Novel material composites for dielectric elastomer actuators

Ankit

2019

Ankit. (2019). Novel material composites for dielectric elastomer actuators. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/136574>

<https://doi.org/10.32657/10356/136574>

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**NOVEL MATERIAL COMPOSITES FOR DIELECTRIC
ELASTOMER ACTUATORS**

ANKIT

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

NOVEL MATERIAL COMPOSITES FOR DIELECTRIC ELASTOMER ACTUATORS

ANKIT

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

22nd July 2019

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Assoc Prof Nripan Mathews

Authorship Attribution Statement

This thesis contains material from 3 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Portions of Chapter 4 are published as Ankit, N. Tiwari, M. Rajput, N. A. Chien, N. Mathews. Highly Transparent and Integrable Surface Texture Change Device for Localized Tactile Feedback. *Small* **14**, 1702312 (2018). DOI: 10.1002/sml.201702312.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof N. Mathews and performed all the laboratory work and analysis at the School of Materials Science and Engineering, NTU.
- N. Tiwari performed the UV-Vis measurements for the samples.
- M. Rajput helped with the spray coating of silver nanowires for initial samples and process optimization.
- I prepared the manuscript drafts and the manuscript was revised by Dr N. A. Chien and Prof N. Mathews.

Chapter 5 is currently being prepared as a manuscript – Ankit, F. Ho, N. Tiwari, F. Krisnadi, S. J. A. Koh, N. Mathews. Bioinspired liquid filler based soft elastomeric composites for electrically powered soft actuators.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof N. Mathews and performed all the laboratory work and analysis at the School of Materials Science and Engineering, NTU.
- F. Ho. prepared the initial samples for proof of concept experiments.
- N. Tiwari helped with the Fourier transform infrared spectroscopy.
- F. Krisnadi prepared the schematic sketches for the manuscript.

- Prof S. J. A. Koh at Department of Mechanical Engineering (NUS) helped with the dielectric spectroscopy measurements.
- I prepared the manuscript drafts and the manuscript was revised by F. Krisnadi, Prof S. J. A. Koh and Prof N. Mathews.

Chapter 6 is published as Ankit, N. Tiwari, M. Rajput, N. A. Chien, N. Mathews. Highly Transparent and Integrable Surface Texture Change Device for Localized Tactile Feedback. *Small* **14**, 1702312 (2018). DOI: 10.1002/sml.201702312.

Portions of Chapter 6 are published as Ankit, J. Y. Chan, L. L. Nguyen, F. Krisnadi, N. Mathews. Large-area, flexible, integrable and transparent DEAs for haptics. *Proc. SPIE 10966, Electroactive Polymer Actuators and Devices (EAPAD) XXI*, 109661W (13 March 2019). DOI: 10.1117/12.2514267.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof N. Mathews and performed all the laboratory work and analysis at the School of Materials Science and Engineering, NTU.
- J. Y. Chan carried out the device integration with Arduino and capturing the images.
- L. L. Nguyen performed the synthesis of conductive hydrogels.
- I prepared the manuscript drafts and the manuscript was revised by J. Y. Chan, L. L. Nguyen and Prof N. Mathews.

Portions of Chapter 6 are also published as Ankit, N. A. Chien, N. Mathews. Surface texture change on-demand and microfluidic devices based on thickness mode actuation of dielectric elastomer actuators (DEAs). *Proc. SPIE 10163, Electroactive Polymer Actuators and Devices (EAPAD) 2017*, 101632G (17 April 2017). DOI: 10.1117/12.2260300.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof N. Mathews and performed all the laboratory work and analysis at the School of Materials Science and Engineering, NTU.
- I prepared the manuscript drafts and the manuscript was revised by N. A. Chien and Prof N. Mathews.

Chapter 7 is currently being prepared as a manuscript – Ankit, F. Krisnadi, D. Accoto, S. J. A. Koh, N. Mathews. Thermally activated reversible rigidity composites for next generation soft actuators.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof N. Mathews and performed all the laboratory work and analysis at the School of Materials Science and Engineering, NTU.
- F. Krisnadi helped with sample preparations and sample characterizations. F. Krisnadi also prepared the schematic sketches for the manuscript.
- Prof D. Accoto at School of Mechanical and Aerospace Engineering (NTU) helped with the analysis of data from mechanical characterizations.
- Prof S. J. A. Koh at Department of Mechanical Engineering (NUS) helped with the dielectric spectroscopy measurements.
- I prepared the manuscript drafts and the manuscript was revised by F. Krisnadi, Prof D. Accoto, Prof S. J. A. Koh and Prof N. Mathews.

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Abstract

Conventional robotics, made from rigid components, are known for their accuracy and precision, and have been extensively utilized in industries for large scale manufacturing. There has been a constant focus to improve the existing robots and make them fit in our natural world, leading to the development of modern era humanoids and animal-inspired robots. However, they suffer from the absence of compliance and do not provide a safe and comfortable environment for human interaction. On the other hand, biological systems make use of their inherent softness and structural compliance to produce complex and fluidic motions. An emerging area of research, soft robotics, promises to address these issues of rigidity and non-dexterity in conventional robots and mimic the systems found in nature. They make use of soft materials and demonstrate fluidic deformation of their bodies to achieve more complex and compliant motions. Different strategies like embedded pneumatics and fluidics, thermally activated polymers, magnetic fields, chemical reactions and electroactive polymers have been adopted for actuating these soft materials. Dielectric elastomer actuators, under the family of electroactive polymers are an attractive option for producing actuation, and they utilize electric fields to deform elastomers and can produce very large actuation strains. However, in their current form, dielectric elastomer actuators suffer from specific limitations like high electric fields, low versatility and need for rigid frames, which calls for investigation into new material systems and novel device configurations. This dissertation attempts to tackle the material and device configuration issues with these field driven soft actuators.

The performance of dielectric elastomer actuators is dependent on intrinsic material properties like dielectric constant and Young's modulus of the elastomer. Commonly used elastomeric systems suffer from low dielectric constant and comparatively high Young's modulus. Conventional approaches to improve these material properties involve chemical modification of the elastomeric backbone and addition of solid fillers, often producing undesirable effect on other material parameters. Drawing inspiration from biological materials like skin and tissues, it is hypothesized that addition of a high dielectric constant liquid filler into a polymer matrix with favorable compatibility, could lead to significant reduction in mechanical stiffness accompanied with the

improvement in the dielectric constant of the resulting composite. Theoretical models are adopted to predict the properties of such a self-contained liquid filler-polymer composite. Ionic liquid and water are investigated as liquid fillers and the role of their interaction with the polymer on the resulting composite is established. Owing to their favorable interaction and other desirable properties, ionic liquid is chosen as the suitable filler, and they produce synergetic effects on the electrical and mechanical properties of the resulting composite. Benchmarking of the actuation behavior against the conventional elastomeric matrix reveals a considerable improvement in the electromechanical performance at significantly low electric fields. Owing to the suitable choice of filler and adoption of a liquid-solid composite approach, these composites also show high stability and transparency, opening the possibilities for next-generation low voltage driven dielectric elastomer actuators.

One of the specific application areas where soft actuators and dielectric elastomer actuators (in particular) have convincing advantage over the conventional rigid actuators is in adaptive surfaces with a focus on improving user interaction at human-machine interfaces. Haptics and tactile feedback are of great importance owing to new generation technologies such as display touchscreens, touchpads, virtual and augmented reality and on-demand buttons. However, state-of-the-art technologies for haptics seek to simulate the texture change without creating actual topographical transformations, making it challenging to provide localized feedback. And dielectric elastomer actuators in their current form suffer from visible obstructiveness and non-integrable architecture. Hence, a new device architecture for dielectric elastomer actuators capable of producing on-demand surface texture change and local topographic features in any pre-designed pattern is demonstrated. Owing to its unique architecture, a transparent, flexible and integrable configuration of the device, comprised of transparent system of electrodes and transparent active elastomer matrix, is demonstrated. Desired surface textures can be controlled by pre-designed pattern of electrodes, which operates as independent or interconnected actuators. Surface deformations and blocked force output from the devices are shown to be well above the perceptual threshold of mechanoreceptors present in human fingers. High transparency levels are achieved owing to the choice of the materials and novel device configuration. The capability of localized and controlled deformation, together with the high integrability to both flexible and rigid substrates is demonstrated. A design approach of

stacking of active layers is also shown to improve the actuation performance of devices in this architecture.

In contrast to biological appendages, the current generation of soft actuators lack the critical attribute of reversibly modulating the mechanical properties upon demand. Although rigidity leads to intermittent motion in conventional robots, a soft actuator capable of modulating rigidity on demand could reduce the power consumption for actuators and haptic devices to remain under electrical stimuli. Most of the current approaches fail to provide rigidity modulation and only demonstrate reversible stiffness; and involve utilization of a passive component which involves augmentation of a reversible stiffness component on the existing actuator. There is a need for an intimate integration which provides reversible modulation of mechanical properties and can contribute directly to the actuation behavior as well. Thermal stimulus is chosen as the method for controlling the modulation of mechanical properties, owing to its lightweight design and scalability. Low-temperature phase change materials are evaluated for their thermal, mechanical strength and electrical properties. A novel glycol-based phase-change filler is chosen due to its low melting point, significant gap between melting and solidification, superior thermal stability, high mechanical strength and high dielectric constant. The fabricated reversible rigidity composites show impressive variations in Young's modulus, flexural modulus and Shore hardness. Owing to its ability to melt and re-solidify, the composites also demonstrate a healing behavior with the ability to regain complete structural integrity and mechanical strength. The composite is integrated with a low-resistance flexible joule heater capable of producing high temperatures within few minutes, to imbibe the composites with the ability to demonstrate the phase change behaviour by remote control. This could lay the foundation for novel soft actuators capable of mimicking nature at a closer level.

In summary, a liquid filler strategy for fabricating polymer composites with high dielectric constant and low Young's modulus has been demonstrated, paving the way for low-field driven actuation DEAs for shape morphing applications. PEG filler based reversible rigidity composites were fabricated enabling novel adaptive surfaces. New device configuration enabling transparency and integrability was achieved by thickness mode actuation of DEAs with potential of development of next generation transparent haptic devices and adaptive-informative surfaces.

Lay Summary

Robots have been around us for quite some time now. Robots are machines capable of performing tasks on their own with high accuracy and precision and minimal supervision to reduce human effort. Our daily lives are touched by different forms of robots around us, be it a direct interaction in form of robotic helpers at the airport or indirectly in the case of industrial arm robots assembling the electronics and machines. Traditionally, there are several component systems to robotics and one of the prominent one is actuation, which is made from hard and rigid components in these conventional robots. However, this is responsible for their intermittent motion. A new field of research, soft robotics, makes use of soft materials for their fabrication and draws inspiration from natural organisms and how they produce fluidic and complex motions. There are different ways by which these soft materials can be actuated and include techniques like applying pneumatic and hydraulic pressure, applying heat, making use of a chemical process like combustion, applying varying magnetic fields and applying electric fields. Among these, the class of actuators employing soft materials deformed by applying the electric field, known as Dielectric elastomer actuators, are preferred owing to their advantages of simple fabrication, large actuation strain and control by electrical stimulus.

The architecture of these actuators resembles a variable capacitor with electrodes on either sides of the elastomer, and their performance depends on material properties like dielectric constant and mechanical stiffness. Generally, researchers have tried to modify either of these properties with addition of solid conductive or ceramic fillers, or chemical modification of the elastomer, and this has led to undesirable changes on the other material properties. Drawing inspiration from biological materials like skin, which is a soft material system filled with fluids, a novel composite is synthesized utilizing a solid polymer matrix and a high dielectric constant liquid filler, an ionic liquid. An increase in dielectric constant is observed accompanied with significant reduction in mechanical stiffness. The novel composites show significant improvement upon the actuation performance of the commonly used elastomeric system at considerably low electric fields. Owing to the judicious choice of material systems, the composites also show high stability and transparency.

With emergence of new generation technologies such as display touchscreens, touchpads, virtual reality and augmented reality, human machine interaction and haptics has become ever more important. Soft actuators and dielectric elastomer actuators (in particular), owing to their inherent softness, have convincing advantage over the conventional rigid actuators. Additionally, state-of-the-art technologies for haptics primarily seek to simulate the perception of texture change with sensory manipulation. Furthermore, dielectric elastomer actuators in their current form suffer from visible obstructiveness and non-integrable architecture. A new device architecture for dielectric elastomer actuators, capable of producing on-demand surface texture change and local topographic features, is demonstrated. Owing to its unique architecture, a highly transparent, flexible and integrable configuration of the device is showed. Out-of-plane deformations and force feedback from the devices are shown to be well above the perceptual threshold of sensors, known as mechanoreceptors, present in our fingertips.

Another attribute of the biological appendages in natural organisms is the ability to reversibly modulate its mechanical properties upon demand, which still eludes the field of soft robotics. One of the best examples of this is found in human body, where muscles modulate their stiffness in accordance to the load distribution and movement. Most of the current approaches manage to only demonstrate reversible stiffness and involves combination of a passive reversible stiffness component with the existing actuator. Hence, a novel low-temperature phase change material is identified for enabling reversible rigidity in the soft actuators owing to its low melting point, significant gap between melting and solidification, superior thermal stability, high mechanical strength and high dielectric constant. Thermal control is chosen the modulation of mechanical properties, owing to its lightweight design and scalability. The fabricated reversible rigidity composites show impressive variations in stretchability, bendability and hardness. Owing to its ability to melt and re-solidify, the composites also demonstrate a healing behaviour with the ability to regain complete structural integrity and mechanical strength.

These novel ultra-soft, high-k liquid filler-based polymer composites, reversible rigidity composites and transparent and integrable device architectures for field-driven soft actuators could pave the way for next generation applications such as shape morphing, adaptive surfaces and transparent haptic devices.

Acknowledgements

First and foremost, I would like to express my sincere gratitude and thanks to my supervisor, Associate Professor Nripan Mathews, for his continuous support and invaluable guidance through the course of my dissertation. I am thankful to him for providing a congenial and motivating research environment. I am obliged to him for contributions of time, ideas, and funding that has made my research experience productive and fulfilling.

I would like to take this opportunity to sincerely appreciate the constant feedback, critical reviews and valuable advice from members of my Thesis Advisory Committee.

