdown field \( \varphi_B \) is independent of the stretch \( \lambda \) [139].

![Diagram showing six failure points](image)

**Fig. 2.7 (a) and (b) six failure points, depending on where the two curves \( \Phi(\lambda) \) and \( \Phi_B(\lambda) \) are positioned [43, 44].**

Based on these considerations, six failure modes of DEs can occur and are depicted in Figs. 2.7 (a) and (b) in terms of EMI, electrical breakdown and tensile strength. As shown in Fig. 2.7 (a), the first mode (T1) indicates a DE achieving a small voltage-induced strain and being punctured at \( \lambda e_1 \) due to electrical breakdown voltage \( \Phi_{B1} \) prior to the onset of EMI. Other researchers [43, 44] have
described the portion of the voltage-stretch curve beyond T1, where a DE is capable of large voltage-induced deformation, as a region of snap-through instability [44]. They and others [160] recognised that an elastomer may survive pull-in instability without electrical breakdown and stabilise with a much reduced thickness. In this region, the voltage again increases and attains point T2 where the DE fails when the voltage reaches the electromechanical instability voltage $\Phi_{EMI}$. If failure does not occur at T2 the DE continues to exhibit more pronounced EMI and the film thins excessively, finally resulting in electrical breakdown at the point $(\lambda e_2, \Phi_{B2})$. Points T3 and T4 indicate where DEs survive EMI, but the failure at T3 is a result of electrical breakdown voltage $\Phi_{B3}$ at a stretch ratio of $\lambda e_3$. The failure at T4 is as a result of reaching the tensile strength limit of the material at $\lambda_{lim1}$ without experiencing electrical breakdown. Fig. 2.7 (b) depicts two modes of DE failure when EMI is eliminated. At point T5 the DE fails due to electrical breakdown voltage $\Phi_{B5}$ at a stretch ratio of $\lambda e_5$. At point T6 the DE fails at the limit of tensile strength $(\lambda_{lim2})$.

### 2.8 DE Applications

DEs are functional materials that have particularly promising potential as muscle-like actuators due to their inherent compliancy and good overall performance. The combination of large deformations, high energy densities, high efficiencies and prompt response times is unique to dielectric elastomer actuators [161]. Furthermore, DEs are easily shaped into many different kinds of configurations such as diamonds [8, 162], cones [17], springs [163-166], rolls [167-169] and folded shapes [170, 171].
Fig. 2.8 The action of a “pick-and-place” actuator made from an elastomer beam with a few vertical fibres is illustrated. Though not obviously apparent in the figures, at (a) the elastomer bends to conform to the shape of both the cylinder and grape; at (b) another example of “pick-and-place” using horizontal wrap action is shown; at (c) a dual action actuator is depicted consisting of a bilayer of two dielectric actuators bonded together with fibres oriented in one direction in one layer and fibres oriented at 90 degrees in the other. When the side with horizontally aligned fibres is actuated, the bending curvature is vertical (second picture) whereas in the third picture, when the side with vertically aligned fibres is actuated, the bending curvature is horizontal [16].

Fig. 2.8 shows a number of ‘gripper’ actions made possible by incorporating a few stiff fibers into voltage-actuated dielectric elastomer beams [16]. In the first example, a wrap-around gripper using vertically aligned fibres is shown to pick and place a cylindrical metallic object and a grape (Fig. 2.8 (a)). In the second
example, a dielectric elastomer gripper having horizontally aligned fibres is shown to grip and lift a wooden beam structure (Fig. 2.8 (b)). The emphasis in this work on using a small number of fibres is of significance, since incorporating too high a concentration increases the stiffness and detracts from the soft mechanical response desirable in soft robotic devices. Previous approaches use pre-stretched dielectric elastomers which require relatively bulky and stiff frames to maintain structural integrity, causing increases in weight and more importantly reducing the overall flexibility or soft nature of the systems.

Harvesting kinetic energy from sources such as wind, waves and human activity is a challenge. DEs, known collectively as electroactive polymer artificial muscle (EPAM) in the literature, have been shown to offer unique capabilities as actuators and are now being developed for a wide variety of generator applications [172]. They have a high energy density and conversion efficiency allowing for very simple generators. In this type of application, the generator mode is the reverse of the actuator mode. When mechanical energy is applied to the DE, it causes deformation (compression in thickness and expansion of the surface area). Thereafter a voltage is imposed on the DE and the applied electrical energy is stored in the polymer as an electric charge. When the mechanical energy decreases, the elastic recovery force of the DE restores the original thickness and decreases the in-plane area. At this instant, the electric charge is pushed out in the plane of the electrode. The resulting change in the location of the electric charge increases the voltage difference, resulting in an increase of the electrostatic energy [173]. DE transducers have been embedded in heels, small electric power generators for lighting LEDs, water mills and buoys [7, 174].
Fig. 2.9. A DE ocean wave power generator based on an articulated, multi-body system buoy at a sea trial site (top) and concatenated rolls in a generator module (bottom). When a wave passes, the outriggers move relative to the buoy and stretch the rolls using a lever arm. The black material between the rings with green edges (visible in the right-hand photograph) is an electrode-coated dielectric elastomer [173].

An energy harvesting applications designed by SRI International was the ocean wave power generator which effectively converted hydrodynamic energy into electrical power through simple and low-cost solutions. The power generation unit as used in the experiments was a cylindrical tube with a diameter of 40 cm and a height of 1.2 m. Two roll-type DE modules with diameters of 30 cm and heights of 20 cm were inside the tube in the stretched state. About 150 g of DE film including electrodes was used in each roll. The maximum electrical output energy tested in a laboratory was 12 J for one cycle of operation. However, wave height was only of the order of few centimeters, which made it very difficult to carry out tests for wave-powered generators. On occasions, the weather generated waves that were 10 cm high. Despite the low wave activity and non-ideal motion of the
buoy, the generator was shown to function. Even with a small wave height of 10 cm, the researchers were able to generate a peak power of 1.2 W with an average power of 0.25 W (see Fig. 2.9) [173].

Tactile sensation is the most widely spread sensory function in the human body so that it is an essential part of human perception. Using a DE for the construction of a tactile interface can provide stimulation of human skin without any additional electromechanical transmission [175]. Softness and flexibility of the device structure, ease of fabrication, the possibility of miniaturisation, and cost effectiveness are the representative benefits of the devices presented [20]. Currently, several DE based tactile interfaces have been designed and implemented. These include a Braille display [176], a wearable tactile display [20, 177] and a virtual keyboards with a wearable tactile display [175]. Fig. 2.10 shows a successful Braille display developed by Choi et al [176]. A thin cylindrical polymer membrane like a coin is coated with conductive electrodes. The nominal thickness of the elastomer membrane is about 50 mm. In order to obtain a large actuation force of sufficient strength to be used for the tactile display, several DE actuators are stacked and combined with a rigid circumferential loop frame. The total thickness of the stack is about 750 mm. Each unit can be plugged onto a circuit board with ease. Due to this feature, a number of Braille cells can easily be combined so that a Braille tablet may be manufactured by arranging multiple Braille cells in a matrix format as shown in Fig. 2.10.
Each cell is mounted with a Braille dot and is lowered by applying a voltage across the thickness of the selected cell, causing local thickness reduction. Under the control of a computer, dots are activated to create tactile patterns of highs and lows representing the information to be read. A person reads by scanning with the fingertips, as in reading conventional Braille print.

### 2.9 Summary

A large amount of literature was reviewed in this chapter. At the beginning, the basic concepts of DEs were described and terms such as dielectric constant, dielectric loss factor, Maxwell stress, actuated strain, electromechanical energy
density and coupling efficiency were defined. Then, numerous compliant electrodes were presented. Their advantages and disadvantages for use in various applications were also evaluated. Subsequently, the influence of pre-stretch on a DE’s electromechanical properties, (i.e. the dielectric strength, actuated strain, electromechanical energy density and coupling efficiency), was emphasised. Thereafter, a number of DE materials that have been reported on in the past few decades were reviewed. In order to investigate the mechanical behaviour of DEs, a number of mechanical models were presented and critiqued. Thereafter, the phenomenon of EMI which occurs in DEs was described and associated with mechanical models. Finally, some interesting DE applications, such as grippers, energy renewable devices and tactile display devices, were demonstrated. The applications discussed here all require quick response speeds, high energy densities and high electromechanical efficiencies. The research to fabricate SR based DEs having the capability of providing large voltage-induced deformation is described in this thesis. It is suggested that the novel DEs devised can meet these requirements and consequently improve the performance and functionality of each application.
Chapter 3  Materials and Experimental Methods

3.1  Introduction
The materials and experimental methods required to fulfil the aims of the research, are described here. This chapter provides information on a soft silicone rubber (SR) used for the dielectric elastomer (DE) matrices and the high dielectric barium titanate (BT) used as a filler to lower the applied electric field strength. An approach to improve the compatibility between SR and BT is also provided. With the purpose of characterising the fabricated DE materials, a range of equipment was employed in order to observe the morphology of modified BT particles, the microstructure of the DEs, their dielectric spectra and mechanical and electromechanical behaviour.

3.2  Materials
As discussed in Chapter 2, many of the most exciting DE materials were discovered as a result of exploratory testing. New formulations of commercially available elastomers are continually being developed and may well be worth exploring. However, it is expected that research focusing on developing materials specifically for DE applications from highly focused and directed research will provide the best candidates for improved performance in the years to come. Currently, three groups of DE materials (SR, polyurethane and polyacrylate) attract the significant interest of the scientific community because of their promising actuation characteristics. However, the main drawbacks of a high
viscoelasticity for polyacrylate and a high modulus for polyurethane raise
significant concern about their wider application.
SR is capable of superior performance when compared with the other elastomers
in terms of greater electrical stability, flexibility and lower viscoelasticity [90].
This is because the Si-O bonds in the main molecular chains have higher bond
energy than the C-C bonds [178] of the polyacrylate and polyurethane materials.
Also Si-O-Si units have larger bond angles and more compliant molecular
configurations, providing lower internal dissipation [179]. As a result, SRs can
retain their elasticity even at -60°C. Although, they have low dielectric constants
(≈ 2.9), modifications to the material can be made in order to increase the value of
this parameter, such as adding fillers [110], tuning the polymer structure [180] and
grafting on side groups with the required properties [181]. Among all the possible
approaches, the addition of high dielectric constant fillers into the SR matrix is the
most common practice to achieve this end.
In this research, a commercial polymer, polydimethyl methylhydrogen siloxane
(LSR4305 DEV, Bluestar Ltd., U.S.A), consisting of two parts (part A and part B)
was used for fabricating the silicone DE samples. The part A component contains
vinyl functional polymers and a platinum catalyst. The part B component contains
a hydride crosslinker and inhibitor. The two parts were required to be mixed at a
ratio of 1:1 in order to be cured completely. Curing can be achieved in 15 s at
175°C. The curing time can be decreased by increasing the temperature. This kind
of SR has the advantage of excellent biocompatibility, high elongation (about
1100%), low elastic modulus (0.1 MPa) and low viscoelasticity combined with
good dielectric and insulation characteristics. The detailed physical and
mechanical properties of the two components are shown in Appendix A.
Ferroelectric oxides which exhibit a spontaneous electric polarisation can be reoriented in an external electric field. In particular, these oxides possess large dielectric constants. BT, is an example of these oxides. It exists as a white powder and has a perovskite structure [182, 183]. Due to its high dielectric constant and low cost, BT was widely used as a filler integrated into DE matrices to improve their actuation performance. The BT used in this work was purchased from Sigma-Aldrich Co. LLC. The surface morphology of the selected particles is shown in Fig. 3.1. The average particle size of the BT was approximately 1µm and the particle density was 6.08 g/ml at 25°C. The dielectric constant for BT reported in the literature was approximately 1200 [184].

![SEM image of the BT particles.](image)

Polydopamine (PDA) which is found in mussels and is responsible for their adhesion capability in seawater was highlighted as a novel coating material in 2007 [185] as it can be easily deposited on virtually all types of inorganic and organic substrates, including superhydrophobic surfaces, with controllable film thickness and high durability. PDA incorporates many functional groups such as
catechol and amine which can serve as both the starting point for covalent modification with desired molecules and anchors for the loading of transition metal ions [186]. Thus PDA has been used as a coating material deposited on the BT surfaces. It has been proven that PDA improves the compatibility between BT and the elastomer matrix, leading to homogeneous dispersion of the fillers in the matrix [187]. Its monomer, dopamine, can be oxidised and spontaneously self-polymerised under alkaline conditions (at pH > 7.5) [186]. Dopamine hydrochloride, purchased from Sigma-Aldrich Co. LLC, was used to fabricate the PDA in this work.

Carbon grease has been the most widely used compliant electrode material in the DE research environment. It is relatively easy to handle and capable of sustaining large strains while remaining conductive [75]. In the research described here, NYOGEL 756G (Nye Lubricants, Inc., USA) was the conductive carbon grease used as the compliant electrode. In preparing the DE, a shadow mask was placed on the DE film to selectively expose the surface. Then, the carbon grease was coated on the exposed surface.

The acrylate film, VHB 4910, is the most commonly used DE having the capability of large voltage-induced deformation of above 100%. It is normally supplied as a clear adhesive tape and was obtained with a thickness of 1 mm from the 3M Company in the UK. This material was used as a reference DE material throughout in this research. The working temperature of VHB 4910 ranges from -35°C to 90°C. Furthermore, it was reported that the film possessed a dielectric constant of approximately 4.5 and was capable of elongations of above 800% [150]. The other mechanical and chemical properties of VHB 4910 are described in Appendix B.
3.3 Sample Preparation

3.3.1 DP-BT Fabrication

The fabricating process of dopamine coated BT (DP-BT) is presented in Fig. 3.2. Initially 10 g of BT was dispersed in 50 ml of ethanol-water mixture having a mass ratio of 1:1 and stirred for 30 min in order to graft -OH functional groups onto the particle surfaces. The solution was then added to 450 ml of deionised water together with 1 g of dopamine hydrochloride. Thereafter, the suspension was stirred at 60°C overnight before being subjected to ultrasonic shaking for 30 min. The DP-BT particles were subsequently removed and washed using deionised water and finally dried at 60°C in a vacuum oven to avoid oxidisation of the PDA.

![Diagram of Sample Preparation](image)

**Fig. 3.2 Schematic of the fabrication of SR and dopamine coated BT composites.**
3.3.2 DE Sample Preparation

Two methods were used to prepare the DE films for bubble inflation and electromechanical testing. For bubble inflation and deflation, a two-part polymer was first mixed at a ratio of 1:1 before BT with the required filler content was added to the silicone matrix. The DE composites containing BT were mechanically stirred to give consistent high levels of compatibility and dispersibility. The mixtures were then degassed in a vacuum to remove entrapped air bubbles and then poured into moulds. The samples were degassed for 1.5 h and solidified in an oven at a temperature of 80°C for approximately 12 h. This allowed DE samples of 0.3 mm and 2 mm thickness to be fabricated using two different moulds. For electromechanical tests, the two parts of the SR polymer were mixed at a weight ratio of 1:1 and dissolved in heptane. Then, BT or DP-BT particles were added to the solution to provide samples containing the required percentage particle weights of 10%, 20% and 40%. In order to achieve uniform dispersion of the SR and fillers in heptane, the solution was subjected to ultrasonic shaking for 20 min. Finally, the mixture was poured into a watch glass and heated for 8 h at 80°C in a water bath in an airing chamber.

3.4 Sample Characterisation

3.4.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) can not only be used for identifying unknown materials, but also for determining the quality or consistency of a sample and the amount of each constituent in a mixture. Generally, in infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared
radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint, no two molecular structures produce the same infrared spectrum. The measurement made by FT-IR was extremely accurate and reproducible.