I would like to express my thankfulness to Nanyang Technological University, Singapore and School of Materials Science and Engineering for supporting me with the research scholarship, all the facilities and the conducive research environment. I would like to extend my appreciation to the technical and administrative staff at the School of Materials Science and Engineering for helping me in my endeavour.

This journey would not have been possible without the constant support of the current and alumni members of the Mathews Research Group, with special mention to Naveen Tiwari, Dr John Rohit Abraham, Mohit Kulkarni, Dr Nguyen Anh Chien and Dr Amoolya Nirmal. I would like to thank all of them for their time for constant discussions and helpful advice. I would also like to express my appreciation for the support and help I got from the administrative staff, my seniors and my friends at Energy Research Institute @ NTU, Singapore.

I would also like to thank the undergraduate students, Febby Krisnadi, Nguyen Linh Lan, Chan Jun Yu, Muhd Iszaki Bin Patdillah, Marco and Fanny Ho who have worked with me on different projects. Their intriguing questions, constant support, helpful suggestions and never-say-die attitude are truly appreciated.

Above all I would like to thank my family and my friends for their constant love, support, and unwavering belief in me, without whom all this would have been impossible.

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Figure Captions

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Figure 3.2 Fabrication of thin film hydrogels. Schematic for sequential procedure for curing conducting hydrogel on top of the glass substrate of required thickness.

Figure 3.3 Chemical structure of EMIMTFSI. Chemical structure of the ionic liquid, EMIMTFSI (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) showing the cation and the anion part. 3-D schematic of the chemical structure and bond orientation is also provided.

Figure 3.4 Schematic of the fabrication of reversible rigidity composite using acrylic elastomer. Elastomer pouch is created by using a 250 μm thick acrylic tape and sticking it at 3 of its edges. After filling the phase change filler, the pouch is sealed off at the 4th edge as well. Inherent stickiness of the acrylic tape keeps the pouch sealed.

Figure 3.5 Schematic of the fabrication of reversible rigidity composite using silicone elastomer. PDMS is cured in a 3D printed mold to provide the desired shape. It is then filled with the melted phase change material and allowed to solidify. Finally, a thin layer of PDMS is cured on top to seal the composite.

Figure 3.6 Biaxial stretching of the acrylic elastomer (VHB 4910). Elastomer film is placed on the grips of the machine and held in place using acrylic grips. The film is biaxially stretched to 3 times its initial value. A circular rigid frame is then placed on the stretched membrane and the film is taken out on the rigid frame.

Figure 3.7 Device fabrication for transparent surface texture change device. Stepwise fabrication details for a transparent haptic device. Hydrogels of required dimensions are cured directly in the cleaned glass substrate and then a biaxially pre-stretched elastomer membrane is placed on top. Top electrodes are patterned through spray coating followed by curing of a top soft layer.

Figure 3.8 Typical stress strain curve for a polymer film undergoing uniaxial tensile tests. Stress-strain curves provide a lot of useful information and parameters about the mechanical properties of the polymer like Young's modulus, mechanical stiffness and stretchability (ultimate strain at fracture).

Figure 3.9 Polarization mechanisms versus frequency range. Dielectric spectroscopy provides information on different polarization mechanisms contributing to the complex permittivity at different frequency ranges.

Figure 3.10 General setup for measurement of absorption and transmission spectra in UV-Vis spectroscopy. Transmission measurements rely on measuring the intensity of light passing through a sample and compare with the intensity of the light passing through the reference.

Figure 3.11 Typical DSC curve. A typical DSC curve plotting the heat flow with respect to temperature showing thermal transitions like glass transition, crystallization point and melting point.

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Figure 3.13 Setup for frequency bandwidth characterization. Non-active region of the device is kept in contact with the tip of the force gauge. Square wave pattern is fed by function generator the high voltage amplifier, which in turn amplifies the input signal and provides a frequency dependent input to the sample. The measurement is carried out on a vibration isolation table; and the sample is held in place using double sided foam tape.

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Abbreviations

AAm	Acrylamide
AgNW	Silver nanowire
AP	Ammonium persulfate
ASTM	American Society for Testing and Materials
BaTiO ₃	Barium titanate
BN	Boron nitride
CaCu ₃ Ti ₄ O ₁₂	Calcium copper titanate
CNT	Carbon nanotube
CP	Conductive polymer
CuPc	Copper-phthalocyanine
<i>d</i>	Thickness of the elastomer,
DBSA	Dodecyl benzene sulfonic acid
DE	Dielectric elastomer
DEA	Dielectric elastomer actuators
DI H ₂ O	Deionized water
DS	Dielectric spectroscopy
DSC	Differential scanning calorimetry
EAP	Electroactive polymer
EGaIn	Eutectic Gallium Indium
EMIMTFSI	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
ERF	Electrorheological fluid
ϵ_1	Dielectric constant of the matrix
ϵ_2	Dielectric constant of the filler material
ϵ_c	Effective dielectric constant of the composite
FA I	Fast adapting type I
FA II	Fast adapting type II
FGS	Functionalised graphene sheet
FOM	Figure of merit
FTIR	Fourier transform infrared

HASEL	Hydraulically amplified self-healing electrostatic
IL	Ionic liquid
IPA	Isopropyl alcohol
IPMC	Ionic polymer-metal composite
IR	Infrared
kHz	Kilo Hertz
kPa	Kilo Pascals
kV	Kilo Volts
$k\Omega/\square$	Kilo ohms per square
L	Elastocapillary length
LCE	Liquid crystal elastomer
LM	Liquid metal
LMEE	Liquid metal embedded elastomer
LMPA	Low melting point alloy
M	Molar (Unit of Molarity)
MBAA	N, N' – methylenebisacrylamide
MPa	Mega Pascals
MRF	Magnetorheological fluid
MW	Molecular weight
MWCNT	Multiwall carbon nanotube
N	Newton
NaCl	Sodium chloride
$\emptyset$	Volume loading of the inclusions
OM	Optical microscopy
p	Maxwell stress
P(VDF-TrFE)	Poly (vinylidene fluoridetrifluoroethylene)
P3HT	Poly (3-hexylthiophene)
PAAm	Polyacrylamide
PANI	Polyaniline
PDMS	Poly(dimethylsiloxane)
PEDOT: PSS	Poly- (4,3-ethylene dioxythiophene): poly(styrene-sulfonate)

PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PHR	Parts of filler per hundred parts of the polymer matrix
R	Average radii of the liquid inclusion
RH	Relative humidity
S	Actuation strain produced in the thickness direction
SA I	Slow adapting type I
SA II	Slow adapting type II
SEBS	Styrene Ethylene Butylene Styrene Block Copolymer
SEBS-g-MA	Polystyrene-co-ethylene-co-butylene-co-styrene-grafted maleic anhydride
SEM	Scanning electron microscopy
SWCNT	Single-walled carbon nanotube
T_c	Crystallization point
TEMED	N, N, N', N' – tetramethylethylenediamine
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TiO ₂	Titanium dioxide
T_m	Melting point
TPU	Thermoplastic polyurethane
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
V	Applied voltage
v_2	Volume concentration of the filler particle
VHB	Very high bond strength
Y	Young's modulus
Y_c	Effective moduli of the composite
Y_i	Approximated moduli of the liquid inclusions
ϵ'	Real part of the relative permittivity (dielectric constant)
ϵ''	Imaginary part of relative permittivity
ϵ_o	Permittivity of vacuum
ϵ_r	Relative permittivity (dielectric constant)

γ Surface tension

Chapter 1

Introduction

This chapter introduces the field of soft robotics with a brief discussion of different technologies employed for actuation. Advantages of an electrically controlled actuation is highlighted, and focus is brought to the area of dielectric elastomer actuators. Specific application, where these soft actuators have advantage over traditional actuators, is identified. Traditional strategies adopted for improving the electro-mechanical performance of dielectric elastomer actuators are discussed, followed by identifying the shortcomings in the current approaches. Objectives and scope of the dissertation are thus identified following the motivation for the research. It is identified that novel material systems and device configurations are needed to bring significant improvements in the actuation performance of these electrically controlled soft actuators and lend novel capabilities to shift their actuation behavior closer to their natural counterparts. The research objective of this work is to investigate novel liquid fillers for fabricating functional polymer composites with desirable material properties for utilization as the active matrix in dielectric elastomer actuators and investigate novel device configurations that could make them more integrable. The motivation is to mitigate the detrimental effects of conventional solid filler approach and current device configurations and elucidate the effect of liquid filler-polymer composites and novel device configuration on the actuation performance of dielectric elastomer actuators. Subsequently, the hypotheses are listed, and approaches followed for verifying them are detailed. The last section of the chapter provides a synopsis of the framework for the dissertation with a preface for each chapter, ending by highlighting the major findings and outcomes.

1.1 Overview

When the word robot is mentioned, the first thing that comes to our mind are the images of the rigid, motorized robots; be it the industrial robotic arms conventionally used for large scale precise manufacturing or the humanoid robots developed by Boston dynamics and Honda. There have been many developments in the field of robotics, leading to the advanced humanoids as we know today. Industrial automation has been the most successful application of the field of robotics so far. They have managed to reduce human effort tremendously, perform complex tasks with precision and enable mass production to meet rising demands worldwide. But these traditional, hard robots have their intrinsic limitations. One of the major shortcomings is the lack of mechanical compliance. Since they are made from conventionally hard materials, they fail to provide a safe and comfortable physical interaction with humans, which requires compliance matching at the point of contact (Figure 1.1-A). Furthermore, owing to their bulky design and use of several rigid components to produce motion, they lack the dexterity and fluidity to produce complex motions. Additionally, the number of components needed grows exponentially with increased dexterity of the desired outcome. Because of the above-mentioned limitations, rigid robots are fairly unsuitable for many applications such as food handling, human-machine interfacing, space exploration and underwater marine observations to mention a few.

Figure 1.1 Motivation for soft robotics. (A) Human machine interaction necessitates the interface at the point of to be soft and comfortable.¹ (B) An image showing the versatility of the biological systems to produce complex motions in a fluidic fashion.¹ (C) Mechanical

stiffness (approximated) for common engineering and biological materials. Soft robots are primarily composed of materials having mechanical stiffness comparable to soft biological materials like skin and muscles.²

Nature has always been the source of inspiration for the scientific community and the researchers to make ever-more capable machines. Biological systems make use of their inherent softness, structural compliance and integrated sensing to produce fluidic motion with reduced complexity in their interaction with the environment (Figure 1.1-B). These natural systems are elegant in design with fewer components involved and have the ability to interact with unknown and unstructured environment in a non-disruptive manner. While most engineering materials conventionally used in robotics have very high mechanical stiffness (10^9 - 10^{12} Pa), natural organisms are composed of biological materials with low mechanical stiffness (10^4 - 10^9 Pa) (Figure 1.1-C).² An emerging area of robotics, that promises to address the issues of rigidity and non-dexterity in conventional robots and mimic the systems found in nature, is the field of soft robotics. Soft robots are composed of soft materials; inspired by the biological systems found in nature. Soft robots offer the advantage of being highly versatile; they can manoeuvre through constrained locations and adapt their motions accordingly in rugged terrains, for they can flex and turn with high curvatures and great fluidity. These soft actuators are capable of mimicking the natural systems intimately.

Popular strategies adopted for achieving actuation in soft robotics involve the use of embedded pneumatics and fluidics, thermally activated polymers, magnetic fields, chemical reactions and electroactive polymers (Figure 1.2).³⁻¹³ The pneumatic and fluidic systems have embedded channels that are designed to create a specific complex movement with a single source of applied pressure. These systems are very lightweight and can produce complex motion via a combination of crawling and undulation. However, the technology that powers most of today's soft robotics requires complex, noisy air and fluid compressors, hard-to-control valves and awkward hoses which limit mobility and possibility for developing untethered systems. One of the preferred actuation technologies are based on electroactive polymers (EAPs), the family of polymers which respond to electrical stimuli by change in shape or size. The biggest advantage of these systems is the possibility of untethered, autonomous operation, easily controllable by the applied electrical stimuli. This makes them an attractive choice for actuation in soft robotics. Dielectric elastomer actuators (DEAs), under the

family of electronic EAPs, are of particular interest owing to their ability to produce very large actuation strains (greater than 100%).⁸ DEAs in their simplest configuration are variable capacitors, in which a soft elastomer membrane is sandwiched between compliant electrodes (conductive and stretchable with the membrane).^{8, 14} DEAs are easy to fabricate, compared to their counterparts in the EAP family, and can be done at low cost.

Figure 1.2 Popular actuation strategies in soft actuators. (A) Pneumatic actuators.^{11, 15} Pneumatic actuators make use of embedded hoses to apply pressure and require bulky

components like air compressors. (B) Thermally driven actuators.^{10, 12} Thermally driven actuators suffer from energy losses and sluggish actuation times. (C) Dielectric elastomer actuators (DEAs).^{13, 16} DEAs are an attractive actuation technology owing to electrical control and large actuation strains accompanied with facile fabrication.

Soft actuators have been demonstrated successfully to perform designated tasks with superior dexterity and flexibility in a variety of applications such as soft robots, versatile grippers and artificial muscles to name a few.^{10, 16-18} One of the specific areas of application, where soft actuators can outperform the conventional actuator technologies is the field of adaptive surfaces.^{14, 19-22} The area of adaptive surfaces is gathering attention owing to their important role in enhancing the experience at human-machine interface, assisting in optical manipulation through metasurfaces and mimicking shape morphing behaviour found in nature. In particular, adaptive surfaces are poised to play a significant role in enabling superior haptic technologies. Haptics, which refers to perception of objects by sense of touch, is critical specially for humans, owing to its role in feeling the world around us and sorting of information.²³ Haptics has come to the forefront of research focus due to their significant impact on human-machine interaction, which grows to become ever so important owing to rise of technologies like touch-sensitive devices, robotics, medical prosthetics, virtual reality and augmented reality.¹⁴ However, most of the currently adopted technologies like vibration motors and piezoelectric actuators²⁴ create the tactile sensation by simulation of the senses rather than creating actual topographical changes on the surface. Some of the newer technologies like TESLATOUGH, which creates a tactile sensation on the screen by electrovibration, Ambient touch, which creates complex vibrotactile patterns and AIREAL, which hits the user's hand with air vortexes for a force sensation in virtual environments, also aim for sensory manipulation (Figure 1.3). Additionally, these are single actuators requiring an array of them to be assembled for conveying multiple information and do not provide localized feedback to the users. Furthermore, the device architectures for these haptic technologies does not allow for a seamless integration and are cumbersome to be fabricated in flexible configurations for wearable applications. Among various soft actuator technologies, DEAs stand out due to their capability to produce actual topographical changes on the surface for tactile feedback. Haptics enabled by DEAs lends specific advantage of superior control (by electrical stimuli) and untethered actuation. Additionally, their thin film architecture can enable

an integrable and flexible device for haptic applications. However, in their current form, DEAs are non-integrable, have limited actuation performance, need complicated fabrication for defect-free integration of multiple layers and face many of the issues alike conventional haptic technologies.

Figure 1.3 State of the art for haptics. Most to the existing haptic technologies like vibration motors aspire to simulate the perception of texture change to convey the tactile information. Even the recent advances in haptics like TeslaTouch, Aired and Ambient touch have focused on sensory simulation rather than producing actual topographical changes.²⁵⁻²⁷ Additionally, they lack the feature of localized feedback and necessitates background integration owing to their bulky and obstructive architecture.

Furthermore, from a materials perspective, the actuation performance of DEAs depends on intrinsic material properties like relative permittivity (dielectric constant) and Young's modulus (mechanical stiffness) of the active elastomer (Figure 1.4). Conventionally used elastomeric matrices have low dielectric constant and high mechanical stiffness. Current approaches for improving the performance of DEAs look at either increasing the relative permittivity or reducing the mechanical stiffness of the elastomer matrix by chemical modifications of the elastomeric backbone or fabricating composites with high solid fillers.²⁸ However, chemical modifications are complex and time-consuming fabrication steps with some long-term stability and reliability issues. Solid fillers, on the other hand, lead to undesirable increase in the mechanical rigidity of elastomer matrix, making effectively no contribution to the overall improvement on the electro-mechanical performance.

Figure 1.4 Material parameters on which performance of DEAs depend.²⁸ The actuation performance of dielectric elastomer actuators is directly proportional to material's dielectric constant and inversely proportional to the Young's modulus.

Finally, appropriate choice of material systems for active elastomeric matrix and compliant electrodes could provide specific performance advantages for these field driven soft actuators, DEAs. Transparent compliant electrodes in combination with transparent elastomers could enable a DEA device with desirable features like transparency in addition to already existing attribute of electrical modulation, which would facilitate integration with real life applications. However, existing DEAs primarily make use of carbon-based compliant electrodes and rigid frames, which limits their integration. Additionally, imbuing soft robots with the ability to modulate their mechanical properties will allow them to mimic nature at even closer level. Biological appendages, which make perfect exemplars of actuators that we aspire to replicate, not only can produce fluidic motion but also have the ability to modulate their mechanical properties making them highly versatile. This particular attribute allows them to adapt to different surface contours, handle objects of different rigidities, and manipulate things with great dexterity. However, current generation of soft actuators lack this important attribute. Existing approaches require amalgamation of a passive component/device with the soft actuators, which does not contribute directly to the actuation and makes the actuator bulky and the fabrication process complicated. Hence, these factors call for investigations into novel material systems which can enable reversible rigidity and contribute directly to the electro-mechanical performance of DEAs with an aim of improving it.

1.2 Problem Statement

Soft robotics is an emerging field of research that makes use of soft materials to mimic fluidic motion produced by biological organisms. DEAs are versatile soft actuators that can produce large actuation strains, are electrically controllable and enable easy fabrication; and are promising candidates for adaptive surface applications. However,

currently used device configurations limit the integrability of DEAs for such applications. Even in their current configurations, the performance of the DEA based actuators are limited by the conventionally utilized material systems. While elastomeric matrices suffer from intrinsic material limitations, currently used compliant electrodes are non-transparent, rendering the devices non-suitable for many applications. The conventional approaches to improving the actuation performance of DEAs are quite limited. Whilst trying to improve the actuation performance of DEAs, alteration in one of the material properties, dielectric constant or mechanical stiffness, leads to undesirable effect on the other, offsetting the intended improvement to device performance. Addition of passive components for enabling rigidity modulation makes them bulky and their fabrication complex.

Hence, for making DEAs more versatile and suitable for real-life applications, and to bring them closer to biological systems in terms of actuation behaviour, novel device arrangement for DEAs is required to improve their integrability and enable transparent device architectures; along with new approaches to alter the material properties to produce synergetic effects on the electro-mechanical properties and enable an intimate integration of the ability to reversibly modulate rigidity within DEAs.

1.3 Objectives and Scope

Moving away from the conventional approaches adopted for providing solutions to the problems identified above, the primary approach of this dissertation is to investigate novel material systems and novel device configuration to improve the performance of DEAs, make them more integrable and imbibe them with abilities to mimic biological systems closely. A novel approach of using liquid fillers is explored that can produce synergetic effects on the electro-mechanical properties of the active elastomeric layer in DEAs and to lead to enhanced actuation performance. A novel device configuration is explored for making DEAs more transparent and integrable compared to their current forms and enable an electrically controlled adaptive surface. Additionally, a new material system is investigated to imbibe DEAs with the ability to reversibly modulate rigidity and make them actuate in a way resembling their biological counterparts.

Study of conventionally used elastomeric matrices and compliant electrode systems for DEAs is carried out initially to understand and benchmark the material properties and actuation behaviours. Different liquid fillers and their nature of interaction with the

elastomeric material are investigated, establishing their importance in final resulting composite and its properties. Choice of an ionic liquid with high dielectric constant and high thermal stability is made for a self-contained liquid-filler polymer composite. These composites exhibit superior material properties and are utilized to realize field driven soft actuators with improved actuation performance. A novel device configuration is realized making use of transparent and conventional compliant electrode systems for demonstrating programmable surface deformations using integrable DEA devices. Finally, to imbibe the DEAs with intrinsic reversible rigidity, a low temperature phase-changing material is identified for fabricating bulk composites. The composites show reversible stiffening and flexing behavior and superior actuation capabilities in a DEA configuration.

Specific objectives of this dissertation include the following:

1. Investigate the conventionally used elastomeric matrices, acrylates and silicones, for their material properties like dielectric constant and mechanical stiffness. This is needed since several reports on dielectric and mechanical properties of the conventional elastomeric materials, revealing different material parameters, suggesting a direct impact of the environmental conditions on them. Subsequently, evaluate the performance of traditionally used carbon-based electrodes and novel compliant electrode systems, silver nanowires network and conductive hydrogels, in terms of actuation strains realized and compliancy versus conductivity. Compare the electrode systems and establish their specific advantages and disadvantages. Identify a suitable elastomeric matrix for further composite fabrication.
2. Predict the electro-mechanical properties of liquid-filler polymer composite using theoretical models. Evaluate high dielectric constant liquid fillers like 1-Ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) Imide (EMIMTFSI) and water for self-contained liquid filler polymer composite fabrication based on the nature of interaction. Establish the suitable filler for further studies and composite fabrication. Investigate the electrical and mechanical properties of the fabricated composite and compare with the pristine matrix. Investigate the stability of these composites. Demonstrate the application of the composite in a DEA configuration. Calculate the actuation performance and compare with the acrylate elastomeric matrix.

3. Demonstrate a novel device configuration for DEAs for realizing transparent and electrically controllable adaptive surfaces using acrylate elastomeric matrix. Investigate the device's physical attributes and actuation performance. Demonstrate the capability of the novel DEA architecture for improved integrability and versatility. Demonstrate the ability of novel fabricated composites for developing other adaptive surface configurations.
4. Identify a suitable low-temperature phase change filler for enabling reversible rigidity modulation by evaluating material systems like paraffin wax and polyethylene glycol (PEG). Investigate the modulation of mechanical properties of the fabricated composite, controlled by melting and solidification of the PEG. Quantify the reversible rigidity behaviour in terms of variation of mechanical properties like Young's modulus, flexural modulus and hardness. Integrate with a heating element for electrically controlled phase change and reversible rigidity modulation; and characterize the heater for its performance characteristics.

Note: - This dissertation focusses on developing the strategies for novel material composites with desirable electro-mechanical properties and phase change behavior separately. Although this is the initial step towards next generation soft actuators, fabrication challenges in terms of integration of all individual material systems in the final demonstrated device configuration has not been tackled and lies outside the scope of this dissertation.

1.4 Hypotheses

This dissertation attempts to address specific scientific hypotheses which are listed below.

1.4.1 A liquid filler-polymer composite approach can simultaneously improve the dielectric constant and mechanical deformability.

An appropriate choice of high dielectric constant liquid filler, having favorable compatibility with the elastomer matrix, can result in a homogeneous self-contained liquid-filler polymer composite with desirable dielectric and mechanical properties, resulting in enhanced electro-mechanical performance of DEAs.

1.4.2 Coupling of a soft layer with a DEA and appropriate design choice for compliant electrodes could enable an integrable device configuration for adaptive surface.

Intimate coupling of a soft polymeric layer with a DEA could capture the strains produced in the active layer upon application of electric field and produce detectable surface deformations. Proper design of compliant electrodes could allow for the device to be integrated with both rigid and flexible substrates, improving the integrability of such devices.

1.4.3 High-k, Low temperature phase change filler for bulk composites can enable reversible rigidity modulation.

A low temperature phase change material employed as an active matrix in a DEA configuration could lend these actuators versatility and bring their actuation behavior closer to their natural counterparts. The introduction of such a material could enable the property of reversible rigidity modulation enabling the DEAs to change their stiffness and flexibility on demand.

1.5 Organization of thesis

- Chapter 1 provides an introduction to the field of soft robotics and details the motivation for choosing dielectric elastomer actuators. Then the problem statement for this research is identified, objective and scope are clearly defined and hypotheses that this dissertation attempts to address are laid out. A preface to the arrangement of the dissertation is provided. Finally, the critical findings are highlighted, and original contributions are indexed.
- Chapter 2 provides a brief introduction to the family of electroactive polymers followed by a detailed insight into the field of dielectric elastomer actuators identifying the critical parameter affecting their performance. A critical review of the literature is presented concerning the recent advances in the field of dielectric elastomer actuators and approaches for improving their actuation performance. Research gaps are clearly identified for development of new material systems justifying the motivation for this work.
- Chapter 3 discusses the rationale behind the selection of materials chosen for study under the scope of this dissertation. It describes the steps involved in material and

device fabrication. It also details about the various characterization techniques employed.

- Chapter 4 illustrates the electro-mechanical properties for conventionally used elastomeric matrices, acrylates and silicones, in DEA configuration. Performance of traditionally used carbon powder electrodes and novel compliant electrode systems; carbon powder-paste hybrid electrodes, silver nanowires network and conductive hydrogels; is measured and compared in terms of actuation strains realized and compliancy versus conductivity. Based on the measurements, silicone is established as a suitable elastomeric matrix for further composite fabrication and novel compliant electrode systems are chosen based on their suitability for the application.
- Chapter 5 investigates the synergetic changes in the dielectric and mechanical properties of the composite by addition of an ionic liquid (EMIMTFSI) to the silicone polymer matrix as self-contained fillers. Design of such a material system based on theoretical models is predicted. It also illustrates the critical role of nature of interaction between the liquid filler and the polymer matrix in determining the resulting composite's morphology and characteristic properties. Stability of these composites is evaluated. Comparison of the actuation performance of these composites against the conventionally used acrylic matrix is done for benchmarking the improvements achieved by addition of ionic liquid fillers.
- Chapter 6 discusses the novel device configuration enabling the seamless integration of DEAs for adaptive surface applications. Design principles for the device architecture and underlying principles are explained. An all transparent configuration is realized and characterized for its actuation performance, accompanied with benchmarking against non-transparent electrode systems. Specific advantages of localized activation, large detectable deformations and integration with rigid and flexible substrates are demonstrated. Possible utilization of new fabricated composites for adaptive surface applications is also demonstrated.
- Chapter 7 examines the material property of low temperature high-k phase change materials and identifies PEG as a suitable choice for the bulk composite fabrication. Reversible stiffening and flexing behavior of the fabricated composite are examined and benchmarked against some common engineering materials. This is done by quantifying the reversible rigidity behavior in terms of modulation of Young's

modulus and Flexural modulus. Electrical control of the reversible rigidity behavior is investigated by integration of a flexible heating element with the composite accompanied with the physical characterization of the heating element.

- Chapter 8 summarizes the results and findings of the dissertation, also highlighting the possible shortcomings. Conclusions are drawn to validate the hypotheses put forward in the Chapter 1. A brief perspective is provided for the future direction with a focus on approaches to amalgamate different material systems in a single device configuration and ways to mitigate the shortcomings.

1.6 Findings and Outcomes/Originality

The findings and outcomes of the dissertation highlighting the original contributions are listed below:

1. Drawing inspiration from nature, a liquid filler strategy is adopted for fabricating novel functional composites. Novel self-contained liquid-filler composites have been successfully fabricated using EMIMTFSI, an ionic liquid, as filler for silicone elastomeric matrix resulting in two-fold increase in the dielectric constant accompanied with 100 times reduction in the mechanical stiffness, in comparison to the pristine polymer matrix. Owing to the favorable interfacial interaction, composites demonstrate 5 times improvement in the stretchability as well. These composites show superior thermal stability showing no degradation effects at high temperature (200°C) for prolonged duration (60 minutes); and stability against moisture uptake showing no weight change for 12 days at 60% RH. In addition, there is negligible change in the thermal degradation behavior. Owing to the appropriate choice of filler, these composites show high transparency (80%) even at high filler loadings (20%). When utilized in a DEA configuration, the composites demonstrate superior actuation performance with 2.5 times improvement in longitudinal strains and 4 times enhancement in areal strain compared to conventional acrylic elastomer, at half the applied electric fields. Their actuation behavior resembles that of their natural counterparts.
2. Novel device configuration for DEAs is successfully demonstrated enabling highly integrable devices; compatible with both rigid and flexible substrates. This is made possible by utilizing the unique thickness mode actuation of DEAs. An all transparent adaptive surface DEA device is realized demonstrating high

transparency (76%) in the visible region of the spectrum. Evaluation of the actuation performance in terms surface deformations produced and blocked force output is done, revealing superior out-of-plane deformations (0.16 mm, 160 μm) and high blocked force output (47 mN), well above the detectable thresholds of receptors in our fingers. Further characterizations show the frequency bandwidth of the device as 20 Hz (for similar performance) and 1000 Hz (for half the value of maximum output), limited by the material systems used and not the design or electrical circuitry of the device. A design approach to improve the actuation performance is demonstrated by stacking of 3 active layers, leading to a surface deformation of 0.3 mm (300 μm) and a blocked force output of 90 mN. Specific advantages of the device configuration such as localized feedback, pixelation of large area devices and flexibility are highlighted through demonstrations.¹⁴

3. A low temperature high-k phase change matrix, PEG, is identified as suitable material for fabricating bulk composites to serve as active layer in a DEA configuration. Investigations reveal specific material properties like high dielectric constant (~ 10 @ 1 kHz), high compressive strength (failure @ 244 N for 0.58 mm compression), low temperature melting ($\sim 55^\circ\text{C}$) and wider temperature operating window (temperature between melting and solidification, $19^\circ\text{C} - 55^\circ\text{C}$) which makes PEG an attractive option. Reversible modulation of mechanical properties of the fabricated composite are evaluated, with the composite showing ~ 700 times modulation in Young's modulus, ~ 100 times modulation in flexural modulus and ~ 10 times change in Hardness value between rigid and soft state. Flexible heating elements are printed and characterized for their performance. Following that, the heating element is integrated with the composite and electrically controlled phase change and reversible rigidity modulation is demonstrated. Owing to its unique material properties, PEG stands out as a suitable candidate for electrically driven actuators, imbuing them with reversible mechanical properties, enabling a soft actuator for the first time with the ability to modulate its mechanical parameters without the need of a passive element.