All spectra were obtained using an FTIR spectrometer (PerkinElmer Spotlight 400) equipped with a germanium crystal (refractive index of 4.0) controlled by Spotlight 400 software. An attenuated total reflectance (ATR)-accessory was used to collect all spectra with 32 scans at a resolution of 4 cm\(^{-1}\) in the range of 4000-650 cm\(^{-1}\). Prior to each spectral acquisition, the background was recorded. The ATR crystal was cleaned thoroughly with acetone to remove any residue before testing every sample.

### 3.4.2 Scanning Electron Microscopy

The microstructures of all materials in this work were observed using Scanning Electron Microscopy (SEM) (Zeiss Supra). DE films were cut at room temperature to create new surfaces using a blade. The samples were then coated with a fine layer of gold to make them conductive prior to observation. All images were taken with an accelerating voltage of 5 kV using a Secondary Electron (SE) image detector. The elemental analysis of these particles was carried out on an Energy Dispersive X-Ray Spectrometer (EDS) (Oxford Inca Xmax) which was coupled to the SEM.
3.4.3 Dielectric Spectroscopy

The interaction between the material and a dynamic electric field was measured over a broad frequency and temperature range. The two interaction mechanisms observed are polarisation, associated with the orientation of permanent dipoles and conduction, related to dissipative effects. By using dielectric spectroscopy, molecular movement of segments or molecules within the material were detected under an external electric field.

Dielectric measurements of SR/BT and SR/DP-BT films were conducted on a broadband dielectric spectrometer, Novocontrol BDS 40, as shown in Fig. 3.3 at 20 °C in the frequency range of 0.1 Hz to 10 MHz. The film of approximately 0.3 mm thickness was placed on a cell which comprised a disposable gold-plated flat electrode with a diameter of 20 mm and thickness of 2 mm.

Fig. 3.3 Experimental setup of the broadband dielectric spectrometer.
3.4.4 Bubble Inflation Test

![Diagram of bubble inflation test system]

**Fig. 3.4** The bubble inflation test system and a sample under test.

The bubble inflation test system [188] shown in Fig. 3.4 induces dynamic equibiaxial mechanical stresses in elastomer samples by hydraulically inflating and deflating them using inert silicone oil as the inflation medium. Disc samples of 2 mm thickness and 50 mm nominal diameter were prepared for physical testing. The samples were held in the bubble inflation system’s inflation orifice. In initial static tests, pressure was applied to the samples causing them to inflate (inflation rate = 41%). During inflation (or deflation) the system’s vision system uses two complementary metal-oxide semiconductor (CMOS) cameras to record the movement of the centres of specific points aligned at the pole on the surface of
each sample. Stress values were simultaneously derived from the applied pressure
and bubble geometry, with strain (or stretch ratio) values calculated from the
change in circumferential distance between the centres of the points on the bubble
surface using three dimensional position coordinates obtained from the vision
system output. Hence, the relation between stress and strain (or stretch ratio) is
obtained in real time.

3.4.5 Electromechanical Test
The voltage-induced deformations of all the composites were measured in the
electromechanical test system, which consisted of a camera, a biaxial clamp to
apply pre-stretching and a high voltage power supply (Fig. 3.5). Prior to use, the
square test samples were bonded in the clamping system and their sides were
equibiaxially stretched in plane to a ratio \( \lambda_{\text{pre}} \). The samples were then held at this
pre-stretch in the clamps. The equibiaxially pre-stretched DE films were patterned
with the compliant electrode. The electrode used in the experiment was carbon
grease. A shadow mask was placed on the elastomer membrane to selectively
expose the surface that needed to be coated with the electrode [75]. In order to get
an improved uniformity, the electrode was printed on the DE film using a rubber
roller. Subsequently, DC voltages were applied with a ramped load increase of 0.5
kV per 10 s following a 10 s interval. A camera recorded area changes of the
samples for each increment. Thereafter, the initial area \( A_0 \) and the actuated area
\( A \) were accurately measured using AutoCAD software. The area strain \( s_a \) was
calculated from the following expression.

\[
 s_a = \frac{(A - A_0)}{A_0} \tag{3-1}
\]
For the application of Eqn. (3-1) it is assumed that the two equal mutually perpendicular principal strains are orthogonal to the transverse (thickness) strain, \( s_z \) and are considered to be constant along their respective principal axes.

![Image](image.png)

**Fig. 3.5** The electromechanical test system in this research: (a) the working schematic of the test system; (b) the pre-stretch frame used for equi-biaxially pre-stretching DE films; (c) the image of the system.

### 3.5 Summary

The materials used in this research were initially summarised including the SR, BT and the acrylate VHB 4910 film. The SR is soft and has an elongation of above 1000% at breaking point. The dielectric constant of BT is very high (>
1200 at 1 kHz). It was used in conjunction with SR to fabricate DEs in the experiments. The processes for modifying the BT particles, employing dopamine which was used to increase the compatibility between the filler and the matrix, were also respectively presented. To characterise the properties of the modified particles and DE films with respect to mechanical properties, dielectric properties and electromechanical properties, required tests such as using FTIR, SEM, dielectric spectroscopy, bubble inflation and the in-house electromechanical test system. This chapter concluded with a description of all the equipment used.
Chapter 4  The Influence of Equi-biaxial Pre-stretch on the Electromechanical Properties of DEs

4.1 Introduction

Pre-stretch is of importance for the electromechanical performance of dielectric elastomers (DEs). In particular, different kinds of pre-loading conditions induce quite different electromechanical properties in DEs. As described previously, pre-stretching DEs gives the possibility of improving their voltage-induced deformation, dielectric strength and energy density, electromechanical coupling efficiency and eliminating electromechanical instability (EMI). In this chapter, preliminary research into the influence of equi-biaxial pre-stretch on the electromechanical properties of DEs is described using a silicone rubber (SR)/30 wt% BT composite and VHB 4910 membranes. This insight gained into the influence of equi-biaxial pre-stretch allowed the next phase in the experimentation to be designed.

4.2 Dielectric Tests

Generally, the dielectric constant increases with the enhancement of polarisability of molecules in materials. Polar groups are reoriented under an electric field to promote the elongation of molecular chains to which they are attached. Therefore, in a DE the voltage-induced deformation results from not only the external Maxwell stress, but also the internal polarisation. Fig. 4.1 shows a plot of the
dielectric constant as a function of frequency for SR, SR with 30wt% BT and VHB 4910.

![Graph showing dielectric constant as a function of frequency for pure SR, SR with 30 wt% BT and VHB 4910.]

**Fig. 4.1** Dielectric constant of pure SR, SR with 30 wt% BT and VHB 4910 dependent on frequency.

As can be seen from the figure, the dielectric constant of VHB 4910 fell dramatically from approximately 4.9 to 3.7 at a frequency of 1 MHz indicating that the polarisation group had an obviously hysteretic response to the applied electric field. The dielectric constant of the pure SR was measured at around 2.9 and remained largely unchanged over the range of test frequencies and was lower than that of VHB 4910. This was probably due to the larger polarisability of the ester group in VHB 4910 by contrast with that of the non-polar structure of the molecules of SR. When the high dielectric BT particles of 30 wt% were added in the silicone matrix, $\varepsilon'$ increased to 5 and also was observed to maintain this value over a wide frequency range from 100 Hz to 10 MHz. The appearance of dielectric enhancement with the addition of the filler is related to the Maxwell
Wagner effect in the thin SR based DE film [189]. This indicated that SR based DEs were more stable than VHB 4910 in terms of dielectric properties when subject to changes in frequency.

4.3 Electromechanical Tests

In these experiments, 3 cm × 3 cm square samples of SR with 30 wt% BT were equi-biaxially stretched from their initial size in steps of 1 cm to a final size of 6.5 cm × 6.5 cm which was achieved just prior to tearing. The 2.5 cm square VHB 4910 samples were equi-biaxially stretched, also in steps of 1 cm, from their original size to a final size of 9.5 cm × 9.5 cm before experiencing tear.

4.3.1 The Behaviour of Fabricated Silicone DEs with 30 wt% BT

![Graph showing strain in area versus electric field applied to SR containing 30 wt% BT.]

Fig. 4.2 Strain in area versus electric field applied to SR containing 30 wt% BT.
Fig. 4.2 shows samples of fabricated DEs with increased deformation depending not only on the applied electric field but also on the equi-biaxial pre-stretch ratio (\(\lambda_{pre}\)). In the absence of a mechanical pre-stretch, the maximum strains of no more than 3% were obtained below the breakdown voltage; while equi-biaxially pre-stretching the samples to a ratio of 1.6 achieved an increase in area of approximately 32% for the SR/30 wt% BT composite. As can be observed from the plots, the voltage-induced area strain for each sample used in the experiment increased with the increase in electric field strength. However, the electric stimulus was negligible due to the small electric field strength below 10 V/\(\mu\)m.

Fig. 4.3 Actuated area strain of SR with 30 wt% BT at break related to equi-biaxial pre-stretch ratio.

Fig. 4.3 shows changes in area strain achieved by varying the equi-biaxial pre-stretch ratio. For the fabricated DEs, the actuated area strain increased steadily for equi-biaxial pre-stretch ratios up to \(\lambda_{pre} = 1.6\). After this threshold value, the area strain went down to 10% at a equi-biaxial pre-stretch ratio of 2.2. Thereafter, the
samples fractured at higher equi-biaxial pre-stretch ratios. Equi-biaxially pre-stretching can induce the molecular chains to rearrange to have approximate linearity and thus promote larger strains, but there is a material-dependent limit on the equi-biaxial pre-stretch that induces maximum strain.

![Dielectric strength of SR with 30 wt% BT at break, related to equi-biaxial pre-stretch ratio.](image)

**Fig. 4.4** Dielectric strength of SR with 30 wt% BT at break, related to equi-biaxial pre-stretch ratio.

Pre-stretch also has a beneficial effect on the enhancement of dielectric strength [140, 190]. Dielectric strength increased with increasing pre-stretch ratio, mainly due to a decrease in thickness. As can be seen from Fig. 4.4, the dielectric strength changed little under an equi-biaxial pre-stretch ratio of 1.4, whereas the dielectric strength increased linearly up to 90 V/µm beyond this ratio. As is well-known, polymer molecular chains are rearranged by the application of mechanical stress. Moreover, the mechanical stretch can generate free volume by driving the segmental motions of chains, which is propitious to increase the dielectric strength [191]. Furthermore, as a result of the thickness of the material being reduced when strained, the heat in DEs produced by the applied electric field can more readily
dissipate through the electrodes, which can also further enhance dielectric strength [192].

**Fig. 4.5 Maximum pressure of SR with 30 wt% BT related to equi-biaxial pre-stretch ratio.**

The maximum pressure caused by the electrostatic force was calculated according to the dielectric strength and the relative permittivity of the composites. The maximum stress increased to nearly 0.4 MPa for a equi-biaxial pre-stretch ratio of 2.2, which was 10 times larger than the stress produced without equi-biaxial pre-stretch (refer to Fig. 4.5). Notably, equi-biaxial pre-stretch can greatly influence the pressure produced in DE materials.
As observed from this figure, the maximum energy density achieved was 0.05 MJ/m$^3$ among all the DE films with varied equi-biaxial pre-stretch ratios. The energy density increased with increasing equi-biaxial pre-stretch ratio when the equi-biaxial pre-stretch was below 2. However, it appeared to decline for pre-stretching beyond ratios of about 2. This is probably because the actuated strain achieved by the sample was relatively low, though the membrane was considerably stiffened by applying a equi-biaxial pre-stretch ratio above 2.
The electromechanical coupling efficiency exhibited a parabolic distribution for equi-biaxially pre-stretched samples. As can be observed in Fig. 4.7, the peak of the curve (0.42) corresponded to a ratio between 1.6 and 1.9. The efficiency was directly dependent on the thickness strain induced by the electric field in accordance with Eqn. (2-16) in section 2.2.4. $K^2$ increased monotonically up to about 0.42 which corresponded to a deformation of 32% as can be seen from Fig. 4.3. It is expected that the maximum energy density would be experienced at a ratio between 1.6 and 1.9.

4.3.2 The Influence of Equi-biaxial Pre-stretch on Electromechanical Properties of VHB 4910

Fig. 4.8 shows that the actuated area strain of the acrylate VHB 4910 is dependent on the applied electric field strength. It can be observed from this figure that the films obtained a maximum actuated area strain at breakdown of approximately 75%
for an equi-biaxial pre-stretch ratio between $\lambda_{\text{pre}} = 2.6$ and $\lambda_{\text{pre}} = 3.0$. However, the change in shape of the samples was minimal in the absence of equi-biaxial pre-stretch. At other values for equi-biaxially pre-stretched samples, slight changes occurred when applying electric fields under approximately 8 V/µm, while a steep increase occurred when the electric field was raised above this threshold value. However, as the transverse strain reached 37%, corresponding to an area strain of 59%, the films became wrinkled, indicating the onset of EMI in the samples. As can be observed from Fig. 4.8, for the samples with equi-biaxial pre-stretch ratios of 2.2, 2.8, 3.0 and 3.4, a plateau caused by the EMI was reached before the samples punctured, while below the threshold, wrinkles were not evident. EMI could be eliminated under these equi-biaxial pre-stretch ratios for DEs if it was not essential to constrain DE test samples at their perimeters [83, 193]. However, it should be considered that the maximum deformation of the samples was constrained by the frame employed in the test and this contributed to the wrinkles (instability) observed in these experiments.

![Fig. 4.8 Actuated area strain versus electric field strength for VHB 4910.](image-url)
Fig. 4.9 The actuated area strain of VHB 4910 at break related to equi-biaxial pre-stretch ratio.

Pre-stretch plays an important part in electro-active deformation when applying high electric fields to DEs. Using this mechanical approach, the maximum actuated area strains at break were monotonically increased from almost 0% without equi-biaxially pre-stretching to 75% at equi-biaxial stretch ratios of about 3. The area strain diminished to 34% at an equi-biaxial pre-stretch ratio of 3.8 (refer to Fig. 4.9). This is probably because the strain stiffening effect prevented larger actuated area strains occurring at higher equi-biaxial pre-stretch ratios. Furthermore, equi-biaxial pre-stretch increased the tendency for the material to be inhomogeneous making mechanical failure more likely. Due to this, the film is susceptible to breakdown at higher equi-biaxial pre-stretch ratios. This is a significant factor contributing to the decrease of actuated area strains when applying large equi-biaxial pre-stretch ratios.
Fig. 4.10 Dielectric strength of VHB 4910 versus equi-biaxial pre-stretch ratio.

Fig. 4.10 shows that dielectric strength can be enhanced by the equi-biaxial stretching of DE samples. The dielectric strength was above 70 V/µm for VHB 4910 at the largest pre-stretch ratio of 3.8. This was possibly because, firstly the equi-biaxial pre-stretch reduced the thickness of the DE samples and secondly, equi-biaxial pre-stretch promoted molecular alignment. However, the equi-biaxially stretched samples suffered from relaxation in the elastomer and mechanical failure during the test process. This may have resulted in slight variations in electromechanical properties for all samples at different constant equi-biaxial pre-stretch ratios.
Fig. 4.11 Maximum pressure of VHB 4910 versus equi-biaxial pre-stretch ratio.

An electrostatic pressure is created from the high electric field that is generated between the top and bottom surfaces of a DE material. Fig. 4.11 shows the relation between the electrostatic pressure and equi-biaxial pre-stretch ratio. Stress increased with larger equi-biaxial pre-stretch ratio and reached a maximum value above 0.16 MPa at an equi-biaxial pre-stretch ratio of 3.8. However, stress increased only slightly, by approximately 0.02 MPa up to a ratio of 2.2, before increasing markedly to a maximum after this value.
Fig. 4.12 Energy density of VHB 4910 related to equi-biaxial pre-stretch ratio.