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Chapter 2

Literature review

This chapter provides a critical review of the literature regarding recent advances in the field of dielectric elastomer actuators (DEAs), their utilization in different applications and ways adopted to improve their performance. First, an overview of different categories within the family of electro-active polymers (EAPs) has been provided. Working principle of DEAs, factors effecting their performance and recent advances in the field of DEAs has been discussed next. Then, a critical discussion about the conventional material systems utilized in the DEAs has been presented. This is followed with a critical review of the strategies adopted so far for improving the performance of DEAs concerning the modification of the material systems. Next, an overview of the literature on the utilization of liquid fillers for fabrication of functional composite materials has been given, followed by the critical review of literature for reversible rigidity strategies adopted for DEAs. The section ends with identifying the research gaps found during literature review and questions that this dissertation attempts to address.

2.1 Electroactive polymers (EAPs)

Electroactive polymers (EAPs) are polymers/elastomers that respond to an electrical stimulus by exhibiting change in shape or size.¹ Based on their underlying actuation mechanism, polymers belonging to the family of EAPs are broadly classified into 2 categories.²

Ionic EAPs

In ionic EAPs, actuation is caused by the movement of ions under the application of electrical stimuli.² Diffusion of ions across a solid or wet electrolyte is driven by an external electric field and produces electro-mechanical changes in the material's configuration. There are different sub-categories under the family of ionic EAPs. Ionic polymer-metal composites (IPMCs) comprise of an ion-exchange polymer membrane which has been swollen by a solvent.³ The membrane is sandwiched between electrodes on either side.³ Upon application of voltage, movement of mobile ions to the oppositely charged electrode within the membrane takes place.³⁻⁴ This leads to swelling of one side of the membrane while the other side contracts; resulting in a bending motion.⁴ They require low voltages of operation but suffer from low actuation strains, need for encapsulation and slow response speeds which limits their application. Ionic polymer gels are formed by crosslinking a polymer, like polyacrylic acid solution, in an electrolyte solution.⁵ They produce actuation by swelling and deswelling of the gel caused by the diffusion of ionic species.⁵ The actuations are small and response speeds are slow added to the need for encapsulation of the device. Another category in ionic EAPs is based on carbon nanotubes (CNTs), in which CNTs are dispersed in an electrolyte and are capable of elongating in length due to double-layer charge formation upon application of bias.⁶ Application of voltage between the CNTs and a counter electrode leads to movement of the ions to the surface of the CNTs, the formation of a double-layer at the CNT-electrolyte interface which induces quantum-chemical effects in the CNTs.⁶ Quantum chemical effects cause the carbon-carbon bond lengths to vary with injected charge, resulting in nanotube dimension variation.⁶⁻⁷ This mechanism offers the advantage of higher lifetime and faster actuation rates compared to other ionic EAPs as it does not involve ion intercalation but poses difficulty in terms of cost and manufacturability. Conductive polymers (CPs) produce actuation by expanding vertically to the direction of the polymer chain, caused by the uptake of counter-ions

during electrochemical redox cycling, and incorporation of ions and solvent between the polymer chains.⁸ They suffer from poor coupling efficiencies and sluggish actuation speeds.

Electronic EAPs

Electronic EAPs are driven by electric field or Coulomb forces.⁹ Electrostatic forces arising due to applied electric field leads to mechanical changes in shape and size of the material. Under the category of electronic EAPs, there are different sub-categories. Ferroelectric polymers are polymers with a non-symmetric structure having a permanent electric polarization.¹⁰ Dipoles present in the material can be aligned under the influence of an applied electric field and resort back to their original polarization upon removal of the field. Ferroelectric polymers have worse piezoelectric actuation properties compared to that of the ceramic piezoelectric crystals, but they provide the advantage of being lightweight, formable and flexible.¹¹ Polymer electrets are dielectric materials having a non-uniform space charge distribution resulting in them showing piezoelectric effects.¹² A highly porous polymer with a polarization gas is subjected to corona charging (at voltages ranging 5-10 kV) resulting in build-up of charges at the gas-polymer interface.¹² Opposing charges will get aligned on opposite sides of the pore under the influence of the applied electric field, forming macroscopic dipoles.¹² Upon application of voltage across the electrodes placed on either side of the film, a change in thickness of the material leads to observable actuation.¹² Electrostrictive polymers are polymers with molecular or nanocrystalline polarizations that can be aligned under the influence of the electric field; they have a spontaneous electric polarization.¹³ Actuation in electrostrictive polymer is the result of the variation in the dipole density of the polymer when placed in an electric field. Liquid crystal elastomers (LCEs) are combination of elastomeric networks and liquid crystals.¹⁴ They possess the orientational ordering properties of liquid crystals in conjunction with the elastic properties of elastomers.¹⁴ During a phase transition, the reorientation of mesogens in liquid crystals leads to significant bulk stresses and strains.¹⁵ Elastomer network permits for the rotation of the mesogens without allowing the free flow and maintaining a solid shape, leading to observable actuation.¹⁵ Dielectric elastomer actuators (DEAs) are group of polymers that provide actuation on the principle of Maxwell stresses.¹⁶ They are of particular interest for their ability to produce very large actuation strains, ease of fabrication and lower costs.¹¹ Owing to these reasons, the focus of this

dissertation is on the dielectric elastomer actuators and has been explained in detail in the next section.

2.2 Dielectric elastomer actuators (DEAs)

Figure 2.1 Basic configuration of DEAs. DEA resembles a compliant capacitor in its architecture, with an elastomeric layer sandwiched between two compliant electrodes.¹⁷ Upon application of voltage, electric field induces charges on opposing sides and resulting electrostatic force induces stress in soft material.¹⁷

Dielectric elastomer actuators (DEAs) belong to the family of electronic EAPs and are known to produce high actuation strains.^{1, 17-20} DEAs in their simplest configuration, resembles a variable capacitor with an elastomeric layer sandwiched between compliant electrodes on either side.^{17-18, 21-22} They work on the principle of Maxwell stresses, which is induction of stress due to electric field pressure from the free charges on the surface of insulating material.¹⁷⁻¹⁸ The induced Maxwell stresses depend on external stimulus like applied electric fields, thickness and area of the sandwiched region; and intrinsic material property like relative permittivity and Young's modulus.¹⁷⁻¹⁸ Compliancy of electrodes (the ability of conducting material to stretch out with elastomeric film while maintaining the conductivity) is extremely critical for the performance of DEAs.¹⁷⁻¹⁸ The elastomeric area which overlaps the compliant electrodes is referred to as the active area and the surrounding area is the inactive area.¹⁷⁻¹⁸ Under applied electric field, the active area experiences compressive Maxwell stresses forcing the sandwiched elastomeric film to stretch out, hence providing in-plane deformation.¹⁷⁻¹⁸ The effective Maxwell stress (p) acting on the material and the relationship of material parameters and operating conditions with actuation performance for DEAs can be broadly understood with the help of following equations, where p is the electrostatic stress, ϵ_r is the relative permittivity (dielectric constant) of the elastomer, ϵ_o is the permittivity of vacuum, V is the applied voltage, d is the

thickness of the elastomer, S is the actuation strain produced in the thickness direction, and Y is the Young's modulus of the elastomer.^{16-18, 23-24}

$$p = \epsilon_o \epsilon_r (V/d)^2 \quad (1)$$

$$S = p/Y = \epsilon_o \epsilon_r (V/d)^2 (1/Y) \quad (2)$$

Figure 2.2 Few of the recent advances in DEAs. (A) Schematic of actuation produced in a HASSEL actuator as the applied voltage is increased gradually.²⁵ (B) Schematic showing the deformation of the actuator to create a donut shape upon application of voltage and this can be used to apply force onto an external load.²⁵ (C) Muscle-like configuration of a contracting DEA attached to the replica of human arm bones by rigid metallic wires.²⁶ (D) Applied voltage actuates the device, producing a contracting motion lifting the arm, with similar behavior to a human bicep muscle.²⁶ (E) Image showing the construction of such a contracting actuator, with multiple stacks of active elements (dark grey) alternating with passive elements (light grey) for enhanced adhesion.²⁶ (F) Zoomed-in image of a few stacks of actuators; each individual stack constructed with 25 dielectric elastomer layers.²⁶ (G) Fabrication sequence for such multilayer stack actuators.²⁶

Owing to the intrinsic advantages of DEA configuration for soft actuators, different applications have been made possible. Field driven actuation and significant strains generated by DEAs have allowed them to be utilized in applications such as artificial muscles, soft grippers, thin film speakers, adaptive surfaces, mechanically active cardiac tissue analysis and biomimetic fish robots.²⁵⁻³³ Acome et. al. demonstrated an artificial muscle making use of a DEA configuration, where the actuation was amplified hydraulically (Figure 2.2-A and Figure 2.2-B).²⁵ Electrostatic forces acting on a

dielectric fluid encapsulated in a chamber made from soft polymeric membranes manipulates the hydraulic pressure, enabling a versatile actuator with tunable strain and force output. Duduta et. al. demonstrated an artificial muscle made of multilayer configuration of DEAs achieved by careful stacking of several individual DEA devices (Figure 2.2-C to Figure 2.2-G).²⁶ These artificial muscles bear close similarity to their natural counterparts in terms of energy density and actuation strains produced.

As mentioned in the previous chapter, adaptive surface is one of the particular areas where soft actuators have significant advantages over conventional actuators.^{17, 30, 33-35} Significant role of adaptive surfaces has been identified in improving the user experience at human-machine interfaces by providing tactile feedback.^{34, 36} Whereas conventional haptics relies on sensory simulation, as seen in the previous chapter, electrical modulation of these adaptive surfaces through DEAs is more favoured owing to advantages of ability to produce actual topographical changes and greater control. Traditionally, the DEAs have been explored for haptic applications.³⁷⁻⁴¹

Figure 2.3 DEAs for haptics. (A) A DEA coupled with rigid link for tactile feedback.³⁸ (B) Hydrostatically coupled DEAs with augmentation of forces generated in active DEA layer through confined fluid.⁴² (C) Multiple layers stacked together to produce detectable deformations.⁴¹

Since the deformations produced in the active layer is quite small, researchers adopt the strategy of coupling DEAs with rigid components (Figure 2.3-A) or non-compressible fluids (Figure 2.3-B) to augment the deformations.^{38, 42} Stacking of multiple active layers (Figure 2.3-C) has also been investigated to simulate the perception of tactile

feedback by varying the pitch and amplitude of vibrations produced.³⁹⁻⁴¹ However, in their current form, they are non-integrable, are single actuators requiring an array of them to be assembled for conveying multiple information and sometimes need complicated fabrication for defect-free integration of multiple layers. Hence, novel device configuration for DEA needs to be investigated to make them more integrable and suitable for adaptive surface applications and haptics in particular. Recently, there have been a few other applications where for DEA based adaptive surfaces have been investigated.^{17, 21-22, 30, 33, 43}

2.3 Conventional material systems used in DEAs

Active elastomeric layer

For DEAs, two elastomeric materials have been conventionally utilized and explored exhaustively; acrylic elastomers and silicones, and both of them provide an equitable cluster of electro-mechanical properties desirable for such actuators.⁴⁴⁻⁴⁹ Most commonly used acrylic films are the commercially available VHB (very high bond strength) series from 3M Corporation, which are composed of mixtures of aliphatic acrylate based on the structure of a vinyl group and a carboxylic acid terminus.¹¹ They have been observed to have a relative permittivity of 4.5 – 4.8 (@ 1 kHz) and a theoretical energy density value of 3.4 MJ/m³.^{11, 50} They have managed to provide very large actuation strains demonstrating a suitable electro-mechanical performance.^{20, 24} However, these acrylic films necessitate the need for pre-stretching for superior electro-mechanical performance and display poor actuation strains without pre-stretch. Additionally, these commercially available acrylic films have significant viscoelastic behavior, which in turn shows up in their actuation performance in form of moderate response times and leads to gradual relaxations. They are extremely sensitive to their surrounding environment and get affected by humidity and temperature, with unmodified acrylates showing an optimal device performance at operational temperatures of around 20°C.¹¹ On top of all that, it is a propriety material belonging to 3M Corporation, limiting any possible modification to tailor the material systems for unique applications. Poly(dimethylsiloxane) (PDMS), commonly referred to as silicones, are a blended inorganic–organic polymer based on silicon and oxygen backbone (Si–O).¹¹ They have low mechanical stiffness and high mechanical dissipation factors. However, silicones have a low dielectric constant (2.5 – 3.0 (@ 1 kHz) compared to the acrylates

and have an energy density of 0.75 MJ/m^3 .¹¹ They have been able to produce actuation strains of about 120% (linear strain), displaying a modest electro-mechanical performance when compared against their acrylic counterparts.⁹ Nonetheless, they have the specific advantage of lower viscoelasticity, which leads to a rapid response and reduced electro-mechanical losses in the actuators. And they have also proven their versatility by being able to withstand a wider temperature range from -100°C to 260°C .¹¹ They have limited rates of moisture absorption, which have resulted in their use in most applications.¹¹ Silicones also provide the advantage of easy processability, and since it can be synthesized from scratch, it provides the option of being modified to suit the applications. Other material matrices like SEBS (Styrene Ethylene Butylene Styrene Block Copolymer) (low electric breakdown strength) and polyurethanes (high mechanical stiffness) have also been utilized for DEAs, but with limited success, and acrylates and PDMS still remains the top choice of researchers.⁵¹⁻⁵²

Compliant electrodes

Apart from the active elastomeric matrix, electrodes are also an important aspect of a DEA. Different materials have been tested to achieve superior actuation performances of these actuators. Original experiments in DEA configurations were carried out with thin metal films being employed as the electrode material, which could only provide very limited actuation strains of approximately 1%, even though they possessed high electrical conductivity.¹¹ Electrode materials used for DEAs should not compromise the stretchability of the sandwiched elastomeric layer while maintaining their conductivity over large strains without showing huge variations in conductivity, giving rise to the term “compliant electrodes”.⁵³ Moreover, they are expected to remain defect-free at the same time.⁵³ A wide variety of microfabrication technologies like electron beam evaporation, cathodic sputtering, electroplating and photolithographic processes can deposit thin metal layers even in the nanometre scale.¹¹ Even though they possess good electrical conductivity, they suffer from major disadvantages like several orders of magnitude higher Young’s modulus than that of elastomers, very limited elasticity (typically around 2–3%) and a tendency to form an insulating oxide layer at the surface.¹¹ These characteristics lead to poor actuation strains and cracking of metal films under high strains, limiting their application as compliant electrodes for DEAs. New approaches such as patterned electrodes, out-of-plane buckled electrodes and corrugated membranes promises applicability of thin metal electrodes for DEAs.⁵⁴⁻⁵⁵

Carbon-based electrodes are the most commonly employed electrode materials for DEAs owing to their ability to provide acceptable electrical conductivities over very large strains.⁵³ They have been used in 3 prominent form factors – carbon powders, carbon greases and carbon composites.¹¹ Carbon powders, such as carbon black and graphite, are deposited directly on the active elastomer layer.¹¹ They contribute minimally to the stiffness of the elastomer membrane attributed to the absence of strong binding forces between the particles. However, their application relies on the stickiness of the underlying membrane for binding to the surface, raising concern over long term stability and limiting their application to intrinsically sticky acrylic and silicone elastomers. Carbon greases consist of carbon particles dispersed in a viscous media such as oil and are known for sustaining very high strains while maintaining their conductivity.⁵³ However, they pose long-term instability concerns owing to their nature of drying or diffusing into the elastomeric membrane. Carbon composites, or more commonly referred to as carbon compounds, are formulated by dispersing carbon black particles in a polymeric matrix (Figure 2.4-A).⁵³ In most of the cases, they are cured on the membrane post application. These composites work on the principle of percolation theory and require high filler loadings to maintain compliancy. This, however, leads to significant contribution of these electrodes to the stiffness of the elastomeric membrane and cannot be neglected. Additionally, they also pose some delamination issues, leading to reduction of the device's life expectancy.

Figure 2.4 DEA configurations with different compliant electrode systems. (A) A versatile soft gripper using compliant carbon electrodes made from a carbon black and silicone composites.³¹ (B) Thin film transparent loudspeakers demonstrated using conductive hydrogels

as compliant electrodes.²⁹ (C) A multi-segmented multilayer DEA realized by using SWCNTs as compliant electrodes.⁴⁵

However, recently new material systems like silver nanowires (AgNWs), single-walled carbon nanotubes (SWCNTs) and conductive hydrogels are also being explored for application as compliant electrodes in DEAs.^{29, 45, 47, 49, 56} This arises from the fact that carbon-based electrodes are not transparent, which limits their widespread application. Keplinger et. al. demonstrated conductive hydrogels made from acrylamide network and sodium chloride as highly stretchable and transparent ionic conductors for DEAs (Figure 2.4-B).²⁹ Duduta et. al. demonstrated a multi segment multilayer DEA architecture making use of SWCNT electrodes (Figure 2.4-C).⁴⁵

2.4 Existing approaches to improve the performance of DEAs

It is evident from the governing equations for DEAs that the actuation performance depends on intrinsic material properties like dielectric constant (relative permittivity) and mechanical stiffness (Young's modulus), apart from the external factors like applied voltage and elastomeric film thickness. Most of the efforts to improve the actuation performance of these soft actuators via the material approach has been directed in either increasing the dielectric properties of the matrix or reducing the mechanical stiffness of the elastomer.¹¹

2.4.1 Reducing the mechanical stiffness

One of the traditional ways of reducing the mechanical stiffness for polymers involves the addition of plasticizers to the polymer backbone and the approach works for elastomeric matrices as well. Lowe et. al. investigated the addition of different plasticizers (81-R, 81-F and 81-VF) in the commercially available silicone elastomer (DC3481) and found out that this leads to tuning of the mechanical stiffness depending on the type and concentration of the plasticizer, which in turn results in the improvement of the actuation performance of DEAs.⁵⁷ A similar approach has also been employed by researchers in investigation of rubber membranes (acrylonitrile-butadiene) softened by addition of plasticizer (dioctyl phthalate).⁵⁸ This led to a significant improvement in the actuation performance owing to the reduction in Young's modulus of the matrix. However, the key issue with this approach, addition of plasticizers to the polymer matrix, is the volatile and migrating nature of these plasticizers resulting in long term stability and reliability issues for the actuators. It is

also important to note that some of these plasticizers like dioctyl phthalate are extremely toxic in nature.¹¹

Figure 2.5 Imperfections caused in the polymer network by imbalanced stoichiometry.

(A) Schematic of the reactants for a linear telechelic polymer and a 3-functional crosslinker for the polymerization.⁵⁹ (B) In case of a balanced stoichiometry, an ideal elastic junction is realized with black dotted lines representing an infinite network.⁵⁹ (C) Schematic of dangling chains of first order showing different combinations of missing constituents.⁵⁹ (D) A primary inelastic loop caused by the stoichiometric imbalance.⁵⁹ (E) Schematic of sol fractions caused by excess of polymer (E) and excess of crosslinker (F).⁵⁹

Another route adopted by researchers for tailoring the mechanical properties of the polymer is by the chemical modification of the polymer backbone. It is achieved by varying the stoichiometric ratio, changing the molecular weight or altering the degree of cross-linking in the polymer. Niu et. al. showed the fabrication of DE films using

UV curable acrylate precursors containing mixture of co-monomers, and varying the concentration of cross-linkers resulted in tunable stress-strain behavior.⁶⁰ Opris et. al. demonstrated the tuning of mechanical properties by addition of different kinds of crosslinkers (ethyltriacetoxysilane, methylhydrosiloxane-dimethylsiloxane copolymer, and tetraethoxysilane) to the silicone networks.⁶¹ However, these chemical modifications often lead to detrimental effects on the viscoelastic properties and require tedious and complex chemical reactions. On the other hand, commercially available silicone elastomers generally come in 2 parts, an elastomer base and a curing agent, which can be mixed in different stoichiometric ratios other than the prescribed one to get silicone matrices with different mechanical properties. However, stoichiometrically imbalanced reactants lead to incomplete polymerization reaction, resulting in disconnected polymer constituents and sol structures (fraction of polymer not covalently connected to the polymer active network) (Figure 2.5).⁵⁹

2.4.2 Increasing the relative permittivity (dielectric constant) of the elastomer

The need for improving the relative permittivity arises from different application areas and is heavily pursued in literature. The improvement in the relative permittivity improves the overall capacitance and hence reduces the required electric field. The different approaches adopted by researchers for improvement of the relative permittivity of the elastomer film is discussed in detail in later sections.

Chemical alterations to the polymeric backbone

An appropriate strategy to get higher dielectric constant values for the elastomer is either by chemical alterations to the existing elastomeric matrices or synthesis of new polymeric matrices. Stoyanov et. al. demonstrated an increase of 470% in the dielectric constant values by addition of π -conjugated conducting macromolecule, namely polyaniline (PANI), doped with dodecyl benzene sulfonic acid (DBSA) to the chemical backbone of polystyrene-co-ethylene-co-butylene-co-styrene-grafted maleic anhydride (SEBS-g-MA, thermoplastic copolymer).⁶² Even though this method of chemical bonding showed an improved performance, the shift from non-conductive to conductive behavior occurred at very low concentrations (2%). Following the similar approach of chemical bonding, Kussmaul et. al. demonstrated a two-fold increase in the dielectric constant by grafting of N-allyl-N-Methyl-p-nitroaniline (push-pull dipole) in a PDMS matrix (Figure 2.6-A and Figure 2.6-B).⁶³ However, presence of large dipole

content leaves the material susceptible to moisture uptake. Racles et. al. pursued the path of synthesis of silicone networks including cyanopropyl groups resulting in a threefold increase in the dielectric constant (Figure 2.6-C and Figure 2.6-D).⁶⁴ However, it was accompanied with the increased brittleness rendering the film unusable for DEA applications. Madsen et. al. carried out the functionalization of siloxane copolymer by a pendant polar group (1-ethynyl-4-nitrobenzene) using catalyst assisted cycloaddition reaction resulted in a 70 % increase in the relative permittivity.⁶⁵

Additionally, although these strategies for chemical modification of the elastomeric backbone show promise in improving the electro-mechanical performance of the DEAs, they require careful fabrication process to be carried out in controlled environments.

Figure 2.6 Chemical modification of the elastomeric backbone to improve permittivity.

(A) Schematic showing the addition of the dipole group to the silicone network. Functionalization by the dipole follows the same chemical route as that of network formation, with the dipole and the PDMS chains being grafted to the crosslinker in single step.⁶³ (B) Permittivity and loss factor spectra for different loading concentrations of the dipoles.⁶³ (C)

Chemical synthesis of cyanopropyl-modified polysiloxanes by 3 different routes [(a) hydrosilylation (b) anionic ring opening polymerization (c) cationic ring opening polymerization].⁶⁴ (D) Dielectric spectroscopy of polysiloxanes with different concentration of cyanopropyl groups showing an increase in the relative permittivity values.⁶⁴

Elastomer Composites

A simpler and highly pursued approach to increase the dielectric constant value involves fabricating elastomeric composites incorporating conductive fillers. At lower concentrations of the conductive particle inside the dielectric medium (below the percolation threshold), the particles are distanced from each other and the electrical properties of the composite is governed by the medium itself.⁶⁶ The behavior of nanoparticle and micro-particle conductive filler composites have been observed to be different depending on the nature and quantity of nanofillers along with the interfacial interaction of nanofiller and polymer.⁶⁷ Different conductive fillers have been investigated for increasing the relative permittivity of different elastomeric matrices; nickel nanoparticles in neoprene, silica-supported copper nanoparticles in poly-styrene (co-ethylene-co-butylene-co-styrene) (SEBS), iron nanoparticles coated with silicon dioxide in silicone and carbon black microparticles in SEBS and ethylene acrylic to mention a few.⁶⁸⁻⁷¹ Focus has also been given on the graphitic nano-materials for improving the dielectric constant. Park et. al. added the commercially available multiwall carbon nanotubes (MWCNTs) into the PDMS matrix which resulted in nearly twofold rise in the permittivity values.⁷² A strong relation between the alignment of the MWCNTs and the relative permittivity was established by Liu et. al (Figure 2.7-A).⁷³ Romasanta et. al. demonstrated the incorporation of functionalised graphene sheets (FGS) in a PDMS matrix resulting in significant increase in the relative permittivity.⁷⁴ Microencapsulation of the conductive fillers has also been investigated by the researchers to increase the loading of these conductive fillers in the PDMS matrix, helping to achieve an even better dielectric permittivity values and prevent the formation of percolative networks leading to electrical breakdown.¹¹ However, addition of these fillers, which are almost exclusively solid, leads to detrimental effects on the mechanical properties of the elastomer; a higher Young's modulus accompanied with a decrease in the ultimate strain at fracture.

Another approach to fabrication of elastomer composites involves mixing of high-k, inorganic, ceramic fillers into the elastomeric matrix. Generally utilized inorganic

fillers for high-k composites are titanium dioxide (TiO_2), boron nitride (BN) and barium titanate (BaTiO_3).^{9, 11} Carpi et. al. demonstrated an increase in the relative permittivity and improvement in the actuation performance in a DEA configuration by addition of rutile-type TiO_2 in the silicone rubber.⁷⁵ Romasanta et. al. evaluated the effect of addition of calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) in the silicone matrix on the resulting dielectric and mechanical properties (Figure 2.7-B to Figure 2.7-E).⁷⁶ However, as with their conducting counterparts, high filler loadings result in detrimental effect on the mechanical properties.

Figure 2.7 Elastomeric composites fabricated by addition of ceramic and conductive fillers. (A) MWCNTs addition in the silicone matrix leads to increase in the dielectric constant and depends on the alignment of the MWCNTs as well.⁷³ (B) Schematic showing the crystal structure of a unit cell of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO).⁷⁶ (C) SEM image of a PDMS-CCTO (8.4%) composite.⁷⁶ Dielectric spectroscopy of PDMS-CCTO composite at different filler loadings showing increase in the dielectric constant (D) with no change in the loss behavior of the composites (E).⁷⁶

Elastomer Blends

A relatively new strategy for improving the relative permittivity involves mixing of 2 polymers, miscible or immiscible, to create elastomer blends. Zhang et. al. designed composites by dispersing an organic polymer (copper-phthalocyanine (CuPc)) in a ferroelectric polymer matrix (poly (vinylidene fluoridetrifluoroethylene) (P(VDF-TrFE))), electrostrictive elastomer) showing a convincing improvement in the relative permittivity values (Figure 2.8).⁷⁷ Carpi et. al. demonstrated blending of poly (3-hexylthiophene) (P3HT) with PDMS matrix resulting in highly polarizable conjugated polymer matrix demonstrating a large increase in permittivity values accompanied with a reduction in Young's modulus.⁷⁸ Gallone et. al. took advantage of strong interfacial

polarization (Maxwell-Wagner-Sillars relaxation) arising due to mixing of PDMS and PU elastomers to create blends with high relative permittivity values.⁷⁹ Tian et. al. also exploited the strategy of improving the interfacial polarization by incorporating polyethylene glycol (PEG) in thermoplastic polyurethane (TPU) resulting in a coactive effect on electrical and mechanical properties of the TPU.⁸⁰ However, the strategy of elastomer blends has long term stability issues and some of them require careful execution of complex chemical reactions.