The energy density also increased dramatically from zero to a maximum value of above 0.05 MJ/m$^3$ (refer to Fig. 4.12) in the test. Energy density mainly depends on the electrostatic force and the strain in the thickness direction. Below an equi-biaxial pre-stretch ratio of around 3.4, the electrostatic force contributed more to the energy density output than to the change in strain. Thereafter, the strain decreased as a result of the energy density decreasing.

The curve relating electromechanical coupling efficiency to equi-biaxial pre-stretch ratio was observed to be parabolic in form (see Fig. 4.13). As can be seen from the figure, a maximum value of about 70% was achieved at a peak equi-biaxial pre-stretch ratio between 2.6 and 3. Also, the efficiency increased with increases in actuated area strain at fracture in the range of 0 to 75%. Hence, the form of the trend-line for the efficiency related to the equi-biaxial pre-stretch ratio is similar to that for the thickness strain related to the equi-biaxial pre-stretch ratio.
Fig. 4.13 Electromechanical coupling efficiency of VHB 4910 related to equi-biaxial pre-stretch ratio.

4.4 Summary

The dielectric constant of VHB 4910 was approximately 4.7 at low frequencies but was seen to decrease to 3.7 in the frequency range from 100 Hz to 1 MHz. The dielectric constant of pure SR was about 2.9, but this increased to 5.0 with the addition of 30 wt% BT. Values for dielectric constant did not vary in the wide frequency range. It was also found that the voltage-induced strains of all DE films were clearly increased by application of equi-biaxial pre-stretch compared with the films for which equi-biaxial pre-stretch was absent. In addition, the largest area strain of above 75% for the acrylate membrane was achieved at an equi-biaxial pre-stretch ratio of approximately 2.0; while the SR/30 wt% BT achieved a maximum area strain of 32% with an equi-biaxial pre-stretch ratio of around 1.6. Moreover, other properties of these DEs, such as dielectric strength, Maxwell
stress, energy density and electromechanical coupling efficiency, were also significantly increased with an increase in equi-biaxial pre-stretch ratio.
Chapter 5  The Influence of Filler Content on the Electromechanical Properties of DEs

5.1 Introduction
Composites of silicone rubber (SR) and barium titanate (BT) are commonly used dielectric elastomer (DE) materials due to an ability to provide large voltage-induced deformations as a result of their high dielectric constants, high elongations at break and low elastic moduli. Filler content can significantly affect the properties of a DE composite due to the change in elastic modulus and dielectric constant. In this chapter, the morphology of SR/BT composites is described. This morphology was observed by employing scanning electron microscopy (SEM). Thereafter, the influence of filler content on the mechanical properties of SR based DEs was studied using a bubble inflation test system. Simultaneously, a critical equi-biaxial pre-stretch ratio was determined from stress-stretch curves where the secant elastic modulus of the material was seen to be at a minimum. Moreover, the influence of filler content on both the electrical and electromechanical properties was investigated using dielectric spectroscopy and an electromechanical test system described in this chapter.

5.2 Microstructure of DEs
Morphology and particle distribution in the SR composites were studied using SEM. Figs. 5.1 (a)–(f) display the micrographs for variations in BT content
ranging from 0 wt% to 50 wt%. It is evident that the particles were uniformly dispersed in the SR matrices. In addition, agglomerations of BT particles of different size were found to be dependent on particle content. These micrographs reveal that at higher filler loadings, the BT particle tended to produce larger agglomerations and therefore large voids were capable of occurring at interfaces between the filler particles and the SR matrix.

Fig. 5.1 Micrographs of SR composites with different filler loadings: (a) 0 wt%; (b) 10 wt%; (c) 20 wt%; (d) 30 wt%; (e) 40 wt%; (f) 50 wt%.
5.3 Stress-Stretch and Secant Modulus-Stretch Behaviour

Fig. 5.2 shows the relation between equi-biaxial true stress and stretch ratio for the silicone rubber composites with varied BT contents by weight. As can be observed, the true stress was less than 8 MPa for all samples when subjected to equi-biaxial stretch, up to a stretch ratio of 5. The stress increased approximately linearly with increases in stretch ratio for equi-biaxial stretch ratios from 1 to about 1.2. The slope of the initial linear portion of the stress-stretch curve was less for higher filler concentrations indicating that stiffness reduced as filler loading increased. All samples used in this test exhibited large deformation.

![Graph showing true stress related to stretch ratio for silicone rubber with various BT contents.](image)

**Fig. 5.2 True stress related to stretch ratio for silicone rubber with various BT contents.**

The curves of secant modulus related to stretch ratio for these composites are depicted in Fig. 5.3. As can be observed from Fig. 5.2, the linear elastic portion of all the stress-stretch curves occurred below a stretch ratio of 1.2 where the slope of each curve indicates the composite’s initial modulus of elasticity [194].
Therefore, it can be observed that the stiffness of these composites (apart from the sample with 10 wt% BT) was lower than that of the pure silicone. The increased stiffness of the DE sample with 10 wt% BT is probably due to enhanced intermolecular forces occurring for particle contents around this specific particle content. Furthermore, as shown in Fig. 5.3, these curves, which are influenced by the intermolecular forces between particles and matrices, approximately exhibit a single critical point of inflection indicating that the stiffness of these materials can be reduced by stretching them to small material specific ratios. It was observed that the minimum elastic moduli were obtained at stretch ratios of approximately 1.6. In line with Eqn. (2-10) in section 2.2.3, it is reasonable to assume that a maximum voltage-induced area strain from pre-stretching can be obtained at this stretch ratio.

Fig. 5.3 Secant modulus of silicone composites with varied BT content, related to stretch ratio.
5.4 Dielectric Properties of DE Composites

Fig. 5.4 Effect of BT content on the dielectric constant of SR as a function of frequency.

The applied electric field necessary to produce a required deformation can be decreased by increasing the dielectric constant in a DE composite in line with Eqn. (2-10) in section 2.2.3. The complex dielectric constant which is also known as the relative permittivity, \( \varepsilon = \varepsilon' - j\varepsilon'' \), comprises the real part (\( \varepsilon' \)) and the imaginary part (\( \varepsilon'' \)) which contributes to the energy loss. The dielectric spectra of the unfilled silicone matrix and the composites are shown in Fig. 5.4 and Fig. 5.5 respectively for \( \varepsilon' \) and the dielectric loss tangent (\( \tan \delta = \varepsilon'' / \varepsilon' \)). As observed in Fig. 5.4, the relative permittivity \( \varepsilon' \) increased gradually with increasing content of filler for the silicone possessing a permittivity of about 2.9 at 1 kHz, due to the strong presence of Maxwell-Wagner interfacial polarisation [195]. The silicone rubber with BT loading of 50 wt% displayed the highest relative permittivity value of approximately 6.3 at 1 kHz. All curves fluctuated slightly in the wide band
frequency from 0.1 Hz to 1 MHz. Because the particles bonded more strongly with the matrices at low filler loadings, the molecular networks in the polymers restricted the mobility of molecular chains. Additionally, polymer chain entanglements were regarded as a factor in restricting the movement of polymer chains. Thus, as in other reported research, the dielectric constant was hardly affected by changes in frequency [196]. Furthermore, there is evidence that the amorphous SR is not influenced by dipole orientation due to its molecular structure at room temperature [197].

![Graph showing the effect of BT content on the dielectric loss tangent of SR composites as a function of frequency.]

**Fig. 5.5 Effect of BT content on the dielectric loss tangent of SR composites as a function of frequency.**

The dielectric loss tangent is a physical parameter of a DE useful for characterising its inherent dissipation of electromagnetic energy. When the value of loss tangent increases, it indicates that greater polarisation occurs as energy losses increase. Fig. 5.5 shows that tan δ decreased markedly for all samples up to a frequency of approximately 10 Hz. The unfilled silicone had a minimum tan δ of about 0.012 at 0.1 Hz. In addition, the dielectric loss tangent increased with
increasing filler content at frequencies above 1 Hz. This is possibly due to the presence of agglomerations and defects in the SR/BT composites [196]. However, there is no general trend for the change of dielectric loss tangent versus BT contents at frequencies below 1 Hz, because the conductivity of polymer composites also contributed to the dielectric loss in this low frequency range [198].

![Graph showing dielectric constant related to BT content.](image)

**Fig. 5.6 Dielectric constant related to BT content.**

A relationship was evident between the volume fraction and the weight percentage dependent on the densities of both the matrix (1.07 g/cm³) and the filler (6.08 g/cm³) in these experiments. This relationship can be expressed by Eqn. (5-1)

\[
\nu_2 = (m/6.08)/(m/6.08 + (100\% - m)/1.07)
\]  

(5-1)

where \(\nu_2\) is the BT volume fraction, \(m\) is the weight percentage of BT and thus the weight percentage of the SR matrix is equal to 100\% - \(m\).

The curve fitting for the dielectric constant of SR/BT composites by means of these equations (2-4 to 2-8) in section 2.2.1 in conjunction with the volume fraction expression (Eqn. (5-1)) above is shown in Fig. 5.6. As can be seen from
this figure, the result obtained by utilising the Rother-Lichtenecker equation with \( \kappa = 0.2 \) was the best fit to the experimental data. However, the dielectric constant of all the DE films calculated from the other equations was significantly smaller than the experimental data. The best-fit \( \kappa \)-value (0.2) determined from the modified Rother-Lichtenecker expression indicates that the ceramic BT particles are reasonably well-dispersed. This \( \kappa \)-value lies between that of low values associated with small (often nano-sized) particles [199] and larger ceramic particles [59]. In practice \( \kappa \) often reflects the size and orientation of embedded ceramic particles [199].

### 5.5 Voltage-Induced Strain

![Graph](image)

**Fig. 5.7** The actuated area strain related to the applied electric field.

Samples of SR, fabricated with different filler loadings ranging between 0% and 50% in 10% increments by weight were bonded to the equi-biaxial clamps at a pre-stretch ratio of 1.6 prior to high voltages being applied to them. Fig. 5.7 shows
that area strains for all samples actuated by high voltages increased greatly with increases in electric field strength, mainly due to the voltage-induced strain dependency on electric field strength as expressed in Eqn. (2-10) in section 2.2.3. All the samples containing BT exhibited higher actuated area strains than the pure SR sample. As can be seen from the curves, the actuated area strains increased with increasing content of BT. The SR composite with 20 wt% BT achieved an area strain of 57% under an electric field of 46 V/µm which was larger than that obtained by the unfilled silicone rubber which only produced an actuated area strain of 34% with an electric field strength of 43 V/µm. Hence, the composite with 20 wt% BT displayed the most pronounced electromechanical effect.

![Graph](image)

**Fig. 5.8** The ratio of dielectric constant to secant modulus at \(\dot{\lambda}_{pre} = 1.6\) and the voltage-induced strain related to the BT filler content in SR composites.

The electromechanical sensitivity (\(\beta\)), which is the ratio of dielectric constant to elastic modulus, was considered a significant parameter in determining voltage-induced deformation [72]. As can be seen from Fig. 5.8, sensitivity increased with an increase in BT content in the SR composites. However, the voltage-induced
area strain displayed a maximum value of 57% for a filler content of 20 wt%, but was surprisingly lower at 28% for the SR composite with 50 wt% BT. This is possibly due to the viscoelasticity of the samples with higher filler content restricting large voltage-induced deformations. Also, defects in DE composites were regarded as contributing factors towards lowering breakdown voltage [191]. This also led to small voltage-induced deformations. In addition, energy loss increased with increasing dielectric loss tangent. This possibly relates directly to the heat increase associated with an increase in filler content [200]. Consequently, the energy loss contributed to the reduction of breakdown voltage for the DE films.

**Fig. 5.9** The dependence of electromechanical energy density and electromechanical coupling efficiency on BT content.

The dependence of electromechanical energy density and electromechanical coupling efficiency ($K^2$) on filler content is shown in Fig. 5.9. As can be observed from this figure, both energy density and electromechanical coupling efficiency rose with increased filler content to about 20 wt%, then decreased with an increase in filler content thereafter. Hence, the energy density for SR composites
with 50 wt% BT was smaller than for DEs with 30 wt% BT which exhibited the largest electromechanical energy densities in the region of 0.042 MJ/m³, (3 times greater than that of pure silicone rubber) and the maximum electromechanical coupling efficiency $K^2$ of 0.59.

5.6 Summary

The influence of filler content on electromechanical properties of SR/BT composites was investigated. It was found that the BT particles have good dispersibility in the matrix. However, a large amount of agglomerates appeared in the DE films with filler contents of above 30 wt% indicating a poor compatibility between SR and BT. Furthermore, the key equi-biaxial pre-stretch ratio of 1.6 for the fabricated DEs was determined by means of the secant modulus-stretch curves. SR based DEs containing 20 wt% BT obtained the largest voltage-induced deformation of 57% and an electromechanical coupling efficiency of 62% at an electric field strength of 46 V/µm when applying an equi-biaxial pre-stretch ratio of 1.6. However, the maximum energy density was obtained by the SR composite with 30 wt% BT. This was ascribed to a higher dielectric constant in the composite containing 30 wt% BT combined with a large voltage-induced strain.
Fig. 5.10 A schematic of the configurations of a DE actuator (a) and its improved design (b).

Notably, the results in these electromechanical experiments obtained with VHB 4910 and SR/30 wt% BT differed from those presented in Chapter 4. This is mainly because (see Fig. 5.10) i) both the compliant electrodes on the DE film were coated over a smaller area and ii) the copper electrode used for applying the high voltage on the compliant electrode was moved from the centre of the coated area to the edge. Due to the changes, the DE samples suffered from fewer restrictions, such as those caused by the frame during large deformation and less friction between the copper electrodes and the DE samples. As a consequence, a larger deformation could be achieved when applying a voltage.
Chapter 6  The Improvement of Electromechanical Properties of DEs using SR and Modified BT

6.1 Introduction

As expected, the overall dielectric constant of composites increased with higher levels of filler due to the fillers’ higher dielectric constants. However, the inorganic barium titanate (BT) particle has a poor compatibility with the silicone rubber (SR) matrix. In order to resolve this problem, a coating can be used to enhance the adhesion between BT and the SR matrix. In recent years, many extensive efforts have been made to achieve composites with good particle dispersion by modifying the inorganic particles with organic coatings such as silicones [201], phosphonic acid [115] and glycidyl methacrylate (GMA) [202]. However, most treatment processes were complicated and difficult to achieve. In this chapter, the introduction of an easy and effective way of modifying the BT particles with dopamine (DP-BT) is described. Taking this into consideration, the elastic modulus, $E$ is given by [203]

$$E = 3\alpha RT$$  \hspace{1cm} (6-1)

where $\alpha$ is the crosslink density, $R$ is the gas constant and $T$ is the absolute temperature at which the experimental modulus is determined. Thus, decreasing cross link density will lead to a lowering of the elastic modulus. In addition, as confirmed in Appendix A, the SR used in this work can be devulcanised by the amine group because it can deactivate the platinum catalyst which is contained in the SR part A component. Therefore, DP-BT containing an amine group can
potentially tune the cross-linking density of SR and decrease the modulus of SR composites.

6.2 Microstructure and Morphology of BT and DP-BT

The morphology of BT and DP-BT particles was studied using SEM. Figs. 6.1 (a) and (b) show the micrographs of BT and DP-BT respectively. It is evident that the BT particles have a uniform size and approximately spherical shape of about 1 μm diameter, while the shape of DP-BT particles was observed to be irregular. Their surfaces appeared rougher than those of the BT particles. This is mainly attributed to the growth of dopamine chains on the surface of BT particles.

Fig. 6.1 SEM micrographs of particles used in the experiments: (a) BT; (b) DP-BT.

EDS analysis (Fig. 6.2) shows the presence of elemental barium (Ba) along with the elements titanium (Ti) and oxygen (O) indicating the fundamental constituents of BT. Carbon (C) was also detected in each of the particles, most likely due to the presence of residual hydrocarbon HC contamination of the BT. This was possibly because the chamber surfaces and vacuum pumps allowed sample surface migration and reaction with the electron beam to form a carbon rich environment [204]. The content of C in DP-BT (46 wt%) is more than that in BT (35 wt%) which could be used as an indicator of the successful deposition of
dopamine on BT particles. Nevertheless, the increase of carbon content in Fig. 6.2 is not regarded as significant and could also be caused by the chamber background or carbon coating. The content of element O changed only slightly after the deposition of dopamine with the O atomic mass fraction of dopamine nearly equal to that of BT.

Fig. 6.2 EDS spectra of (a) DP-BT and (b) BT.

Fig. 6.3 shows the FT-IR transmittance spectra of BT and DP-BT. It can be observed that the transmittance intensity in the range from 650-4000 cm\(^{-1}\) was enhanced by coating BT with dopamine. Due to the deposition of dopamine on BT, the C-H bond appeared at 2916 cm\(^{-1}\). The transmittance peaks located at 1607 cm\(^{-1}\) and 1286 cm\(^{-1}\) corresponded to aromatic amine N-H bending vibrations and C-N stretching vibrations respectively. In addition, the appearance of the peaks at
2568 cm\(^{-1}\) and 2168 cm\(^{-1}\) was interpreted as indicating the presence of the Ba-OH and Ti-OH [183] formatting which was probably due to the addition of ethanol during the fabrication of DP-BT.

![Fig. 6.3 FT-IR spectra of BT and DP-BT.](image)

6.3 Microstructure of SR/BT and SR/DP-BT Composites

Fig. 6.4 (a-c) and (d-f) present the microstructures of SR with BT and DP-BT composites respectively. As can be seen from Figs. 6.4 (a-c), some considerable agglomeration of BT particles were exposed on the fractured surfaces of the compound. This can be attributed to the large difference in surface energy between the filler and matrix [72]. Conversely, very few agglomerates were found in the SR/DP-BT composites. With increasing DP-BT content, the packing of particles became denser. The SR/DP-BT composites exhibited good dispersibility even at the higher DP-BT content of 40 wt%. Moreover, the interface between DP-BT and SR was particularly indistinct indicating improved compatibility
between the filler and the matrix probably due to the hydrogen bonds between dopamine and SR.

Fig. 6.4 SEM micrographs of SR based DE films with different content of BT and DP-BT, respectively: (a) 10 wt% BT; (b) 20 wt% BT; (c) 40 wt% BT; (d) 10 wt% DP-BT; (e) 20 wt% DP-BT; (f) 40 wt% DP-BT. (Inserts show particle agglomerations)

6.4 Mechanical Properties of DE Composites

The stress-stretch curves and secant modulus-stretch curves of SR composites with different BT and DP-BT contents are presented in Fig. 6.5. As shown in the
figure, the true stresses of SR/DP-BT composites were in the approximate range of 3 MPa to 6 MPa for all films when subjected to an equi-biaxial stretch ratio of 5, while the equi-biaxial stresses for the SR/BT composites were in the approximate range of 1.5 MPa to 8 MPa at the same equi-biaxial stretch ratio and for the same particle contents. The true stress increased approximately linearly with the increases in equi-biaxial stretch ratio for stretches from 1 to about 1.2 in two mutually perpendicular directions for both SR/BT and SR/DP-BT samples. The rate of increase in stress tended to be less for increases in stretch as the filler concentration grew indicating that stiffness generally and predictably reduced as filler loading became higher. All samples used in these tests exhibited large deformation. For the particle content range tested, it appeared that the 40 wt% of particle compounds were the weakest and the 10 wt% the strongest. This is probably due to the greater presence of agglomerates in the compounds with more particles, which has been observed in previous work [205]. These agglomerates were large enough to act as stress raisers and also could contribute to a decrease of filler-matrix interactions [72]. Moreover the increased quantity of amino groups in the composite significantly reduced the cross-link density in the silicone rubber by reacting with the curing agent [198, 206] in a competing side reaction.
Fig. 6.5 Plots of true stress related to stretch for SR composites with various (a) BT content and (c) DP-BT contents; secant modulus of SR composites with varied filler content related to stretch ratio: (b) SR/BT composites and (d) SR/DP-BT composites.

The curves of secant modulus versus stretch ratio for SR/BT and SR/DP-BT composites are depicted in Figs. 6.5 (b) and (d) respectively. The initial linear elastic portion of the stress-stretch curve was taken as the value of the elastic modulus [194] for small strains. As stated, for all the DE composites, as observed in Figs. 6.5 (a) and (c), the linear stage occurred below a stretch ratio of 1.2 and it is likely that the secant modulus is approximately equal to the elastic modulus in this region. The stiffness of each of the DE films used in the test was lower than that of the initial stiffness of unfilled silicone (0.3 MPa). Furthermore, as shown in
Figs. 6.5 (b) and (d), these secant modulus-stretch curves exhibit a material specific minimum in modulus indicating that their stiffness can be reduced by pre-stretching them to relatively small ratios. This phenomenon is considered to be as a result of the influence of intermolecular forces and chain entanglements between particles and the matrix material. It can be observed that the minimum elastic moduli were obtained at a stretch ratio of around 1.6 for both SR/BT and SR/DP-BT composites. This means that the application of an external force could have initially unravelled chain entanglements resulting in the elastic modulus initially falling at small stretch ratios. Thereafter, as the stretch ratio increased, intermolecular forces rose due to the hydrogen bonds between DP-BT and SR and the reorientation of molecular chains. In line with Eqn. (2-10) in section 2.2.3, it is likely that a maximum voltage-induced area strain from pre-stretching can be obtained at a stretch ratio close to 1.6.

### 6.5 Dielectric Constant and Dielectric Loss Tangent of DE Composites

Increasing the dielectric constant in a DE composite provides the opportunity to reduce the applied electric field in line with Eqn. (2-10) in section 2.2.3. Fig. 6.6 shows the plots of dielectric constant and dielectric loss tangent related to frequency for SR/BT composites and SR/DP-BT composites respectively. As can be seen from Figs. 6.6 (a) and (c), unfilled SR possessed a dielectric constant of about 2.9 at 1 kHz and the dielectric constant \( \varepsilon' \) of both SR/BT composites and SR/DP-BT composites increased with additional filler content due to the strong presence of Maxwell-Wagner interfacial polarisation [53, 95]. The composite of SR/DP-BT exhibited a maximum dielectric constant of approximately 7.9 at 1
kHz for a filler content of 40 wt%, which is larger than that of the SR composites containing 40 wt% BT.

Fig. 6.6 Dielectric constant as a function of frequency for (a) SR/BT composites and (c) SR/DP-BT composites; dielectric loss tangent as a function of frequency for (b) SR/BT composites and (d) SR/DP-BT composites.

All the curves in the figure fluctuated slightly in the wide brand frequency range of 0.1 Hz to 1 MHz. The reason for this is unclear but may be because the particles bonded strongly with the matrices at low filler loadings and the molecular networks in the polymers restricted the mobility of molecular chains. Polymer chain entanglement has been proposed as a factor in restricting the movement of polymer chains [196]. Furthermore, it seems likely that the amorphous SR was not influenced by dipole orientation at room temperature.
Thus, the dielectric constant was affected minimally by changes in frequency. The dielectric loss tangent (tan δ) is often used to characterise the energy loss in dielectric materials. Figs. 6.6 (b) and (d) show the variation of loss tangent as a function of frequency for unfilled SR and the SR/BT and SR/DP-BT composites. All materials had a low loss tangent mainly due to the weak polarisability of the silicone matrix material [134].

**Fig. 6.7 Plots showing the effect of BT and DP-BT versus filler content: (a) dielectric constant; (b) dielectric loss tangent.**

Figs. 6.7 (a) and (b) show the dielectric constant at 0.1 Hz and dielectric loss tangent at 0.1 Hz related to BT content and DP-BT content each at room temperature. As can be observed from the figure, the dielectric constant of SR composites increased as the BT or DP-BT content became larger. Also, the dielectric loss tangent decreased markedly for all samples up to a frequency of approximately 10 Hz. Unfilled silicone had the minimum loss tangent of about 0.012 at 0.1 Hz, while a maximum loss tangent of just below 0.015 was achieved by the film with 40 wt% DP-BT. This is probably due to the presence of agglomerations and other defects such as voids in the SR/DP-BT composites.
However, it can be seen that the dielectric loss tangent of SR composites was decreased by modifying the surface of BT with dopamine.

6.6 Voltage-Induced Strain of DE Composites

The relation between actuated area strain and applied electric field for SR/BT composites and SR/DP-BT is shown in Fig. 6.8. Samples of silicone rubber doped with a range of filler loadings were bonded to equi-biaxial clamps to introduce a pre-stretch ratio of 1.6 in two mutually perpendicular planes to be applied prior to the samples being subjected to high voltages. From Figs. 6.8 (a) and (b), it can be observed that area strains for all samples subjected to high voltages (HV) increased greatly with increases in electric field strength. All the samples containing BT and DP-BT exhibited higher actuated area strains than the unfilled SR samples. The unfilled SR films achieved area strains of around 34% for an applied electric field of 43 V/µm. For the SR/DP-BT composites, the sample with 20 wt% DP-BT exhibited the maximum deformation of approximately 80% for the application of an electric field of approximately 53 V/µm.

Fig. 6.8 The actuated area strain of (a) SR/BT composites and (b) SR/DP-BT composites related to the applied electric field.
Though silicone rubber with 20 wt% BT achieved a relatively small area strain of around 57% under an electric field of 46 V/µm, this was the maximum value reached by any of the SR/BT composite samples. It also can be seen that the voltage-induced strains of the SR composites with fillers were larger than those of the unfilled SR samples for the same electric field strength due to the effect of the increased dielectric constant of the SR composites. Moreover, the incorporation of BT and DP-BT enhanced the breakdown strength of DE composites. This is consistent with previous research into other polymer-based composites [187, 207].

![Graph](image)

**Fig. 6.9** The ratio of dielectric constant to secant modulus at λ<sub>pre</sub> = 1.6 related to the BT and DP-BT weight ratios of SR composites.

For all samples, area strain increased as the voltage applied to the surfaces of the DE samples increased. The electromechanical sensitivity, which is the ratio of dielectric constant to elastic modulus, was regarded as a significant value in the determination of voltage induced deformation [72]. As can be seen from Fig. 6.9, the sensitivity (β) increased with increasing BT and DP-BT content in all the SR composites. With the addition of more dopamine coated BT particles in the SR,
more platinum catalyst was deactivated. Consequently, a greater number of SR molecules were not crosslinked. This mainly contributed to a sticky SR film having a high viscoelasticity occurring for the SR with 40 wt% DP-BT. This composite exhibited the maximum sensitivity but didn’t result in the largest voltage-induced area strain. This was probably due to electrode instability and the sample having inherent material defects [28] such as the agglomerates that can be observed in Fig. 6.4. Voids may also have been present in the samples.

![Figure 6.10](image.png)

**Fig. 6.10** The dependence of (a) electromechanical energy density and (b) electromechanical coupling efficiency on BT and DP-BT content.

The dependence of electromechanical energy density and coupling efficiency on filler content is shown in Fig. 6.10. The DE with added BT exhibited the largest energy density of 0.04 MJ/m³ at a filler loading of 40 wt% and a maximum electromechanical coupling efficiency of 0.59 at a filler loading of 20 wt%. However, an SR composite with 20 wt% DP-BT obtained a maximum energy density of 0.07 MJ/m³ and had a maximum electromechanical coupling efficiency of 0.68.
6.7 Summary

The modified BT using dopamine exhibited high compatibility with the SR matrix due to the presence of hydrogen bonds. Also, as a result dopamine containing amine groups SR cross-linking was inhibited. The elastic moduli for all composites used in this work were very small allowing them to achieve high area strains when high electric fields were applied. Prior to the application of the electric fields, the key equi-biaxial pre-stretch ratio of 1.6 was determined by means of equi-biaxial mechanical testing. By comparison with conventional uniaxial testing, the method described here is more accurate in defining the optimum mechanical properties for loading DE specimens. Furthermore, the dielectric constant of the SR based composites was increased by filling the SR samples with dopamine coated BT, while the dielectric loss tangent was decreased. Finally, the SR composites with 20 wt% DP-BT displayed the highest electromechanical performance in terms of a maximum voltage-induced area strain of approximately 80% together with an electromechanical energy density of 0.07 MJ/m$^3$ and a coupling efficiency of 0.68.
Chapter 7  The Elimination of EMI in Fabricated DEs

7.1 Introduction

Electromechanical instability (EMI) has been regarded as a great problem preventing dielectric elastomers (DE) from achieving large voltage-induced deformations and hence preventing them from finding use in the numerous applications for which the material has been proposed. It has been reported that pre-stretch is an effective way to eliminate the occurrence of EMI in DEs mainly due to the strain stiffening effect. According to the theory expounded by Suo [41], as expressed in Eqn. (7-1)

$$\Phi(\lambda) = H \lambda^{-2} \sqrt{\left(\sigma(\lambda) - \sigma_{pre}\right)/\varepsilon' \varepsilon_0}$$ (7-1)

where $H$ is the thickness of the DE film, $\lambda$ is the equibiaxial stretch ratio, $\sigma_{pre}$ is the stress due to prestretch, $\varepsilon_0$ is the dielectric constant of the vacuum, $\varepsilon'$ is the dielectric constant of the DE film. The voltage in a DE is a function of stretch when the material has a Maxwell stress imparted to it. Thus, the investigation of the stress-stretch behaviour for all DEs is essential in their development and application.

Generally, stress-stretch curves can be acquired by tensile testing or deduced from a free energy function for a mechanical model under conditions of different loading modes such as uniaxial, equi-biaxial and pure shear loading. Research has been carried out based on the Neo-Hooken [208-210], Arruda-Boyce [211], Mooney-Rivlin [212, 213], Yeoh [214, 215], Ogden [39, 216] and Gent models [10, 43, 44, 84, 160, 217]. However, most of these investigations were only
conducted by theoretical simulation without fitting experimental data obtained from equi-biaxial tensile testing. Furthermore, the Neo-Hooken, Yeoh and Gent models do not employ the second strain invariant $I_2$, so were considered inappropriate for accurately modelling the predominant stiffening effect [154] at higher strains if only two or three terms were used in the constitutive equation. As with other material models, for the Ogden model, errors can occur when it is applied outside the deformation range for which its parameters were calculated [153]. In this chapter, the influence of equi-biaxial pre-stretch on EMI was primarily investigated by employing the modified Gent model under the condition of equi-biaxial loading.

7.2 The Influence of Pre-stretch on Dielectric Constant

Though pre-stretch has an influence on the dielectric constant ($\varepsilon'$) of DE materials, in previous research it was considered that this minimal influence could be ignored [41]. It was shown that the dielectric constant of polyacrylate film decreased by a few percent when equi-biaxial pre-stretch reached $\lambda = 5$ [161]. Furthermore, it was found that the dielectric constant of SR was virtually unchanged during pre-stretch in the experiments previously described in this thesis [218]. Thus, the dielectric constants of VHB 4910 and the silicone rubber (SR) based DEs were regarded as independent of the deformation in the research described here. The dielectric constants obtained at 1 kHz for VHB 4910 and the pure SR were 4.7 and 3.0 respectively. The dielectric constants of SR/barium titanate (BT) composites and SR/dopamine coated BT (DP-BT) composites were as shown in Table 7-1.
Table 7-1 The dielectric constants of SR/BT composites and SR/DP-BT composites.