Figure 2.8 Elastomer blend using CuPc and P(VDF-TrFE). (A) Schematic of the chemical structure of copper-phthalocyanine (CuPc) oligomer.⁷⁷ (B) Plot of relative permittivity as a function of frequency for the pristine P(VDF-TrFE) and the composite of P(VDF-TrFE) containing 40 wt.% CuPc showing huge increase in the dielectric constant.⁷⁷

2.5 Liquid-filler approach for novel polymer composites

The option of solid fillers has been thoroughly exhausted for fabrication of functional composites for a varied array of applications, including active layer for DEAs. A relatively new strategy explored by researchers to fabricate functional material composites is to make use of liquid fillers.⁸¹⁻⁸⁴ However, it is worth mentioning here that no such approach existed at the beginning of this dissertation. One particular filler, eutectic gallium indium (EGaIn), which is a low melting point ($\sim 15^\circ\text{C}$) liquid metal (LM), has been gaining widespread attention.⁸⁵ Barlett et. al. incorporated EGaIn in a silicone matrix to fabricate liquid metal embedded elastomers (LMEEs) with high dielectric constant and very small increase in the mechanical stiffness.⁸¹ The liquid metal inclusions exist as globular phases dispersed in the polymer matrix (Figure 2.9-A). Later, making use of a similar elastomer-EGaIn composite, Markvicka et. al. demonstrated an autonomously electrically self-healing soft conductor for application as flexible and stretchable conductors in soft robotics and wearable electronics (Figure

2.9-B and Figure 2.9-C).⁸² Liquid metal droplets inside the elastomer matrix are interconnected by rupturing the globular phases via trace patterning and forming an electrically conducting path.⁸² However, owing to huge difference in the specific gravity between the metal and the polymer, these composites suffer from the issue of phase separation.

Figure 2.9 Liquid metal elastomer composites. (A) Schematic of the material composite formed by dispersing liquid metal droplets inside a stretchable elastomer matrix.⁸¹ Stretchability and patternability of an EGaIn-PDMS composite is also demonstrated.⁸¹ (B) An intricate electrical circuit formed by trace patterning on an EGaIn-PDMS composite maintains integrity while being stretched and twisted.⁸² Micrograph showing dispersion of EGaIn microdroplets inside the elastomer matrix.⁸² (C) Even after severe damage forced on the stretchable conductor, the electrical path is maintained.⁸²

Apart from liquid metals, researchers have been looking for other compatible liquid fillers. Miriyev et. al. demonstrated the fabrication of a soft composite making use of ethanol as liquid fillers inside the silicone matrix (Figure 2.10-A).⁸⁶ The composite was used for demonstrating application in soft robotics by thermally controlled (joule

heating) phase transition of ethanol from a liquid to a gaseous phase (Figure 2.10-B).⁸⁶ Apart from being slow in their actuation speeds, they also suffer from long term stability and reliability issues owing to very high vapor pressure of ethanol. Mazurek et. al. investigated the effect of addition of glycerol in silicone matrix and demonstrated an increase in the relative permittivity (Figure 2.10-C).⁸⁷⁻⁸⁸ However, it was accompanied with very slight change in mechanical stiffness and reduction in ultimate strain at break. Additionally, high loadings of filler were required for significant changes in the figure of merit for the electrochemical performance.

Figure 2.10 Other liquid filler-elastomer composites. (A) Schematic of the microstructure of ethanol-PDMS composite with a stereoscope image of the composite showing ethanol globules inside the silicone matrix. (Scale bar – 1 mm).⁸⁶ (B) A soft actuator fabricated from the ethanol-PDMS composite actuated by a thin resistive wire causing the phase transition of ethanol by joule heating (8V, 1A).⁸⁶ (C) Schematic of fabrication of a green silicone composite by dispersing glycerol in PDMS and the SEM image shows the glycerol globular phases inside the silicone matrix.⁸⁷

2.6 Reversible rigidity modulation in DEAs

Different approaches for modulating the rigidity of soft actuators has been demonstrated by the researchers. Various mechanisms for modulating the stiffness of the soft actuators have been broadly classified into two categories; namely active and semi-active technologies.⁸⁹ Active technologies have the capability to introduce energy into the system, either to perform positive work or negative work and include examples like flexible fluidic actuators, shape memory materials and tendon-driven compliant actuators.⁸⁹⁻⁹¹ On the other hand, technologies such as material jamming, electrorheological fluids (ERFs), magnetorheological fluids (MRFs) and low melting point materials fall under the semi-active category, characterized by systems that are only capable of energy dissipation.^{90, 92-94} Out of these systems, a reversible stiffening mechanism based on thermal transition has advantages in terms of scalability and lightweight. Reversible rigidity devices controlled by thermal transition are able to maintain high rigidity in load bearing state without energy consumption as compared to systems.⁸⁹

Figure 2.11 Reversible rigidity in DEAs. (A) A variable stiffness DEA made by a DEA structure in combination with silicone substrates embedded with a low melting point alloy.⁹⁵

(B) Schematic of the structure of a variable stiffness DEA employing a number of active DEA units with chucking electrodes to enable electroadhesion for stiffness modulation.⁹⁶ (C) Demonstration of variable stiffness DEA claw supporting different loads, with loads increasing from left to right.⁹⁶

In context of DEAs, a few arrangements have been explored for enabling stiffness modulation (Figure 2.11). These approaches are also quite new and reversible stiffening has not been studied extensively. Shintake et. al. demonstrated a variable stiffness soft gripper making use of a DEA structure in combination of silicone substrates embedded with a low melting point alloy (LMPA) (Figure 2.11-A).⁹⁵ DEA accounts for the bending actuation of the structure whereas the joule heating of LMPA causes the phase change to occur leading to reversible stiffness. Imamura et. al. made use of electroadhesion in a multilayer DEA architecture for producing reversible stiffness (Figure 2.11-B).⁹⁶ Although these systems show reversible stiffness, they require a rigidity modulation system augmented on the actuator system and do not contribute directly in the actuation process. Additionally, use of LMPAs and EGaIn raises cost concerns as they are very expensive metal eutectics, incorporating rare earth elements.

2.7 Summary and Research Gap

Soft robotics and soft actuators are emerging field of research, which draws inspiration from biological materials and makes use of soft systems for producing fluidic motion with enhanced dexterity. Many applications like artificial muscles, soft robots, adaptive surfaces, and versatile grippers have been explored using these soft machines. One application where soft actuators stand out from the conventional actuators is the area of adaptive surfaces owing to the fact that these can enable superior human-machine interaction at the interfaces. An electric-field driven adaptive surface is preferred owing to the advantages of electrical control of actuation and low power consumption. However, DEAs explored so far for adaptive surface applications suffer from major shortcomings; they necessitate the use of rigid frames, are bulky in their architecture and rely on coupling with other components to produce detectable actuation.

Generally used active elastomeric matrices in a DEA configuration, acrylates and silicones, are limited in their electro-mechanical performance owing to their intrinsic material properties. While commercially available acrylates have low Young's modulus and reasonable dielectric constant, they suffer from significant viscoelastic effects and

show good actuation performance only after prestretching, which necessitates rigid frames to support the stretched membranes. Silicones on the other hand, have high elastic stiffness and low dielectric constant, which affects their actuation performance. Conventional approaches to improve the performance of DEAs by materials approach involves reducing the mechanical stiffness and increasing the dielectric constant. As discussed in detail above, most of these approaches are unidimensional in their results, with positive effect on the intended material property accompanied with undesirable effect on the other material properties. Chemical modifications always require careful execution of reactions, most of the times in a controlled environment. Composites fabrication relies heavily on solid fillers, which not only increases mechanical stiffness, but reduces the stretchability as well.

Based on the gaps identified in the existing literature, this dissertation attempts at investigating a new material approach of incorporating liquid fillers in an elastomer matrix for modifying the material properties which produces a synergetic effect on both mechanical and dielectric properties leading to enhanced actuation performance. For imparting more versatility to the DEAs, a low temperature phase change material is also being investigated for fabrication of bulk composites, which will not only enable reversible rigidity modulation but also act as the active matrix in the DEA configuration and improve the actuation performance. Finally, a new device configuration is explored that imparts integrability and flexibility to DEA devices enabling localized deformations, pixelation of the surface and transparency.

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Chapter 3

Experimental methodology

This chapter briefs the rationale behind the selection of materials and device configurations adopted for this study. The chapter provides the fabrication details for material synthesis and device assembly. Underlying principles for characterization techniques and experimental details employed to investigate the physical, optical and electrical properties of the materials and characterization of devices are briefly explained.

3.1 Rationale for selection of materials and device configurations

Acrylates and silicones are the two commonly utilized elastomeric matrices for dielectric elastomer actuators.¹ Most of the reports on DEAs and their different configurations utilizes either of these elastomeric matrices. However, reports on dielectric and mechanical properties of these elastomeric materials have claimed different material parameters, suggesting an impact of the environmental conditions on the material properties.¹⁻² Hence, the electro-mechanical properties of the commercially available acrylic elastomer (3M VHB 4910) and silicone elastomer (PDMS, Sylgard 184), predominantly used active elastomeric matrices in DEAs, has to be investigated and important material parameters like Young's modulus and dielectric constant have to be identified from these measurements. This, in turn, will also provide the benchmark for the characteristic properties on which novel material systems for active layer have to be evaluated.

For compliant electrodes, carbon-based electrodes in form of powder and paste are the commonly used compliant electrodes for DEAs.³ Hence, they are investigated for their conductivity, compliancy (variation in resistance with strain) and actuation performance. This provides the yardstick for evaluating performance of novel compliant electrode systems. Major shortcomings of the carbon-based electrodes are high resistances and non-transparency. Hence for novel compliant electrodes, silver nanowires (AgNWs) and conductive hydrogels are chosen for investigation, owing to their high transparency and facile fabrication. Commercially available AgNWs can be deposited to fabricate electrodes by simple spray-coating method using shadow masking and physical masking. Owing to electronic conductivity, they have been reported to possess very low resistances. Conductive hydrogels, on the other hand, follow a simplistic fabrication process involving stirring (without heating) and are UV curable. They have superior transparency with nearly 100% transmittance in the visible region of the spectrum.

For self-contained liquid filler-polymer composite fabrication, PDMS is chosen as the host elastomer owing to factors such as cost effectiveness, biocompatibility, good viscoelastic properties and facile fabrication suited for large scale manufacturing. Ionic liquids (ILs) are essentially a disparate group of salts which are liquid at ambient temperatures. Aprotic ionic liquids like EMIMTFSI possess high dielectric constants

(in the range of 10-12), have a big electrochemical window and very high decomposition temperatures which make them attractive for applications such as electronic recycling and electrolytes for batteries.⁴⁻⁵ Water is chosen as the other liquid filler owing to its very high dielectric constant and easy availability. Additionally, highly hydrophobic nature of PDMS elastomer makes water an interesting choice for understanding the behavior of such liquid filler-polymer composites.

For reversible rigidity composite fabrication, acrylics and silicones are both selected owing to their specific advantages like facile fabrication (PDMS) and lower mechanical stiffness (acrylics). Polyethylene glycol (PEG) and paraffin wax are chosen as low temperature phase change material over liquid metal alloys. This is due to the fact that liquid metal alloys are quite expensive and are conductive in nature; whereas PEG and wax are easily available at very low costs and are dielectric in nature.

Although different device configurations like isotonic and pure shear have been investigated for DEAs, for enabling an integrable DEA device, thickness mode actuation of DEAs is selected, in which a soft passive layer is integrated on the DEA and capture the changes in the underlying active layer to produce desirable surface patterns.⁶⁻⁸ This mode allows for specific topographical changes by straightforward patterning of electrodes, resulting in deformations as desired. Additionally, the thickness mode actuation of DEAs is more suitable for tactile applications as the soft insulating layer on top of the electrically active layer provides the user with additional safety. Although, commercially available and conventionally used 3M acrylic tape is used for device fabrication to benchmark the performance of the device with other haptic devices, novel transparent electrodes (AgNWs and conducting hydrogels) are utilized as compliant electrodes.

3.2 Material fabrication

3.2.1 Carbon electrodes

Carbon powder (Graphite, Sigma Aldrich) and carbon conductive grease (MG Carbon conductive grease) were used for carbon-based compliant electrodes for fabricating the devices. Application of the electrodes is done by simple brushing, with the inherent stickiness of the underlying elastomeric layer binding the powder/paste together. For patterning of the electrodes, wax paper masks (Parafilm) are used and given desirable design by cutting. This helps in creating well-defined electrode patterns.

3.2.2 Spray coated AgNW network⁶

Silver nanowire (AgNW, Sigma- Aldrich, diameter - 115nm, length - 20-50um, 0.5% in IPA) dispersion was prepared by further dilution of the as-received AgNW in isopropyl alcohol (IPA), mixed in a ratio of 1:4 by volume and ultrasonicated (Thermo Fischer Scientific, FB15055) for 20 mins. AgNW dispersions in IPA have been found to be very stable and uniform. Patterning of AgNWs was done by automated spray deposition (HOLMARC Model HO-TH-04) with dry nitrogen gas as a carrier (flow pressure of 15 psi), substrate distance of 11cm from spraying nozzle and hot plate temperature maintained at 50°C; making use of wax paper masks. Samples were annealed in oven (Mettler, UFE 500) at 70°C for 5 minutes. Stock PEDOT: PSS (Heraeus, Clevious PH1000) solution was filtered through a PVDF filter (0.45 um pore, Membrane Solutions) and the filtered solution was further diluted in IPA in a ratio of 1:8 by volume. A fine layer of PEDOT: PSS (poly- (4,3-ethylene dioxythiophene): poly(styrene-sulfonate)) was deposited on top of AgNW network, again by the automatic spray pyrolysis machine, with 4 cycles of coating over an area of 18 cm². Finally, the samples were annealed at 70°C for 5 minutes inside the oven.

3.2.3 Conductive hydrogels^{6-7, 9-10}

Polyacrylamide (PAAm) hydrogels was synthesized following the reported procedure for solution polymerization.^{6, 10} 2.2 M of AAm (Acrylamide, Sigma-Aldrich, A8887) was dissolved in deionized water (DI H₂O). Crosslinking agent N, N' – methylenebisacrylamide (MBAA, Sigma-Aldrich, M7279) (0.0009 times the weight of AAm), photo-initiator ammonium persulfate (AP, Sigma-Aldrich, 248614) (0.0017 times the weight of AAm) and crosslinking accelerator N, N, N', N' – tetramethylethylenediamine (TEMED, Sigma-Aldrich, T9281) (0.0025 times the weight of AAm) were added to the solution in the same order as listed here. The hydrogel solution was kept for degassing for 5 minutes. Reaction mechanism for polymerization of PAAm hydrogels has been shown in Figure 3.1. NaCl (Sodium chloride, Sigma-Aldrich, 746398) was dissolved along with the AAm in the DI H₂O for fabricating conductive hydrogels. AP activates TEMED to form an unpaired electron for radical polymerisation in the chain initiation step. AAm and MBAA combine to form an extensive hydrogel network. Hydrolysis transforms aminocarbonyl groups into carboxylic acid groups which affects transition of volume phase.

Figure 3.1 Reaction mechanism for solution polymerization of PAAM hydrogels. AP reacts with TEMMED to form an unpaired electron for radical polymerisation. AAm and MBAA combine to form an extensive hydrogel network. Hydrolysis transforms aminocarbonyl groups into carboxylic acid groups which affects transition of volume phase.

The method used for fabrication of thin films of hydrogel directly on the substrates has been shown in the schematic image in Figure 3.2. Glass substrate was prepared by cleaning via the ultrasonication process; following a cycle of 10 minutes each in Decon soap, DI water, acetone and ethanol. It is then followed by plasma exposure for 10 minutes (Figure 3.2-A). Commercially available acrylic foam tape (VHB F9473PC, 250 microns, 3M) was used to form a boundary for determining the lateral dimensions and thickness of the hydrogel layer (Figure 3.2-B). Conducting hydrogel solution was poured ((Figure 3.2-C) and a 3 mm thick glass slide was placed on top (Figure 3.2-D). This prevents the wrinkling on the hydrogel surface. Curing of the gel was done using an ultraviolet light source (Heraeus Noblelight Fusion UV Inc, Incident Power 16

mW/cm²) and exposing the sample for 8 minutes. Cover glass slide and foam tapes were removed; and the cured hydrogel film was washed with DI water to remove unreacted chemicals before purging is done by Nitrogen gas.

Figure 3.2 Fabrication of thin film hydrogels.⁶ Schematic for sequential procedure for curing conducting hydrogel on top of the glass substrate of required thickness.

3.2.4 Liquid filler-PDMS composites

Liquid filler-PDMS composites were prepared by mixing water (H₂O) and EMIMTFSI (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, Sigma Aldrich) (Figure 3.3) into the polydimethylsiloxane (PDMS, Dow Corning Sylgard 184) matrix using a planetary mixer (Thinky ARE310). A planetary mixer, also known as planetary centrifugal mixer, works on the principle of planetary motion. The vessel containing the constituent materials rotates about its own axis and at the same time revolves around a central axis in the opposite direction of the rotation. Such a motion creates a vertical spiral convection, which in turn disperses and blends the material effectively, ensuring reproducibility of samples.

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

Figure 3.3 Chemical structure of EMIMTFSI. Chemical structure of the ionic liquid, EMIMTFSI (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) showing the cation and the anion part. 3-D schematic of the chemical structure and bond orientation is also provided.

Elastomer base and curing agent (for PDMS) were added to the container in the vendor prescribed stoichiometric ratio of 10:1 (by volume). Different concentrations of water and EMIMTFSI corresponding to different samples were added then to the container. The mixing recipe was set for mixing for 10 minutes and degassing (defoaming) for 5 minutes. This ensured proper mixing and degasification of the mixtures. The samples were then drop casted in a petri dish (for dielectric spectroscopy, mechanical characterization and actuation characterization) and drop casted on cleaned glass substrates for FTIR, thermal tests and UV-Vis measurements.

3.2.5 Reversible rigidity composites

Reversible stiffness composites were fabricated using 2 different elastomeric matrices; acrylates (VHB F9473PC, 250 microns, 3M) and PDMS (Dow Corning, Sylgard 184). For acrylate-based composite, the schematic for fabrication is shown in Figure 3.4. A rectangular area of 250 micron-thick VHB acrylic elastomer, measuring 7.5 cm by 10 cm, was cut with the backing liner kept intact. Parafilm was cut and used as mask for

brushing talcum powder on the elastomer. This is to prevent the internal elastomer region, where the pouch would be filled with phase-change filler, from sticking onto anything. Elastomer sheets are then folded along the dotted line and stick along the 3 edges (after proper aligning). The borders are sealed owing to strong adhesive strength of these acrylic tapes. Phase-change filler (PEG (Polyethylene glycol, Sigma Aldrich) and Paraffin wax (Sigma Aldrich)) is first melted and then filled in the elastomer pouch by removing the backing paper from one side of the elastomer pouch. The elastomer is sealed from the 4th edge as well resulting in the fabricated elastomer pouch filled with phase-change filler. These composites are used for reversible rigidity characterizations and demonstration. The thin acrylic elastomer contributes minimally to the overall stiffness of the composite.

Figure 3.4 Schematic of the fabrication of reversible rigidity composite using acrylic elastomer. Elastomer pouch is created by using a 250 μm thick acrylic tape and sticking it at 3 of its edges. After filling the phase change filler, the pouch is sealed off at the 4th edge as well. Inherent stickiness of the acrylic tape keeps the pouch sealed.

For silicone-based composite, the schematic for fabrication is shown in Figure 3.5. A 3D printed mold is used for creating a PDMS elastomeric box. It is then filled with the melted phase-change material and allowed to solidify. After solidification, another layer of PDMS is drop casted to seal the composite. These composites are also used for certain reversible rigidity characterizations and demonstrations.

Figure 3.5 Schematic of the fabrication of reversible rigidity composite using silicone elastomer. PDMS is cured in a 3D printed mold to provide the desired shape. It is then filled with the melted phase change material and allowed to solidify. Finally, a thin layer of PDMS is cured on top to seal the composite.

3.3 Device fabrication

3.3.1 For actuation characterization of compliant electrodes

For actuation characterization of compliant electrodes, an acrylic tape (3M, VHB 4910) was biaxially prestretched (Figure 3.6) on a custom-made universal stretching machine (CTC Ironworks Pte Ltd). The film (11cm x 11 cm) is placed on the machine (Figure 3.6-A) and held in place using mechanically tightened acrylic grips (1 cm). From an initial dimension of 90 cm square, the film is stretched to 360 cm square, leading to 3 times biaxial pre-stretch (Figure 3.6-B). A circular rigid frame (Figure 3.6-C) is then placed on the stretched membrane and the film is taken out on the rigid frame (Figure 3.6-D). Further, the films are taken out on smaller acrylic frames (Diameter – 10 cm, thickness – 1 cm) for fabrication of devices. A similar stretching strategy is followed for fabrication of haptic devices.

Figure 3.6 Biaxial stretching of the acrylic elastomer (VHB 4910). Elastomer film is placed on the grips of the machine and held in place using acrylic grips. The film is biaxially stretched to 3 times its initial value. A circular rigid frame is then placed on the stretched membrane and the film is taken out on the rigid frame.

3.3.2 For transparent haptic devices⁶

The step-by-step fabrication technique for transparent surface texture change device has been explained in Figure 3.7. All transparent material system was used for the device fabrication; glass slide acting as the hard surface and PET as the flexible substrate, conducting hydrogel as the bottom transparent electrode, acrylic tape (3M, VHB 4910) as the active elastomer, silver nanowire – PEDOT: PSS hybrid electrode as the top electrode, and PDMS (Dow Corning, Sylgard 184) as the top soft passive layer. Glass substrates were cleaned using the same process as mentioned in Section 3.2 (Material Synthesis, Conductive hydrogels), whereas for PET substrates acetone was avoided (Figure 3.7-A). Conducting hydrogel of desired thickness was cured on the top of the cleaned glass substrate (Figure 3.7-B). Acrylic tape was pre-stretched (300 % biaxially) on a rigid frame. The elastomer membrane was then laminated on top of the conducting hydrogel layer, ensuring no air bubble is present between the two layers (Figure 3.7-C). The pre-stretched film was prevented from falling back by sticking the edges of the tape to the substrate. Top electrodes (Figure 3.7-D) were patterned by spray-coating process and using appropriate wax paper masks (Parafilm). Parafilm masks helps to create well-defined patterns and are found to be very convenient to remove after use. Creating thick PDMS layers is quite difficult on planar

surfaces having no boundary. Although PDMS can be cured separately and placed on the device, this does not ensure proper pairing of the two layers. Hence, soft passive PDMS layer (Figure 3.7-E) was cured directly on the top of the device by creating a 1 mm high boundary around the circumference of the device. PDMS was prepared by mixing elastomer base and curing agent in the ratio of 10:1 (by weight), followed by degasification using vacuum desiccator (Cole Palmer) and cured for 24 hours at room temperature.

Figure 3.7 Device fabrication for transparent surface texture change device.⁶ Stepwise fabrication details for a transparent haptic device. Hydrogels of required dimensions are cured directly in the cleaned glass substrate and then a biaxially pre-stretched elastomer membrane is placed on top. Top electrodes are patterned through spray coating followed by curing of a top soft layer.

3.3.3 For carbon-based haptic devices⁸

Acrylic elastomer (3M, VHB 4905) was used for the active elastomeric layer, carbon powder (Sigma-Aldrich, CAS Number 7782-42-5) for patterning compliant electrodes, electrical connections were made by copper tape and polydimethylsiloxane (PDMS) (Dow Corning, Sylgard 184) as the soft passive layer. The acrylic elastomer was pre-stretched on a rigid frame, 300 % biaxially, and carbon electrodes were patterned on both the sides by brushing. The DEA device was transferred on a rigid substrate and

held together by adhesion of acrylic tape with the substrate, reinforced by the scotch tape. A 1 mm thick layer of PDMS was cured on the top of the device. For multilayer devices, active layers were stacked on top of each other ensuring there is no air gap between the two layers. Alternating electrodes were connected to opposite terminals.

3.4 Characterization techniques and Experimental setup

3.4.1 Mechanical characterization

Uniaxial tensile testing¹¹⁻¹²

Uniaxial tensile testing is a fundamental technique in which the sample is subject to a monitored tension until the specimen fails. Specimen are prepared as per the guidelines in ASTM standard D638. The sample is placed between 2 fixtures, on the top and the bottom, where the bottom fixture is fixed, and the top fixture is movable. Uniaxial tensile test provides a stress-strain curve for the sample, which in turn provides various useful material properties like Young's modulus (modulus of elasticity, mechanical stiffness), yield point, stretchability, elasticity, plasticity, ultimate strain at break and ultimate strength of the material. A typical stress strain curve is shown in figure 3.8 demarcating various information obtained from it.

Figure 3.8 Typical stress strain curve for a polymer film undergoing uniaxial tensile tests.¹² Stress-strain curves provide a lot of useful information and parameters about the mechanical properties of the polymer like Young's modulus, mechanical stiffness and stretchability (ultimate strain at fracture).

*Compression testing*¹³

As opposed to tensile tests, compressive tests are done to understand the load bearing ability of materials. It provides the behaviour of material resisting deformation under applied compressive load and is demarcated using shear strength (also known as compressive strength).

*3-point bending test*¹⁴

A three-point flexural test can be used to determine the flexural properties of a material. A test specimen (beam) of rectangular cross-section was placed on two supports. All the test specimen were prepared according to recommended dimensions in ASTM standard D790, with only the span to thickness ratio kept at 10, instead of 16, for practical considerations. A span to thickness ratio of above 8 ensures that the failure occurs only due to the bending moment and not the shear failure. Total length of the specimen was kept at least 20% longer than the support span length to allow overhanging on each end of the support. Load is applied at the centre of the span length through a moving crosshead, moving down at a constant pre-set constant rate. The force applied and the deflection of the test specimen at the point where load is applied are automatically recorded and provides the load-deflection graph. Flexural strength and flexural modulus of elasticity can be calculated using the load-deflection plot.

3.4.2 Dielectric spectroscopy¹⁵

Dielectric spectroscopy (DS), also known as impedance spectroscopy or electrochemical impedance spectroscopy is a technique used for studying the dielectric properties of a material when subjected to an external electric field (either at fixed or variable frequency). DS is a capable tool for determining frequency-dependant complex permittivity of the material and provides information about molecular dynamics (like reorientation of dipoles in an alternating electric field), static dielectric permittivity and DC electrical conductivity. Figure 3.9 demarcates the polarization mechanisms playing dominant role in the complex permittivity of the material at different frequency ranges.

Electronic and atomic polarizations usually occur at high frequencies (in neutral atoms) characterized by a slight displacement of electrons with respect to the positive nucleus. Where electronic polarization occurs in the optical band, atomic polarization occurs in the infrared band, and both are independent of temperature. Dipolar polarization is

usually observed in materials possessing a permanent dipole and characterized by an alignment of these dipoles under an applied electric field. These polarizations are dependent on temperature and observed in the microwave frequency range. Ionic polarization is observed in lower frequency regimes and caused by shifting on ionic species in the material under the applied electric field. These polarizations are also independent of the temperature.

Figure 3.9 Polarization mechanisms versus frequency range.¹⁵ Dielectric spectroscopy provides information on different polarization mechanisms contributing to the complex permittivity at different frequency ranges.

3.4.3 Spectroscopic characterizations

*Scanning electron microscopy (SEM)*¹⁶⁻¹⁷

Scanning electron microscopy (SEM) is a very versatile tool for analysis of micro- and nano-structures, produces high resolution images of a sample and provides useful information about the topography and elemental composition. The underlying principle of SEM is to hit the sample with a focussed beam of electrons and these electrons interact with the atoms on the surface of the sample, which produces different types of

signals containing information about the topography and composition of the surface of the sample. SEM can achieve very high resolution of orders of magnitude less than 1 nanometre. The most commonly used mode of a SEM is the detection of secondary electrons. These secondary electrons are emitted from the k-shell of the specimen atoms when bombarded by the electron beam (inelastic scattering interactions) and the number of detected secondary electrons is dependent on parameters like the sample's topography. The origination of these electrons takes place only a few nanometres from the surface of the sample owing to their low energy.