<table>
<thead>
<tr>
<th>Filler content, wt%</th>
<th>$\varepsilon'$ of SR / BT at 1 kHz</th>
<th>$\varepsilon'$ of SR / DP-BT at 1 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>10</td>
<td>3.4</td>
<td>4.7</td>
</tr>
<tr>
<td>20</td>
<td>3.6</td>
<td>5.3</td>
</tr>
<tr>
<td>40</td>
<td>5.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>

7.3 Stress-Stretch Behaviour of DEs

In this work the equi-biaxial stress-stretch curves for SR based DEs were obtained over a wide equi-biaxial stretch range from 1 to 5 using the bubble inflation test system. However, due to the constraint of the VHB 4910 sample size in the tests, the stress-stretch curve was only determined for equi-biaxial stretch ratios from 1 to approximately 2 (Fig. 7.1) for this material.

Therefore, for VHB 4910 it was necessary to introduce a suitable mechanical model to provide a credible extrapolation of the stress-strain curve and hence an improved understanding of stress-stretch behaviour at larger equi-biaxial stretch ratios up to 5. The strain energy function from a modified Gent model [157, 219] which includes a logarithmic term for $I_2$ is expressed by Eqn. (2-39) in section 2.7. Thus, by substituting Eqns. (2-29), (2-30) and (2-32) in section 2.6.3 into this equation, an expression for true stress was obtained as

$$
\sigma(\lambda) = \frac{2\mu J_m \left(\lambda^2 - \frac{1}{\lambda^4}\right)}{J_m - 2\lambda^2 - \frac{1}{\lambda^4} + 3 + \frac{4C_2(\lambda^4 - \frac{1}{\lambda^2})}{\lambda^4 + 2/\lambda^2}}
$$

(7-2)

For VHB 4910, $J_m$ is about 120 [84, 214]. The experimental data was fitted to Eqn. (7-2) with $\mu = 0.01262$ MPa, $C_2 = 0.02711$ and correlation co-efficiency ($R^2$) = 0.99448.
Fig. 7.1 shows the stress-stretch plots of VHB 4910 and SR and the curve fitting for VHB 4910. As can be seen from the figure, the true stress of VHB 4910 was larger than that of the pure SR sample below an equi-biaxial stretch ratio of around 2.5. However, it was predicted that this situation would be reversed above the 2.5 equi-biaxial stretch ratio. The true stress was approximately 3 MPa for both VHB 4910 and SR at an equi-biaxial stretch ratio of 5.
7.4 The Relationships between Secant Moduli and Voltage-Induced Deformations

As previously mentioned, EMI can be suppressed by stiffening DE films [40]. Pre-stretch can fulfill this aim because of the strain stiffening effect. When materials strain stiffens, the elastic modulus increases with an increase in strain.

![Graph showing secant modulus and actuated area strain](image)

**Fig. 7.2** The secant modulus and actuated area strain of (a) VHB 4910 and (b) SR plotted against equi-biaxial pre-stretch ratio.

Fig. 7.2 shows the secant modulus and actuated area strain of VHB 4910 and SR samples varying with equi-biaxial pre-stretch ratio. It is well known that the magnitude of elastic modulus is related to intermolecular force [220]. As can be seen from this figure, both VHB 4910 and SR are capable of achieving large voltage-induced deformation for low values of elastic moduli where the intermolecular forces are at a minimum, indicating a lower energy barrier to elongation of the molecular chains when subjected to a high voltage. It was reported that the VHB 4910 film achieved a large voltage-induced strain up to 158% by employing an equi-biaxial pre-stretch ratio of 3.0 [63]. In this research, for VHB 4910, a maximum voltage-induced area strain of 200% was achieved at an equi-biaxial pre-stretch ratio of 2.0 by applying a large electric field. Above this level of pre-stretch, the voltage-induced strain unexpectedly decreased, possibly
due to the greater strain inducing a higher modulus as a result of strain stiffening. For SR, the curves of the secant modulus and actuated area strain are broadly parabolic. This is in line with the behaviour of VHB 4910. The maximum voltage-induced strain was achieved at an equi-biaxial pre-stretch of 1.6 but with a lower modulus. By comparison with VHB 4910, SR achieved a smaller voltage-induced strain possibly due to the lower inherent dielectric constant. For SR samples, the possibility of removing EMI existed when applying the equi-biaxial pre-stretch ratio above 1.6 taking the strain stiffening effect into consideration, while VHB 4910 exhibited the absence of EMI with the equi-biaxial pre-stretch ratio above 2.0.
Fig. 7.3 The secant modulus and actuated area strain versus equi-biaxial pre-stretch ratio for SR composites with (a) 10 wt%, (b) 20 wt% and (c) 40 wt% BT and SR composites with (d) 10 wt%, (e) 20 wt% and (f) 40 wt% DP-BT respectively.

Fig. 7.3 shows that the secant modulus and actuated area strain are both dependent on equi-biaxial pre-stretch ratio for the SR/BT and SR/DP-BT composites. As can be observed from the figure, all curves are essentially parabolic. The minimum and maximum for all tests was located within the same range of equi-biaxial stretch ratios from 1 to 3. Furthermore, the maximum actuated area strain was
achieved for all SR based DEs at an equi-biaxial stretch ratio of approximately 1.6. For the SR/BT composites, the maximum voltage-induced strain was strongly dependent on filler content. The minimum strain of 0.34 was achieved by the SR composite containing 10 wt% BT with a secant modulus of 0.3 MPa at an equi-biaxial stretch ratio of 1.6. Meanwhile, the maximum strain of 58%, the largest amongst the SR/BT composites, was achieved by the composite of SR/20 wt% BT with a secant modulus of around 0.19 MPa at an equi-biaxial stretch ratio of 1.6.

Thereafter, the maximum strain decreased with increasing filler content such that at 40 wt% the maximum strain was approximately 40% and this corresponded to a secant modulus of 0.17 MPa for an equi-biaxial stretch ratio of 1.6. For the SR/DP-BT composites, the actuated area strain was a maximum of approximately 80% for a filler content of 20 wt%. Though, out of all the DE films, the SR/40 wt% DP-BT composite had the lowest secant modulus, the largest voltage-induced strain for this composite was surprisingly 40% at an equi-biaxial pre-stretch ratio of 2.0. This was possibly due to defects in the composite contributing to a decrease of dielectric strength. Moreover, it can be observed from Fig. 7.2 and Fig. 7.3 that the onset of the strain-stiffening effect for the SR based DEs is at an equi-biaxial stretch ratio of about 1.6, which is smaller than the corresponding stretch ratio in VHB 4910 where strain stiffening begins at an equi-biaxial stretch ratio above 2.0.
7.5 The EMI of VHB 4910 and SR Based DEs

The dependence of voltage $\Phi$ on stretch ratio for DEs can be determined by applying Eqn. (7-1). For given values of $\lambda_{pre}$ and $\Phi$, the DE was in one of a number of equilibrium states. Fig. 7.4 depicts a range of curves for voltage $\Phi$ versus stretch ratio for (a) VHB 4910 and (b) SR. The curves were obtained by varying the pre-stretch ratio ($\lambda_{pre}$) in the range 1 to 3. $\sigma_{pre}$ was determined for all values of pre-stretch from the $\sigma(\lambda)$ curves shown in Fig. 7.2.

![Fig. 7.4 Actuation of (a) VHB 4910 and (b) SR under equi-biaxial loading:](image)

The plots were created from experimental data. Hence, the $\Phi(\lambda)$ curves were derived from Eqn. (7-1) where the $\sigma(\lambda)$ curves employed were obtained using the Gent modified model for VHB 4910 and bubble inflation test for Pure SR.

As can be seen from Figs. 7.4 (a) and (b), when $\lambda_{pre}$ was small (1 to 1.6) for VHB 4910 and SR, the voltage-stretch curves exhibited a maximum value of $\Phi$ before declining to values of approximately 10 kV and 4 kV respectively. It is possible for EMI to appear on the DE surfaces at and beyond these maximum values before electrical breakdown failure occurs. Initially, for small voltages, the deformation of the DE increased with increasing voltage. Thereafter, when the voltage exceeded the value for $\Phi_{EMI}$, the DE film drastically deformed with a
pronounced increase in area strain and concurrent thinning of the test sample. Ultimately, the applied electric field reached a level where breakdown ensued, resulting in the failure of the DE. When $\lambda_{\text{pre}}$ was large (above 2), the voltage-stretch curve increased monotonically without EMI occurring, so in this case the DEs only suffered failure at electrical breakdown. Furthermore, it can be seen from Figs. 7.4 (a) and (b) that the critical voltage $\Phi_{\text{EMI}}$ decreased as a result of increasing the pre-stretch. For VHB 4910, $\Phi_{\text{EMI}}$ declined from about 28 kV to 10 kV between $\lambda_{\text{pre}} = 1.0$ and $\lambda_{\text{pre}} = 1.6$, while for pure SR, $\Phi_{\text{EMI}}$ decreased from 7 kV to 4 kV for the same pre-stretch range.

Fig. 7.5 The morphology of VHB 4190 films (a) the uniform area without instability; (b) the creased area with instability exhibiting EMI.

Fig. 7.5 shows the different states when a voltage was applied across a VHB 4910 film. As can be observed from Fig. 7.5 (a), the DE surface coated with a carbon grease electrode is uniform without the occurrence of EMI, whereas at a high voltage the surface creases and wrinkles indicating the presence of EMI on the DE (Fig. 7.5 (b)).
Fig. 7.6 The voltage-stretch curves with various equi-biaxial pre-stretch ratios for SR composites with (a) 10 wt%, (b) 20 wt% and (c) 40 wt% BT and SR composites with (d) 10 wt%, (e) 20 wt% and (f) 40 wt% DP-BT respectively. (The plots were created using stress-stretch curves obtained from the bubble inflation test in accordance with Eqn. (7-1) and the individual points shown on the graphs were obtained from experimentation)
Fig. 7.6 shows the voltage-stretch curves obtained with varied equi-biaxial prestretch ratios for SR/BT composites and SR/DP-BT composites respectively. As can be observed from these curves, it was found that the region of ‘snap through’ was reduced by either adding fillers or increasing the equi-biaxial pre-stretch ratio. Additionally, the electromechanical voltage decreased as filler content increased for both SR/BT composites and SR/DP-BT composites. Furthermore, N-shaped voltage-stretch curves for all composites were completely transformed to monotonically increasing curves by applying an equi-biaxial pre-stretch ratio of 2.5 or more, indicating the suppression of EMI. It was also found that EMI was alleviated by the addition of BT or DP-BT. For the SR/BT composites, though EMI persisted without pre-stretch, it was initially eliminated by applying a small equi-biaxial pre-stretch ratio of 1.6 to the SR based DE with 20 wt% BT and then disappeared at an equi-biaxial pre-stretch ratio of 2.0 for all the films tested. For the SR/DP-BT composites, EMI was removed at an equi-biaxial pre-stretch ratio of 1.6 for the composites containing SR/10 wt% DP-BT and SR/20 wt% DP-BT. However this was not the case for the SR/40 wt% DP-BT composite which still exhibited EMI. When comparing SR/BT composites with SR/DP-BT composites, the SR based DE filled with DP-BT was less likely to exhibit EMI at small pre-stretch ratios.

Table 7-2 shows the values of the electric field strength ($\varphi_{EMI}$) at which EMI began to occur during the application of a range of equi-biaxial pre-stretch ratios for all the DEs tested. As can be seen from this table, the $\varphi_{EMI}$ of VHB 4910 barely changed although the equi-biaxial pre-stretch increased from 1.0 to 1.6. However, the $\varphi_{EMI}$ of SR based DEs increased significantly with larger equi-biaxial pre-stretch ratios. It was also observed that with the addition of fillers, the
$\phi_{EMI}$ of all the DE composites without equi-biaxially pre-stretching decreased except for the two composites of SR/10 wt% BT and SR/40 wt% BT.
Table 7-2 The values of the electric field strength ($\varphi_{EMI}$) at which EMI commenced occurring under the condition of different equibiaxial pre-stretch ratios for all DEs in these experiments.

<table>
<thead>
<tr>
<th>Polymer (specific type)</th>
<th>$H$(mm)</th>
<th>$\varphi_{EMI}$, V/µm</th>
<th>((\lambda_{pre} = 1.0))</th>
<th>((\lambda_{pre} = 1.6))</th>
<th>((\lambda_{pre} = 2.0))</th>
<th>((\lambda_{pre} = 2.5))</th>
<th>((\lambda_{pre} = 3.0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>VHB 4910</td>
<td>1.00</td>
<td>44</td>
<td>44</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
</tr>
<tr>
<td>Pure SR</td>
<td>0.30</td>
<td>36</td>
<td>88</td>
<td>151</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
</tr>
<tr>
<td>SR/10 wt% BT</td>
<td>0.34</td>
<td>40</td>
<td>92</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
</tr>
<tr>
<td>SR/20 wt% BT</td>
<td>0.34</td>
<td>31</td>
<td>109</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
</tr>
<tr>
<td>SR/40 wt% BT</td>
<td>0.22</td>
<td>40</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
</tr>
<tr>
<td>SR/10 wt% DP-BT</td>
<td>0.50</td>
<td>31</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
</tr>
<tr>
<td>SR/20 wt% DP-BT</td>
<td>0.46</td>
<td>33</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
</tr>
<tr>
<td>SR/40 wt% DP-BT</td>
<td>0.50</td>
<td>22</td>
<td>53</td>
<td>81</td>
<td>NEI</td>
<td>NEI</td>
<td>NEI</td>
</tr>
</tbody>
</table>

* NEI = No Electromechanical Instability
7.6 The Electromechanical Energy Density and Coupling Efficiency of DEs

Fig. 7.7 Electromechanical energy density versus equi-biaxial pre-stretch ratio for SR based DEs with different filler contents: (a) BT and (b) DP-BT.

Fig. 7.7 shows the electromechanical energy density that was obtained by the SR based DEs with different BT and DP-BT contents by application of various equi-biaxial pre-stretch ratios. As can be seen from the figure, the energy density was very small for all composites without application of pre-stretch. For all the SR composites except the SR/40 wt% BT sample, the energy density increased
reaching a peak with increasing equi-biaxial pre-stretch ratio and thereafter fell away. However, the energy density rose again to its highest value of 0.045 for the SR/40 wt% BT composite for an equi-biaxial pre-stretch ratio of approximately 3. Among the SR composites with BT particles, the largest energy density of 0.065 MJ/m$^3$ was achieved by the SR/20 wt% BT composite. However, the maximum energy density for all SR composites was 0.072 MJ/m$^3$ for the SR/20 wt% DP-BT composite. This corresponded to the largest actuated area strain of approximately 80% and the relatively high measured dielectric constant of 5.3.

![Graphs showing electromechanical coupling efficiency versus equi-biaxial pre-stretch ratio for SR based DEs with different filler contents: (a) BT and (b) DP-BT.](image)

Fig. 7.8 Electromechanical coupling efficiency versus equi-biaxial pre-stretch ratio for SR based DEs with different filler contents: (a) BT and (b) DP-BT.
Fig. 7.8 shows the electromechanical coupling efficiency achieved by SR based DE composites with different equi-biaxial pre-stretch ratios. It was observed that the electromechanical coupling efficiency for all DE composites had a parabolic relation with the applied equi-biaxial pre-stretch ratio and reached maximum values at an equi-biaxial pre-stretch ratio of 1.6. The reason for this is that the coupling efficiency was only determined by the voltage-induced deformation which rose to a maximum at an equi-biaxial pre-stretch ratio of 1.6. The maximum coupling efficiency of 68% was obtained by the SR/20 wt% DP-BT composite when an equi-biaxial pre-stretch ratio of 1.6 was applied. It was larger than that of the SR/BT composites with a filler loading of 20 wt%.

![Graph showing energy density vs. pre-stretch ratio]

**Fig. 7.9 The relations between energy density and equi-biaxial pre-stretch ratio.**

The SR/20 wt% DP-BT DE composite possessed the largest energy density among all the SR based DEs tested in this work. Fig. 7.9 shows the comparison of electromechanical energy density between the in-house made SR/20 wt% DP-BT composite and the commercially available used VHB 4910 DE. It can be seen that the acrylate film had a higher energy density above 0.2 MJ/m$^3$ at larger equi-
biaxial pre-stretch ratios above 2.0. Such values were much larger than those of the SR based DEs. However, it was smaller than that of the silicone DEs when equi-biaxial pre-stretch was either not applied or was less than a critical value of 1.6.

Fig. 7.10 The relation between coupling efficiency and equi-biaxial pre-stretch ratio.

Fig. 7.10 shows the electromechanical coupling efficiency of SR/20 wt% DP-BT composite at the equi-biaxial pre-stretch ratios of 1.0, 1.6, 2.0, 2.5 and 3.0, by comparison with the same equi-biaxial pre-stretch ratios for VHB 4910. As observed from the figure, the electromechanical coupling efficiency was higher than that of VHB 4910 in the absence of equi-biaxial pre-stretch. Although, the efficiency for the silicone composite was less than VHB 4910 at equi-biaxial pre-stretch ratios above 1.6, it was very close to that of VHB 4910 when applying an equi-biaxial pre-stretch ratio of 1.6. It should be noted that the VHB 4910 film with an equi-biaxial pre-stretch ratio of 2.0 exhibited the maximum efficiency of
88% which was 20% larger than that of the SR/20 wt% DP-BT composite when equi-biaxially pre-stretched to a ratio of 1.6.

7.7 Summary

Both the polyacrylate VHB 4910 and SR inevitably suffered from EMI in tests where either no equi-biaxial pre-stretch was applied prior to testing or when low equi-biaxial pre-stretch ratios were applied prior to testing. However, the instability was assuaged by means of the addition of fillers in the SR based DEs. For the composite of SR/10 wt% DP-BT, the EMI was clearly eliminated at a relatively low equi-biaxial pre-stretch ratio of 1.6 and above, while instability disappeared at an equi-biaxial pre-stretch ratio of above 2.0 for the polyacrylate films. Equi-biaxial pre-stretch had a significant influence on the voltage-induced strain of all DE films. For all membranes tested, the maximum voltage-induced strain was achieved when the composites were equi-biaxially pre-stretched to ratios in the range 1.6 to 2.0. Furthermore, with the addition of fillers, strain was increased for the SR composites in all tests. The DE of SR/20 wt% DP-BT possessed the maximum electromechanical energy density of 0.072 MJ/m³ and exhibited a coupling efficiency of 0.68. In conclusion, the composite of SR/20 wt% DP-BT is a potential substitute for VHB 4910 in terms of its capacity to both alleviate EMI and simultaneously undergo large voltage-induced deformation.
Chapter 8  Conclusions and Recommendations for Future Work

8.1 Conclusions

The main objective of this study were to fabricate a dielectric elastomer (DE) using silicone rubber (SR) containing barium titanate (BT) capable of achieving large voltage-induced deformations at relatively low electric field strengths and simultaneously eliminate electromechanical instability (EMI) by using equibiaxial pre-stretch. The initial study on the fabrication of DEs identified various parameters to characterise the electromechanical properties of the material, such as the actuated area strain, energy density and electromechanical coupling efficiency. EMI was studied using both experimental and numerical approaches.

The influence of equibiaxial pre-stretch on the electromechanical properties of DEs was initially explored by investigating the commercially available and widely used polyacrylate DE, VHB 4910 and an SR/30 wt% BT composite material developed in the laboratory. It was found that SR based DEs were more stable than VHB 4910 in terms of dielectric properties when subjected to changes in frequency, because the dielectric constant for the SR/BT composite remained largely constant over the range of test frequencies 0.1–10^6 Hz. The voltage-induced deformations of all DE films were clearly increased by applying equibiaxial pre-stretch to the DE samples compared with films on which equibiaxial pre-stretch was absent. A maximum actuated area strain of above 75% for VHB 4910 film was achieved at an equibiaxial pre-stretch ratio of approximately 2.0; while SR/30 wt% BT achieved a maximum area strain of 32% with an equi-
baxial pre-stretch ratio of around 1.6. It was also found that the dielectric strength and the Maxwell stress increased with increases in the equi-biaxial pre-stretch ratio for all DEs used in these experiments. The energy densities and electromechanical coupling efficiencies increased in the small equi-biaxial pre-stretch ratio range achieving a maximum and decreased at larger equi-biaxial pre-stretch ratios. This is probably caused by the strain-stiffening effect. Comparing the fabricated silicone DE samples with VHB 4910 showed that, though the maximum strain achieved for the silicone samples was slightly smaller, the maximum energy density output of each was roughly equal. Also, the maximum pressure and the maximum dielectric strength were far higher for the fabricated silicone DE samples containing BT particles than for the commercially available VHB 4910 samples. It is noticeable that the results obtained from relatively simple preliminary experiments were slightly lower than those obtained from the later optimised experiments.

For the SR based DEs, the influence of BT content on the electromechanical properties was further studied. The key equi-biaxial pre-stretch ratio of approximately 1.6 was determined using stress-stretch curves obtained from bubble inflation tests. At this ratio, the secant elastic modulus exhibited a minimum. Thus the polymer molecules could be easily driven by the Maxwell stress. Furthermore, the key equi-biaxial pre-stretch ratio of 1.6 for the fabricated DEs was determined by means of the secant modulus-stretch curves. SR based DEs with 20 wt% BT obtained a largest voltage-induced deformation of 57% and electromechanical coupling efficiency of 0.62 at an electric field strength of 46 V/μm, when an equi-biaxial pre-stretch ratio of 1.6 was applied. However, the maximum energy density in all tests on SR composites was ascertained for the
composite with 30 wt% BT and this was considered to be mainly due to a higher dielectric constant as a result of the higher level of BT combined with a large voltage-induced strain. However, the SEM images indicated the occurrence of a large number of agglomerates in DE films with filler contents of above 30 wt%, showing poor compatibility between SR and BT.

Subsequently, BT was modified by coating with dopamine in order to improve the compatibility between particles and matrix and consequently decrease the elastic moduli of the SR based composites. On the one hand, dopamine contains a hydroxyl group and amine group which are capable of forming hydrogen bonds with fillers and matrices; but on the other hand, an amine group could reduce the cross-link density of SR by preventing it devulcanising in the doped samples used in this work. The SEM images showed good compatibility and dispersibility of the dopamine coated BT (DP-BT) particles in SR matrices. It was found that the addition of DP-BT into SR led to increased dielectric constants and decreased dielectric loss tangents for the compounds in comparison with SR/BT composites.

Additionally, the minimum secant moduli of DEs were obtained at an equi-biaxial stretch ratio of approximately 1.6 using the bubble inflation method. The ratio was applied in the electromechanical experiments in order to achieve the maximum voltage-induced deformations obtainable. Significantly, a maximum actuated area strain of approximately 80%, which was 30% larger than that of the SR/BT composites, was achieved for the sample having a DP-BT content of 20 wt%. The electromechanical properties of the SR/DP-BT composites, such as voltage-induced deformation, electromechanical energy density and coupling efficiency, were greatly improved.
EMI in VHB 4910 and SR based DEs can be suppressed by applying equi-biaxial pre-stretch because of the strain stiffening effect that is induced. In experiments where no equi-biaxial pre-stretch was employed prior to testing, or when low equi-biaxial pre-stretch ratios were applied prior to testing, the DEs inevitably suffered from EMI. This was probably due to a decrease in elastic modulus with an increase in stretch. It was noticeable that instability was assuaged by means of the addition of fillers in the SR based DEs.

In SR based DEs it was possible to remove EMI by applying lower equi-biaxial pre-stretch ratios of 1.6 and above, while for VHB 4910 films, instability disappeared at an equi-biaxial pre-stretch ratio of above 2.0. It was also found that the maximum voltage-induced strains were achieved when the range of composites were equi-biaxially pre-stretched to ratios between 1.6 to 2.0 and this corresponded to the lowest elastic modulus in each material. Moreover, the electromechanical energy density and coupling efficiency for both DE materials were substantially increased by equi-biaxial pre-stretch. The SR/20 wt% DP-BT composite possessed a maximum energy density and coupling efficiency among all the SR based DEs. Electromechanical properties for both the SR/BT and SR/DP-BT composites at the low equi-biaxial pre-stretch ratio of 1.6 approached and sometimes exceeded those for VHB 4910.

Thus, composites of SR and BT, especially the SR/20 wt% DP-BT composite, are excellent DEs having the capability of achieving large voltage-induced deformations at low electric field strengths, whilst exhibiting the elimination of EMI when equi-biaxial pre-stretch is applied.
8.2 Recommendations for Future Work

The static properties of DE materials, such as equi-biaxial stress-stretch behaviour, dielectric constant and electromechanical actuation were respectively characterised using dielectric spectroscopy, bubble inflation mechanical testing and electromechanical testing. From the results obtained, it was found that the SR/20 wt% DP-BT composite, having an equi-biaxial stretch ratio of above 5 in two mutually perpendicular planes, a high dielectric constant of 5.3 and a relatively low loss tangent factor of about 0.015, achieved the maximum voltage-induced deformation of about 80%.

However, the dynamic performance, including response time, field-actuated stability after cyclic electric field loading and fatigue life with a high voltage switched on and off, also needs to be comprehensively researched in order to establish that the SR/DP-BT compound has commercial potential. On the basis of these considerations, the future work should focus on:

1) *Coupling the electromechanical test system with the bubble inflation test system to characterise the dynamic performance of the DEs.* Since the latter system requires samples of greater thickness than those used thus far, the power supply device may not be sufficient for actuating the samples to achieve large deformations. Thus, a voltage amplifier would need to be procured to meet this requirement. Additionally, the conductive parts that receive the voltage signal need to be made of insulating materials such as polytetrafluoroethylene (PTFE), polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).

2) *Investigating the relationship between cyclic response behaviour, the applied electric field and the time spent using the coupled test system.* For
an ideal DE, the strain response of the fabricated material should be stable. However, it has been reported that the response behaviour of DEs is related to their viscoelasticity [35, 90, 221]. In order to characterise the viscoelasticity of DEs, a dynamic mechanical analyser (DMA) can be utilised. Moreover, owing to the Mullins effect (stress softening under dynamic loading), the actuated strain normally varies greatly in different loading cycles when a constant high voltage is applied, especially between the first and second cycle. Thus, the effect of varying viscosity on the dynamic response of DEs also needs to be studied.

3) Obtaining the fatigue life of fabricated DEs for situations where high voltages are applied or are absent. As is universally accepted, a commercial material is required to be resilient and hence have a long service life. The DEs made in-house should undergo fatigue tests in the coupled bubble inflation test system. Furthermore, as pre-stretch has a significant influence on the fatigue life of all kinds of elastomers including DEs, the fatigue lives of the fabricated DE related to variations in equibiaxial pre-stretch ratios should also be studied for situations where high voltages are either applied or not.

It’s well known that pre-stretch is important for not only enhancing voltage-induced deformation but also eliminating EMI in DEs [1]. However, due to some drawbacks inherent in using pre-stretch, particularly using a frame for pre-stretching the material complicates the DE function; pre-stretch decreases the lifetime of DEAs due to stress relaxation and fatigue in the pre-stretched material. Hence, DE materials should be required to achieve large voltage-induced deformations without the application of pre-stretch. Therefore, a further aim of
future research should be to develop SR based DEs without the necessity for using pre-stretch to obtain larger voltage-induced deformations. Interpenetrating polymer networks (IPNs) [102, 104, 125] can be used to mitigate EMI in fabricated DEs by using a soft polymer (LSR4305) as the host elastomer and introducing a rigid heat cured SR (Wacker Elastosil LR W 3003/70) as an additive elastomer.

A simplified processing route for preparing IPN based DE is:

1) The components A and B of Wacker Elastosil LR W 3003/70 are mixed at a ratio of 1:1 at room temperature. Then, the heptane solvent is added to the mixture. The resulting solution is sealed in order to prevent the heptanes from volatilising and stirred using a magnetic stirring apparatus for 30 min.

2) The film of SR/20 wt% DP-BT is equi-biaxially pre-stretched to a pre-determined ratio and fixed on a clamp. Subsequently, the solution obtained by step 1) is sprayed onto the upper surface of the equi-biaxial pre-stretched film and heated at 180°C in an oven for 30 min in order to be completely cured. The sample is then reversed so the bottom surface is now the upper surface and is sprayed with the solution and again heated to 180°C.

3) After the heat treatment, the film is released from the clamp and allowed to fully relax for 24 h. The amount of preserved equi-biaxial pre-stretch is calculated from the final dimensions after relaxation with respect to the sample size prior to equi-biaxial pre-stretching. Thus, the preserved equi-biaxial pre-stretch values obtained represent the actual equi-biaxial pre-stretch of the host SR.
It is worth pointing out that the equi-biaxial pre-stretch locking efficiency in the IPN film can be increased by increasing the thickness of the additive films which could be tuned by repeatedly spraying with the solution. However, the thicker the DE film, the higher the actuating voltage required. This factor should be considered when carrying out the proposed further research.

Future work could also focus on the development and design of various DEs based apparatus making use of the unique electromechanical property of this material. Silicone based DEs described in this research have the potential to be used in the design of rotary motors. Most electric motors currently used are made from rigid metallic parts and are electromagnetic. Consequently, they invariably produce noise pollution in service. However, motors consisting of flexible DE components are able to eliminate noise.

Fig. 8.1 A 3-phase DE rotary motor: (a) the schematic of the DE motor; (b) the activation sequence of the electrodes and the displacement of the orbiter caused by the electrode expansion [222]; (c) a motor designed by the biomimetics lab from the University of Auckland, New-Zealand [223].
Figs. 8.1 (a) and (b) depict the schematic of a 3-phase DE rotary motor. The motor consists of a DE membrane stretched on a frame. Three electrodes are patterned on the membrane and a rigid orbiter is placed at the centre of the membrane. The three electrodes are sequentially activated to move the orbiter in a circle-like translation path. The orbiter enters into contact with a rotor located at the centre of the membrane which spins due to the friction forces between the orbiter and rotor. Fig. 8.1 (c) shows a motor designed by in the University of Auckland [223]. The size of the motor can be reduced by further miniaturisation due to its flexibility. Therefore, DEs have a promising future in mobile motors and cooling fans for laptops as the electronic products become thinner and lighter.

Thus, the advantages of fast response, light weight, large voltage-induced strain, relatively high mechanical energy density and coupling efficiency of the DE materials designed, fabricated and evaluated in this research indicate that they could potentially provide the essential characteristics required for this rotary motor and numerous other novel devices. Consequently, future work will also involve assembling this promising DE material into a number of miniaturised products including a rotary motor and a range of actuators.
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New Silicone Composites for Dielectric Elastomer Actuator Applications In


Appendix A. The Properties of LSR 4305

SILBIONE® LSR 4305

Low Durometer Liquid Silicone Rubber

Description
SILBIONE® LSR 4305 is a developmental, 5 durometer, healthcare grade liquid silicone rubber designed for producing high clarity, high strength molded parts.

Applications
- Orthopedic insoles
- Pressure relieving pads
- Prosthetic liners
- Rollers
- Precision molded parts
- Cushioning devices

Features
- Superior clarity
- High tear strength at low durometer
- Very low hardness
- Very high elongation
- Excellent mold release for shorter cycle times
- Rapid cure at elevated temperature
- No post cure is needed

Typical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>As Supplied</th>
<th>Test Method ASTM</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>TP 038</td>
<td>cps</td>
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<td>Viscosity</td>
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<td>TP 013</td>
<td>g/cm</td>
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<th>Test Method ASTM</th>
<th>Unit</th>
<th>Press Cured 1 min, 177°C</th>
<th>Post Cured 10 hrs, 200°C</th>
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<td>Hardness</td>
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<td></td>
<td>Shore OO (A)</td>
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<td>45 (5)</td>
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<tr>
<td>Tensile Strength</td>
<td>D 412</td>
<td></td>
<td>psi (N/mm²)</td>
<td>450 (3.1)</td>
<td>490 (3.4)</td>
</tr>
<tr>
<td>Elongation</td>
<td>D 412</td>
<td></td>
<td>%</td>
<td>900</td>
<td>980</td>
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<tr>
<td>Tear Strength</td>
<td>D 624, Die B</td>
<td></td>
<td>Ppi (N/mm)</td>
<td>60 (10.5)</td>
<td>55 (10)</td>
</tr>
<tr>
<td>Modulus, 100%</td>
<td>D 412</td>
<td></td>
<td>psi (N/mm²)</td>
<td>15 (0.1)</td>
<td>15 (0.1)</td>
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</tbody>
</table>

Instructions for use
Parts A and B components of SILBIONE® LSR 4305 are designed to be mixed in equal parts using standard liquid injection molding processing equipment and techniques. Airless mixing, metering and dispensing equipment are recommended for production operations. Accurate measuring and complete mixing are essential factors in obtaining consistent results.

Curing
Curing is typically achieved in 15 seconds at 175°C. Curing time can be decreased by increasing temperature.

Cleaning
Special care must be taken to assure clean molds and a clean work area with no organic rubbers used on the same processing equipment. Traces of foreign materials can poison the catalyst and inhibit the cure. All metering and mixing equipment should be thoroughly cleaned. Polymer systems, which contain traces of amines, sulfur, nitrogen oxide, organotin compounds and carbon monoxide can interfere with the cure of this product and should be avoided.
**SILBIONE® LSR 4305**

<table>
<thead>
<tr>
<th>Limitation</th>
<th>Silbione® silicone HC products are used for healthcare, medical and pharmaceutical applications within specified limitations. Bluestar Silicones supports the sales of these Silbione® products to customers involved in manufacturing and assembling approved medical devices for skin contact or less than 30-day implantation. The purchaser has the sole responsibility to select a particular Bluestar Silicones SILBIONE® product and determine its application suitability. The purchaser also has the sole responsibility to comply with all applicable statutory, regulatory and industry requirements and standards for compatibility, extractability, testing, safety, efficacy and labeling.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safety</td>
<td>Please read the container labels for SILBIONE® LSR 4305 or consult the Material Safety Data Sheet (MSDS) before handling for safe use, physical and health hazard information. The MSDS is not included with the product packaging, but can be obtained by contacting Bluestar Silicones at 866-474-6342 or consult your Bluestar Silicones representative.</td>
</tr>
<tr>
<td>Storage and shelf life</td>
<td>SILBIONE® LSR 4305 when stored in its original unopened packaging, at a temperature of 24°C (77°F), may be stored for 12 months from the date of manufacture. Beyond this date, Bluestar Silicones no longer guarantees that the product meets the sales specifications.</td>
</tr>
<tr>
<td>Packaging</td>
<td>SILBIONE® LSR 4305 is available in 36 kg or 400 kg kits</td>
</tr>
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Liquid Silicone Rubber – Injection Molding Guide

Injection molding of silicone parts has enabled producers to achieve higher levels of automation and productivity than ever before. Molders and OEMs can now manufacture articles for a variety of devices and components with very demanding performance specifications.

This document is intended to illustrate the basics of injection molding of Sibione® Liquid Silicone Rubber and troubleshooting. Additional sources of information are the tool and injection molding machine manufacturers who are involved in the injection molding process.

Contact your Bluestar Silicons Representative for additional information on specific products and for information beyond the contents of this document.

BLUESTAR SILICONES – DELIVERING YOUR POTENTIAL

**High Performance Physical Properties**

Sibione® LSRs are designed to give the highest physical properties on the market right out of the mold. These high strength products require no post-curing. If the application does require post-curing, the percent change in physical properties is minimal. With high clarity, high resiliency, and low compression set, Sibione® LSRs are ideal for demanding healthcare applications.

**Ease of Processing**

The manufacture of Sibione® LSRs is tightly controlled, providing good lot-to-lot consistency to the molder. With low viscosities, matching A/B extrusion rates and lot-to-lot consistency, fewer process adjustments are required during molding and between lot change-over.

**Improved Productivity**

Sibione® LSR 43xx Series is formulated to give good release from the mold with no sticking. Combine this with the ability to fill cavities faster (low viscosity = lower injection pressures), fast cure rates, and lower part flashing, and the molder now has the right combination to improve injection molding productivity rates.

**Technical & Regulatory Support**

Bluestar Silicons is committed to its customers and to providing fast, high-quality service in the marketplace. Our team of silicone experts can offer the assistance needed to help you mold the Sibione® LSR successfully.

**Product Development**

Bluestar Silicons works closely with customers to develop new products and new opportunities for growth. Contact your Bluestar Silicons Representative for more information on Research and Development project.
General Information

General
For many years, silicones have been used in a wide range of application areas including aerospace, automotive, electrical, construction, industrial, medical and healthcare. The unique properties of silicones make them ideal for very demanding applications.

The injection molding of Silbione Liquid Silicone Rubber (LSR) offers the user ease of processing, high-volume molding, improved productivity, and consistent part quality.

Why use silicones in healthcare applications?
- Excellent biocompatibility
- Inert, odorless, tasteless, stain resistant
- Extreme temperature applications (from -50°C to +200°C continuous)
- Hypo-allergenic
- Can be steam or radiation sterilized. Dishwasher safe.
- Easy to clean
- Flexible and durable
- Resistance to ozone and corona
- Resistance to weathering and oxidation
- Excellent resistance to many chemicals, including low water absorption
- Superior dielectric and insulation characteristics
- High clarity and transparency
- Low compression set and good resiliency
- Long work and shelf life
- Low Shrinkage (no cure by products)

Benefits of LSRs over HCRs
- Molding Cycle Time: Fast cycle times that are typically measured in seconds. Temperature =-170 °C to 200°C, Cycle time =-4 to 6s/mm.
- Secondary Operation: Molds can be designed to be flashless, eliminating the need for secondary operations.
- Contamination: Packaged in a closed system; less chance of contamination because an operator does not physically touch the material, and the material is not in contact with the atmosphere.
- Labor: LSR injection equipment and tooling can be set up to run automatically with only minimal labor to monitor the system and change drums.
- Scrap: LSR does not generate scrap from excess flash to the same degree as high consistency rubber. LSR molds can be designed to run flashless.
- Part Configuration: Because of the flow properties of LSRs, they are ideal for small intricate parts where maintaining tight tolerances is important.
**Injection Molding Guide**

**Limitations**
Bluestar Silicones supports the sales of these products to customers involved in manufacturing and assembling approved medical devices for less than 30 day implantation. The purchaser has the sole responsibility to select a particular Bluestar Silicones product and determine its application suitability. The purchaser also has the sole responsibility to comply with all applicable statutory, regulatory and industry requirements and standards for compatibility, extractability, testing, safety, efficacy and labeling.

**Storage and shelf life**
Silbione® LSRs when stored in its original un-opened packaging, at a temperature of 24°C (77°F), may be stored for a minimum of 6 months (12 months for most products) from the date of manufacture. Beyond this date, Bluestar Silicones no longer guarantees that the product meets the sales specifications.

**Safety**
Please read the container labels for Silbione® LSRs or consult the Material Safety Data Sheet (MSDS) before handling for safe use, physical and health hazard information. The MSDS is not included with the product packaging, but can be obtained by contacting Bluestar Silicones at 866-474-6342 or consult your Bluestar Silicones representative.

**Packaging**
Silbione® LSRs are available in 18 kg (40 lb) pail kits or 200 kg (440 lb) drum kits.

**LSR Chemistry**
Silbione Liquid Silicone Rubbers (LSRs) are two-component platinum-catalyzed silicone elastomers. The Part A component contains vinyl functional polymer(s) and the platinum catalyst. The Part B component contains the hydride crosslinker and inhibitor.

![Diagram of Polydimethyl Methylvinyl Siloxane and Cured Silicone Elastomer]
# Injection Molding Guide

## Product Portfolio

### TYPICAL PROPERTIES

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<tr>
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<th>LSR 4305</th>
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<td>1100</td>
<td>1060</td>
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<td>60 (10)</td>
<td>115 (19.2)</td>
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<td>28 (0.2)</td>
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### BIOCOMPATIBILITY DATA

<table>
<thead>
<tr>
<th>Biocompatibility Tests (1)(2)</th>
<th>LSR 4301</th>
<th>LSR 4305</th>
<th>LSR 4310</th>
<th>LSR 4325</th>
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<tr>
<td>Cytotoxicity</td>
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<tr>
<td>Skin Sensitization</td>
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<tr>
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<td>Hemolysis</td>
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<td>Mucosal Irritation</td>
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<td>Pyrogenicity</td>
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<td>7-Day Implant</td>
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<td>USP Class VI</td>
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<td>FDA Master File (MAF)</td>
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<table>
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<tr>
<th>Extraction Tests (2)</th>
<th>LSR 4305</th>
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<tr>
<td>FDA 21 CFR 177.2600</td>
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<td>Water extraction only</td>
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<tr>
<td>FDA 7117.11 Nitrosamines</td>
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</tbody>
</table>

*Indicates test not performed on the material, however, it is substantially equivalent to another tested Bluestar Silicones LSR.*

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150
### Injection Molding

#### Injection Pressure

The injection velocity and pressure depend on the viscosity of the silicone and the design of the runner system. Cavities are typically filled in 0.5 – 3 seconds. Pressures range from 250 psi to 2000 psi.

During the start-up of a new tool, the injection pressure should be set high enough that the silicone will be completely injected into the mold before the cure of the silicone can begin in order to prevent premature curing at the injection point. A mold filling study is typically done during the start-up to monitor the balance of the cavities and to ensure that, upon complete filling, the mold is not over-loaded.

The point at which the injection is completed and the curing time begins is referred to as the switch over.

#### Holding Time / Pressure

Silicone expands as its temperature increases. Holding pressure is required to prevent the silicone from flowing back into the injection nozzles when this expansion occurs. Typically, 0.5 – 4 seconds is a sufficient holding time.

#### Cavity Pressure

The slow expansion of the curing silicone causes the cavity pressure to gradually increase. To prevent excessive flashing and back-rind, each cavity should be filled to 96-99% of capacity.

#### LSR Supply

The **Silbione** LSR is dispensed from a pressurized pumping unit at a ratio of 1:1. This meter-mix system is typically a double-acting pneumatically driven reciprocating pump with follower plates that move the silicone from the 200 kg drums or 18 kg pails through flexible pipes to the static mixer.

#### Mixing

The **Silbione** LSR and any other additives (typically a pigment/polymer masterbatch) are delivered through a static mixer that will thoroughly mix the components while not imparting additional frictional heat. Some injection molding machines include a dynamic mixer near the end of the screw to achieve additional mixing. Although a dynamic mixer provides additional mixing of the components, it can also impart frictional heat into the silicone shortening the pot life of the material after this point.

#### Injection Unit

The pressure of the LSR drops to approximately 400 – 1000 psi as the material is delivered from the pumps to the screw (injection unit). The rotational speed of the screw should be high enough to deliver the silicone into the mold so as not to prolong the cycle time but not so high that the temperature of the **Silbione** LSR is increased causing partial curing.

Leakage can occur at the non-return valve if the valve closing does not occur immediately or if the valve does not close completely.

Back pressure should be set at approximately 70 – 500 psi.
Curing

The reaction between the vinyl and hydride-functional components takes place very slowly at room temperature but is rapidly accelerated with heat. This fast and efficient addition-cure reaction can be measured on a rheometer. The graph shows cure of the silicone plotted as a function of torque versus time at a given temperature. As the temperature of the sample increases in the testing chamber of the rheometer, the polymerization of the silicone begins. The T90 value is the time at which 90% of the maximum torque is reached, indicating the beginning of silicone cure. The T90 value is the time at which 90% of the maximum torque is reached, indicating the point in an injection molding process that the silicone reaction is approaching completion and demolding is now possible.

Cure Rate measured with MDR 2000 at 115°C

Recommended molding temperature (actual temperature inside the mold) is 150°C - 200°C. At these temperatures, the LSR cures very rapidly. The exact rate of reaction of the LSR depends on the following factors:

- chemical formulation of the Silbione® LSR
- temperature of the mold
- temperature of the Silbione® LSR when it enters the cavity
- surface area of the part being molded versus the volume of the part

For planning purposes, the cure time can be estimated assuming 4 – 6 sec/mm. As the part thickness gets larger, this factor will also increase due to the poor heat transfer characteristics of silicone.

During the start-up of a new tool, the cure time of the article can be decreased until deforming or sticking occurs. This cure time represents the “edge” of the process and the curing time should then be increased by 5 – 10% to guarantee a safe operating range.

For ways to increase productivity after your current process has been optimized, contact your Bluestar Silicones Technical or Sales Representative.
## Injection Molding Guide

### Demolding

Silicone LSR 43xx series products are designed to provide excellent mold release properties and high hot tear resistance. These features allow for high productivity, and automated removal of articles from the hot mold.

### Cavity Surface Finish

The LSR duplicates exactly the surface of the cavity. Polished steel or polished chrome plated surfaced molds should be used to achieve highly transparent parts. Silicone LSR 43xx series products are formulated to provide excellent release from any cavity surface finish.

LSRs adhere more to polished surfaces. A rough surface finish on a mold will provide less adhesion with the silicone and easier demolding when using a LSR that is not designed for good mold release.

A PTFE/Nickel surface coating on the mold provides easier demolding of the cured silicone article. This coating will wear over time and the tool will need to be resurfaced.

A Titanium/Nickel surface coating offers a very high wear resistance.

### Shrinkage

Linear shrinkage of articles molded with Silicone LSR is typically 1.5 – 2.5%. Exact shrinkage depends on the following factors:

- chemical formulation of the Silicone LSR
- molding temperature
- cavity pressure
- where the shrinkage measurement is made (shrinkage is usually slightly higher in the direction of the material flow than perpendicular to the direction of flow).
- dimension of the part (thicker parts shrink less than thinner parts)
- post curing causes an additional 0.3 – 0.5% shrinkage.

### Production Shut-down

Unless otherwise stated, mixed Silicone LSR is designed to remain processable for a minimum of 2.5 days at temperatures less than 35°C. Should the injection molding machine need to be remain idle for more than 2.5 days, the injection unit and cold runner should be purged with the Part A component to prevent polymerization of the silicone. Injection molding machine parts holding mixed material could also be kept in a freezer to prevent curing of the silicone for longer time periods. Care should be taken to ensure that if these steps are taken, condensation inside the machine parts does not occur.

A regular preventive maintenance schedule is recommended for the mixer and injection unit. Even if the injection molding machine is used nearily without interruption, the mixer and injection unit should be cleaned at least every three months to ensure that cured particles do not accumulate and interfere with flow through the colder runner. Cured particles could detach and enter the tool cavity.

### Cleaning

Special care must be taken to assure clean molds and a clean work area with no organic rubbers used on the same processing equipment. Traces of foreign materials can poison the catalyst and inhibit the cure. All metering and mixing equipment should be thoroughly cleaned. Polymer systems, which contain traces of amines, sulfur, nitrogen oxide, organotin compounds and carbon monoxide can interfere with the cure of this product and should be avoided.

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Sylmeca LSR may not cure properly if they come in contact with certain substances. Some common cure inhibitors include:

- chlorinated solvents, acetone, MEK
- adhesive tapes (i.e. duct tape)
- peroxide and peroxide by-products
- sulfur compounds
- amines
- urethanes
- tin based compounds (condensation cure silicones)
- most substances with highly electronegative atoms: N, S, P, Cl
  - that are soluble or partially soluble in silicone
  - some gaseous inhibitors such as some amines, e.g. NH3
- butyl and chlorinated rubbers
- strong acids
- strong bases
# Appendix B. The Properties of VHB 4910

## Technical Data

**Product Description:**
3M™ VHB™ Tapes provide the convenience and simplicity of a tape fastener and are ideal for use in many interior and exterior bonding applications. In many situations, they can replace rivets, spot welds, liquid adhesives and other permanent fasteners. These 3M™ VHB™ Tapes are made with acrylic foam which is viscoelastic in nature. This gives the foam energy absorbing and stress relaxing properties which provides these tapes with their unique characteristics. The acrylic chemistry provides outstanding durability performance.

These tapes utilize a variety of specific foam, adhesive, color and release liner types to provide each product/family with specific features. These features can include adhesion to specific or a broad range of materials, conformability, high tensile strength, high shear and peel adhesion, resistance to plasticizer migration, and UL 746C recognition. All 3M™ VHB™ Tapes have excellent durability and excellent solvent and moisture resistance.

The tapes included in this data page have unique performance features that are not typically required in most common applications. Please refer to “3M™ VHB™ Tapes” technical data sheet for applications that do not require the special features incorporated in these specialty tapes.

### 3M™ VHB™ Tape Products

#### 4950 Family
This family has general purpose adhesive on both sides of firm type foam. This family is typically used on metal, glass and high surface energy plastic substrates. Available in white and black.

<table>
<thead>
<tr>
<th>Tape Number</th>
<th>Color</th>
<th>Thickness in (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4914</td>
<td>White</td>
<td>0.010 (0.25)</td>
</tr>
<tr>
<td>4920</td>
<td>White</td>
<td>0.015 (0.4)</td>
</tr>
<tr>
<td>4929</td>
<td>Black</td>
<td>0.022 (0.8)</td>
</tr>
<tr>
<td>4929AF</td>
<td>White</td>
<td>0.025 (0.96)</td>
</tr>
<tr>
<td>4949</td>
<td>Black</td>
<td>0.045 (1.1)</td>
</tr>
<tr>
<td>4969</td>
<td>White</td>
<td>0.045 (1.1)</td>
</tr>
<tr>
<td>4969 (AF)</td>
<td>White</td>
<td>0.090 (3.5)</td>
</tr>
<tr>
<td>4969 (AF)</td>
<td>White</td>
<td>0.120 (4.7)</td>
</tr>
</tbody>
</table>

#### 4945 Family
This family has multi-purpose adhesive on both sides of firm foam.

<table>
<thead>
<tr>
<th>Tape Number</th>
<th>Color</th>
<th>Thickness in (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4945</td>
<td>White</td>
<td>0.045 (1.1)</td>
</tr>
<tr>
<td>4946</td>
<td>White</td>
<td>0.045 (1.1)</td>
</tr>
</tbody>
</table>

#### 4910 Family
This family of clear tapes is excellent for applications where clear or colorless is desired. The general purpose adhesive on both sides is suitable for high surface energy substrates.

<table>
<thead>
<tr>
<th>Tape Number</th>
<th>Color</th>
<th>Thickness in (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4905</td>
<td>Clear</td>
<td>0.020 (0.5)</td>
</tr>
<tr>
<td>4910</td>
<td>Clear</td>
<td>0.040 (1.6)</td>
</tr>
</tbody>
</table>

#### 4901 Family
This family of tapes is based around the low temperature appliable acrylic adhesive system, utilized on both firm and conformable foam types. These products are suitable for high surface energy substrates. Available in white (firm foam) and gray (conformable foam).

<table>
<thead>
<tr>
<th>Tape Number</th>
<th>Color</th>
<th>Thickness in (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4951</td>
<td>White</td>
<td>0.045 (1.1)</td>
</tr>
<tr>
<td>4951 (AF)</td>
<td>Gray</td>
<td>0.045 (1.1)</td>
</tr>
<tr>
<td>4957 (AF)</td>
<td>Gray</td>
<td>0.062 (2.5)</td>
</tr>
</tbody>
</table>

#### 4952 Family
This family utilizes the low surface energy adhesive on a firm foam.

<table>
<thead>
<tr>
<th>Tape Number</th>
<th>Color</th>
<th>Thickness in (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4922</td>
<td>White</td>
<td>0.025 (0.9)</td>
</tr>
<tr>
<td>4962</td>
<td>White</td>
<td>0.045 (1.1)</td>
</tr>
</tbody>
</table>

#### 4611 Family
This family has a general purpose adhesive on both sides of firm foam. This family of tapes is typically used on metal substrates, and has the added feature of high temperature resistance, making it often suitable for bonding prior to high temperature paint processing.

<table>
<thead>
<tr>
<th>Tape Number</th>
<th>Color</th>
<th>Thickness in (mm)</th>
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<tr>
<td>4611</td>
<td>Dark Gray</td>
<td>0.045 (1.1)</td>
</tr>
<tr>
<td>4648</td>
<td>Dark Gray</td>
<td>0.025 (0.96)</td>
</tr>
<tr>
<td>4655</td>
<td>Dark Gray</td>
<td>0.062 (2.5)</td>
</tr>
</tbody>
</table>

#### 4622 Family
This family has general purpose adhesive on the face side (the side that typically would be bonded first) and multi-purpose adhesive on the liner side (the side exposed when the release liner is removed) of a conformable foam. Available in white.

<table>
<thead>
<tr>
<th>Tape Number</th>
<th>Color</th>
<th>Thickness in (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4618</td>
<td>White</td>
<td>0.025 (0.96)</td>
</tr>
<tr>
<td>4622</td>
<td>White</td>
<td>0.045 (1.1)</td>
</tr>
<tr>
<td>4624</td>
<td>White</td>
<td>0.062 (2.5)</td>
</tr>
</tbody>
</table>

*P or F after the product number designates that both a paper and film liner product version are available, e.g. 4930 (paper liner) and 4600F (film liner). See page 2 for specific details.*
### 3M™ VHB™ Tape Specialty Tapes

**Typical Performance Characteristics**

Note: The following technical information and data should be considered representative or typical only and should not be used for specification purposes.

<table>
<thead>
<tr>
<th>Family</th>
<th>Product Number</th>
<th>Color</th>
<th>Thickness Inches</th>
<th>90° Peel Adhesion B/lb B/in B/cm</th>
<th>Normal Tensile B/lb B/ft² kPa</th>
<th>Dynamic Overlap Shear B/lb B/ft² kPa</th>
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</thead>
<tbody>
<tr>
<td>4950</td>
<td>4914</td>
<td>White</td>
<td>0.010</td>
<td>13 (23)</td>
<td>130 (900)</td>
<td>130 (900)</td>
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<tr>
<td></td>
<td>4920</td>
<td>White</td>
<td>0.015</td>
<td>15 (26)</td>
<td>160 (1100)</td>
<td>100 (690)</td>
</tr>
<tr>
<td></td>
<td>4929</td>
<td>Black</td>
<td>0.025</td>
<td>20 (35)</td>
<td>160 (1100)</td>
<td>100 (690)</td>
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<td></td>
<td>4930F</td>
<td>White</td>
<td>0.025</td>
<td>20 (35)</td>
<td>160 (1100)</td>
<td>100 (690)</td>
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<tr>
<td></td>
<td>4949</td>
<td>Black</td>
<td>0.045</td>
<td>25 (44)</td>
<td>140 (970)</td>
<td>80 (550)</td>
</tr>
<tr>
<td></td>
<td>4950</td>
<td>White</td>
<td>0.045</td>
<td>25 (44)</td>
<td>140 (970)</td>
<td>80 (550)</td>
</tr>
<tr>
<td></td>
<td>4955</td>
<td>White</td>
<td>0.090</td>
<td>20 (35)</td>
<td>95 (660)</td>
<td>70 (480)</td>
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<tr>
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<td>4959F</td>
<td>White</td>
<td>0.082</td>
<td>20 (35)</td>
<td>75 (520)</td>
<td>55 (380)</td>
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<tr>
<td>4945</td>
<td>4945</td>
<td>White</td>
<td>0.045</td>
<td>25 (44)</td>
<td>140 (970)</td>
<td>80 (550)</td>
</tr>
<tr>
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<td>70 (480)</td>
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<td>4957F</td>
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<td>75 (520)</td>
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<td>20 (35)</td>
<td>100 (690)</td>
<td>100 (690)</td>
</tr>
<tr>
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<td>4952</td>
<td>White</td>
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<td>80 (550)</td>
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<td>Dk Gray</td>
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<td>100 (690)</td>
<td>80 (550)</td>
</tr>
<tr>
<td></td>
<td>4655</td>
<td>Dk Gray</td>
<td>0.082</td>
<td>18 (32)</td>
<td>80 (550)</td>
<td>60 (410)</td>
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<td>4916</td>
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<td>80 (550)</td>
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<tr>
<td></td>
<td>4922</td>
<td>White</td>
<td>0.045</td>
<td>20 (35)</td>
<td>70 (480)</td>
<td>65 (450)</td>
</tr>
<tr>
<td></td>
<td>4924</td>
<td>White</td>
<td>0.082</td>
<td>20 (35)</td>
<td>55 (380)</td>
<td>60 (410)</td>
</tr>
</tbody>
</table>

- **90° Peel Adhesion** - Based on ASTM D3330 - To stainless steel, room temperature, jaw speed 12 in/min (304.8 mm/min). Average force to remove is measured. 72 hour dwell.
- **Normal Tensile (T-Block Tensile)** - ASTM D-897 - To aluminum, room temperature, 1 in² (6.45 cm²), jaw speed 2 in/min (50.8 mm/min) Peak force to separate is measured. 72 hour dwell.
- **Dynamic Overlap Shear** - ASTM D-1002 - To stainless steel, room temperature, 1 in² (6.45 cm²), jaw speed 0.5 in/min (12.7 mm/min) Peak force to separate is measured. 72 hour dwell.
## Typical Performance Characteristics

Note: The following technical information and data should be considered representative or typical only and should not be used for specification purposes.

<table>
<thead>
<tr>
<th>3M™ VHB™ Tape Family</th>
<th>Product Number</th>
<th>Color</th>
<th>Thickness (inches)</th>
<th>Static Shear 72°F (22°C)</th>
<th>Static Shear 150°F (66°C)</th>
<th>Static Shear 200°F (93°C)</th>
<th>Static Shear 250°F (121°C)</th>
<th>Static Shear 350°F (177°C)</th>
<th>Temperature Tolerance Short Term (Wet/Heat) °F (°C)</th>
<th>Temperature Tolerance Long Term (Dry/Heat) °F (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4914</td>
<td>White</td>
<td>0.010</td>
<td>1500 500 500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300 (149) 200 (93)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4920</td>
<td>White</td>
<td>0.015</td>
<td>1500 500 500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300 (149) 200 (93)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4929</td>
<td>Black</td>
<td>0.025</td>
<td>1500 500 500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300 (149) 200 (93)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4930(F)</td>
<td>White</td>
<td>0.025</td>
<td>1500 500 500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300 (149) 200 (93)</td>
<td></td>
</tr>
<tr>
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<td>Black</td>
<td>0.045</td>
<td>1500 500 500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300 (149) 200 (93)</td>
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</tr>
<tr>
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<td>4950</td>
<td>White</td>
<td>0.045</td>
<td>1500 500 500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300 (149) 200 (93)</td>
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<td>250 (121) 200 (93)</td>
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</tbody>
</table>

Static Shear - ASTM D3854 - To stainless steel, tested at various temperatures and strain loadings. 0.5 in² (3.23 cm²). Will hold listed weight for 10,000 minutes (approximately 7 days). Conversion: 1500 g/0.5 in² equals 6.6 lb/in²; 500 g/0.5 in² = 2.2 lb/in².

Short Term Temperature Tolerance - No change in room temperature dynamic shear properties following 4 hours conditioning at indicated temperature with 100 g/static load. (Represents minutes, hours in a process type temperature exposure).

Long Term Temperature Tolerance - Maximum temperature where tape supports at least 250 g load per 0.5 in² in static shear for 10,000 minutes. (Represents continuous exposure for days or weeks).
### Additional Typical Performance Characteristics

Note: The following technical information and data should be considered representative or typical only and should not be used for specification purposes.

<table>
<thead>
<tr>
<th>3M™ VHB™ Tape</th>
<th>Units</th>
<th>Test Standard</th>
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<tr>
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<td>4611</td>
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<td>Dissipation Factor</td>
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<td>Dielectric Breakdown Strength</td>
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<td></td>
<td>0.0273</td>
<td>0.0595</td>
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<tr>
<td>Thermal Conductivity (k value)</td>
<td>18 (460)</td>
<td>25 (630)</td>
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<tr>
<td>Volume Resistivity</td>
<td>0.09 (6)</td>
<td>0.16 (1.1)</td>
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<tr>
<td>Surface Resistivity</td>
<td>1.5 x 10¹⁰</td>
<td>3.1 x 10¹⁰</td>
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<tr>
<td>Water Vapor Transmission Rate</td>
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</tbody>
</table>

### Thermal Properties of Modeling

| Shear Modulus (at 25°C, 1 Hz) | 180 (100) | 6 x 10⁹ | 10¹⁴ m²/s°C (10¹⁴ lbf/in²°F) |
| Poisson’s Ratio | 0.49 |

### 3M™ VHB™ Tapes

#### UL746C Livings - File MH 17478

**Category 03922 Compound - Polymeric Adhesive Systems, Electrical Equipment**

<table>
<thead>
<tr>
<th>3M™ VHB™ Tape Product Families</th>
<th>Substrate</th>
<th>Temperature Rating</th>
<th>Minimum</th>
<th>Maximum</th>
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<tbody>
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<td>Poly(ethylene terephthalate)</td>
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<td>-35°C</td>
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</tbody>
</table>

*Substrates can be used with or without primer/Coating. 3M Sure-Lok, 3M Adhesive Promoter 43080 and 3M Tape Primer 39 are used with glass substrates. 3M Primer 4011, 3M Adhesive Promoter 43086 and 3M Tape Primer 34 are used with aluminum and galvanized steel substrates.

### Outgassing

<table>
<thead>
<tr>
<th>3M™ VHB™ Tape</th>
<th>% TML</th>
<th>%ICM</th>
<th>%NMR</th>
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<tr>
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<td>0.77</td>
<td>0.01</td>
<td>0.21</td>
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<td>4932</td>
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<td>0.66</td>
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<tr>
<td>4945</td>
<td>1.24</td>
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</table>

**TML = Total Mass Loss**

**ICM = Inhibitive Characteristic Materials**

**NMR = Non-Resistant Materials**


Available online at http://outgassing.nasa.gov

### Solvent and Fuel Resistance

<table>
<thead>
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<th>Solvent/Fluid</th>
<th>% Adhesive Retention</th>
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<td>Water</td>
<td>100</td>
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<tr>
<td>Methanol</td>
<td>100</td>
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<td>Isopropyl Alcohol</td>
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<td>Jet Fuel</td>
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<tr>
<td>Gasoline</td>
<td>100</td>
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</table>

**Test Method**

- Tape between stainless steel and aluminum foil
- 72 hours dwell at room temperature
- Sorbent immersion for 72 hours
- Test within 45 minutes after removing from solvent
- Peel angle 90°
- 12 in/min rate of peel
- Peel adhesion compared to control

**Note:** Continuous submersion in chemical solutions is not recommended. The above information is presented to show that occasional chemical contact should not be detrimental to tape performance in most applications in ordinary use.

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List of Publications

Journal Publications


Conference Contribution