Fourier transform infrared (FTIR) spectroscopy¹⁸

Fourier transform infrared (FTIR) spectroscopy is a characterization technique used to obtain an infrared spectrum of absorption or emission for materials. Similar to other absorption spectroscopy techniques, FTIR also relies on how well the sample absorbs light at particular wavelengths. The technique is based on the underlying principle that most molecules absorb light in the infrared region of the electromagnetic spectrum. The peaks observed in the absorption spectra corresponds to the specific bonds present in the molecule. The background spectrum of the IR light source is recorded initially, followed by the spectrum of the IR light source passing through the sample. The ratio of the two spectrums provides information related to the material's absorption spectrum. The resultant absorption spectrum shows peaks at wavelengths corresponding to the bond's natural vibration frequencies and confirm the presence of different chemical bonds and functional groups present in the material. FTIR is notably advantageous for recognition of organic molecular groups and compounds due to the range of functional groups, side chains and cross-links involved, all of which will have distinctive vibrational frequencies in the infra-red range of the spectrum.

UV-Vis (Ultraviolet-visible) and Optical microscopy¹⁹

UV-Vis (Ultraviolet-visible) spectroscopy refers to the absorbance (or reflection) spectroscopy done for ultraviolet-visible spectral region. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transitions. These measurements depend on the concentration of compounds and homogeneity of the mixtures. Absorbance (or reflection) in the visible region directly effects the perceived colour of the compound as well. The general setup is shown in Figure 3.10 and the measurements are done against a reference sample.

For doing the transmission measurements, the intensity of light before (I_0) and after the sample (I) should be known and it can be related to the transmission (T) by the formula:

$$T = \frac{I}{I_0}$$

Optical microscopy makes use of visible light and an arrangement of lenses to magnify images of small objects. They are the oldest form of microscopy. Where a simple microscope uses a single lens for magnification, a compound microscope makes use of several lenses to increase the magnification of the object. Magnification obtained by a compound microscope is quantified as the product of the powers of the ocular lens (eyepiece) and the objective lens.

Figure 3.10 General setup for measurement of absorption and transmission spectra in UV-Vis spectroscopy.¹⁹ Transmission measurements rely on measuring the intensity of light passing through a sample and compare with the intensity of the light passing through the reference.

3.4.4 Thermal characterizations

*Differential scanning calorimetry (DSC)*²⁰

Differential scanning calorimetry (DSC) is a thermo-analytical characterization technique used for detecting and understanding the thermal events occurring in a sample material. The heat flux or power to the sample is monitored against time or temperature under a controlled atmosphere. A sample (to be measured) and a reference (with well-defined heat capacity over the range of temperatures) are kept inside a furnace enclosed inside aluminium pans, where both of them are maintained at nearly the same temperature throughout the entire experiment. The difference in the amount of the heat required to maintain the temperature of the sample against the reference, as it undergoes exothermic and endothermic thermal events, as a function of temperature.

The underlying principle is that when the sample undergoes these thermal events like glass transition (T_g), melting point (T_m) and crystallization point (T_c), more or less heat would be required to be supplied to the sample in comparison to the reference.

Figure 3.11 Typical DSC curve.²¹ A typical DSC curve plotting the heat flow with respect to temperature showing thermal transitions like glass transition, crystallization point and melting point.

Glass transition temperature demarcates the temperature region where polymer undergoes a transformation from a brittle, glassy phase to a rubber-like phase. In a typical DSC curve as shown in Figure 3.11, it is characterized by a step-wise increase of the DSC heat flow/temperature curve. Above the glass transition temperature polymer chains have high mobility. At crystallization point, chains have high energy to form ordered arrangements and undergo crystallization. It is an exothermic process and is characterized by a reduction in the recorded heat flow/temperature curve. Melting is an endothermic fusion effect recorded as a thermal event in the heat flow/temperature curve and is characterized by increased heat flow.

*Thermogravimetric analysis (TGA)*²²

Thermogravimetric analysis (TGA) is also a thermo-analytical characterization technique and is rapidly used for understanding the thermal degradation and thermal stability properties. Mass of a sample is monitored with respect to time or temperature under controlled atmosphere as a function of temperature change. By appropriate choice of the program, either thermal degradation behaviour of the material with increasing temperature can be observed or the thermal stability of the material at a constant temperature (isothermal conditions) can be monitored.

3.4.5 Actuation characterizations

Actuation strain measurement⁶

Electric field was applied to the devices by controlling the step-up transformer (XP Power, CB101), which received the input voltage and monitor voltage by a DC voltage supply (Aim-TTi, MX100TP). Strain measurements were done by capturing images (SONY, DSC-WX350) and analysing by Image J (FIJI, Opensource) image processing software.

Blocked force measurement⁶

Setup used for measuring the blocked force output from the haptic devices and adaptive surface devices has been shown in Figure 3.12. Non-active region of the device, where the vertical deformation (positive out-of-plane deformation) takes place is kept in contact with the tip of the force gauge (MARK-10). Electric field is applied by the step-up transformer (XP Power, CB101), which receives the input from the DC power supply (Aim-TTi, MX100TP). The measurement is carried out on a vibration isolation table to prevent surrounding perturbations from affecting the measurements. The sample is held in place using a double-sided foam tape (3M VHB 4910 acrylic tape) to prevent the slippage, resulting in loose contact between the force gauge tip and sample surface.

Figure 3.12 Setup for blocked force measurement.⁶ Non-active region of the device is kept in contact with the tip of the force gauge. Electric field is applied by the step-up transformer, which receives the input from the DC power supply. The measurement is carried out on a vibration isolation table; and the sample is held in place using double sided foam tape.

Frequency bandwidth characterization⁶

Setup used for measuring the frequency response of the haptic devices and adaptive surface devices has been shown in Figure 3.13. Similar to the blocked force measurement setup, then non-active region of the device is kept in contact with the tip of the force gauge (MARK-10). MARK-10 is capable of sorting force signals in millisecond regime as well. The measurement is carried out on a vibration isolation table and the sample is held in place using a double-sided foam tape (3M VHB 4910 Acrylic tape). For generating a square wave pattern of the input electrical signal, an input signal from a function generator (Tektronix AFG3000C) is fed to the high voltage amplifier (Trek 610 B) first, which in turn gets amplified to a high-voltage square wave pattern. This is then applied as the frequency dependent input signal to the sample.

Figure 3.13 Setup for frequency bandwidth characterization.⁶ Non-active region of the device is kept in contact with the tip of the force gauge. Square wave pattern is fed by function generator the high voltage amplifier, which in turn amplifies the input signal and provides a frequency dependent input to the sample. The measurement is carried out on a vibration isolation table; and the sample is held in place using double sided foam tape.

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Chapter 4*

Conventional elastomeric matrices and compliant electrode systems

Acrylates and silicones are the two extensively used elastomeric matrices as active layer in the dielectric elastomer actuators. Different reports have mentioned varying material parameters (dielectric constant and Young's modulus) for these two elastomers. Hence, an investigation of the underlying electrical and mechanical properties, using dielectric spectroscopy and uniaxial tensile test, has been presented. This sets the benchmark for the characteristic properties on which novel material systems for active layer have to be evaluated. Moving ahead, carbon-based electrodes in its powder and paste form, which are the commonly utilized compliant electrodes in DEAs, are evaluated for their resistance, compliancy (variation in resistance with strain) and actuation performance. This provides yardstick for evaluating performance of new compliant electrode systems. Finally, spray coated AgNW (silver nanowire) network and conductive hydrogels, which are novel transparent compliant electrodes for DEAs, are evaluated for their resistance, compliancy, actuation performance and other physical attributes. These transparent compliant electrodes show similar actuation behavior compared to their carbon-based counterparts, have superior compliancy and enable transparent DEA devices to be fabricated.

* Portions of this chapter have been published as Ankit et. al. "Highly transparent and Highly Transparent and Integrable Surface Texture Change Device for Localized Tactile Feedback. Small (2018): 1702312.

4.1 Introduction

Acrylic elastomers (3M VHB) and silicones (PDMS, Sylgard & Ecoflex) are the two commonly utilized elastomeric matrices utilized for dielectric elastomer actuators.¹⁻³ Acrylates, while they possess moderately high dielectric constant and relatively low mechanical stiffness, are known to produce very large actuation strains, but they need to be pre-stretched which necessitates use of rigid frames and have significant viscoelastic effects affecting the response time and long-term stability.^{2, 4-5} Additionally, they are susceptible to surrounding conditions like temperature and humidity and are limited in terms of doping and chemical modification owing to their propriety formulation.⁶⁻⁷ On the other hand, silicones have a lower dielectric constant and offer a range of mechanical properties.⁸ They have demonstrated moderate actuation performance but have the advantage of lower viscoelasticity (leading to faster response times), resistance to moisture uptake and wider operational temperature range.^{2, 7} Their biggest advantage is the easy processability which makes them attractive choice for fabrication composites, and if needed they can be synthesized from scratch. Other material matrices like SEBS (styrene ethylene butylene styrene block copolymer) and polyurethanes have also been utilized for DEAs, but with limited success, and acrylates and PDMS still remains the top choice of researchers.⁹⁻¹²

Apart from the active elastomeric matrix, electrodes are also an important aspect of a DEA. Since there are large mechanical strains associated with the operation of DEAs, the electrode materials need to be compliant. For electrodes to meet the compliancy criterion, they should maintain their conductivity over large strains without significant variations and should not contribute to the mechanical stiffness of the sandwiched elastomer film.¹³ Different electrode materials have been utilized in DEA configurations, starting from thin metal films with very low actuation strain.¹³ Even though the metal films possess excellent electrical conductivity, they pose major drawbacks in form of significantly higher Young's modulus, limited stretchability and oxidizing behavior; leading to poor actuation behavior and cracking of metal films under moderate strains.² Carbon-based electrodes are the commonly used compliant electrodes for DEAs.^{1-2, 5, 13} They are used as powders, pastes or polymer composites and offer specific advantage of easy availability, cheap cost, facile fabrication and no significant contribution to mechanical stiffness to the elastomer. However, different form factors have their own specific limitations; powders pose long term stability issues

owing to their binding relying on the stickiness of the underlying membrane, pastes also pose long term stability concerns owing to their drying and diffusing nature, and composites contribute significantly to the stiffness of the underlying membrane for binding to the surface and face delamination issues. Added to that, they provide moderate electrical conductivity. One significant concern for the carbon-based devices is that they suffer from the issue of opaqueness. This renders DEAs highly impractical to be used for applications such as integrated haptics with display screens and touch panels. Recently, few efforts have been directed at investigation of transparent conductive materials like single-walled carbon nanotubes (SWCNTs), silver nanowires (AgNWs), conducting hydrogels and graphene as compliant electrodes in DEAs for applications such as tunable lenses, soft robotic grippers and multilayer actuators.¹⁴⁻¹⁸ It is relevant to point out that most of the reports on DEAs making use of these transparent compliant electrodes have come out in recent years and only a few reports were there at the start of this dissertation.

There are several reports on dielectric and mechanical properties of the conventional elastomeric materials, revealing different material parameters, suggesting a direct impact of the environmental conditions on them.^{2, 10} Hence, the electro-mechanical properties of the commercially available acrylic elastomer (3M VHB 4910) and silicone elastomer (PDMS, Sylgard 184), predominantly used active elastomeric matrices in DEAs, is investigated and useful material parameters like Young's modulus and dielectric constant are identified from the measurements. Evaluation of the conventional carbon-based compliant electrode systems has been done in terms of conductivity variations with respect to linear strains and actuation performance under applied electric field. Novel electrode systems such as AgNWs and conductive hydrogels have also been investigated for their physical attributes like stretchability and conductivity.

4.2 Results

4.2.1 Electro-mechanical properties of VHB 4910 (Acrylic tape) and Sylgard 184 (PDMS)

Dielectric spectroscopy of acrylic elastomer (VHB 4910) and silicone elastomer (PDMS, Sylgard 184) has been shown in Figure 4.1. Complex permittivity of the material systems has been measured against frequency and provides useful information

about the energy storage behavior and loss behaviour for these matrices. Figure 4.1-A shows the plot of real part of permittivity, commonly known as the dielectric constant, versus the frequency for VHB 4910 and PDMS. As observed from the plot, VHB 4910 shows a higher dielectric constant value (@1 kHz) of ~ 5.2 compared to the PDMS (~ 3.7) and compares well with the values reported in the literature.^{2, 10} The high value corresponds to higher energy storage capacity of the VHB 4910 material. It is interesting to note here that VHB 4910 displays a frequency dependent variation in the measured dielectric constant values, whereas PDMS has a nearly frequency-independent behaviour. This particular behaviour observed in the VHB 4910 is typical of materials with ionic species present inside them, and the applied electric field causes the movement and reorientation of ionic species which is intrinsically a slow process.¹⁹ The dielectric constant measurement shows strong frequency dependence in the ionic polarization regime, with the dielectric constant value decreasing with increasing frequency. Figure 4.1-B shows the plot of imaginary part of the relative permittivity, which provides information about the loss behaviour of both the materials. Both the material systems show low loss behaviour, typical to insulating materials.²⁰ On a closer look, it is clearly observed from the plot that PDMS has a lower loss behaviour compared to the VHB 4910 acrylic tape, which in turn implies towards reduced losses in the PDMS material system by leakage.

Figure 4.1 Dielectric properties. (A) Plot of dielectric constant (real part of relative permittivity) versus frequency for VHB 4910 (3M) and PDMS (Sylgard 184). (B) Plot of imaginary part of relative permittivity versus frequency for VHB 4910 (3M) and PDMS (Sylgard 184).

Figure 4.2 Mechanical properties. Stress-strain curves for VHB 4910 (3M) and PDMS (Sylgard 184) measured by uniaxial tensile testing.

Figure 4.2 shows the measured stress-strain curve for VHB 4910 and PDMS (Sylgard 184) by a uniaxial tensile testing apparatus. Both materials show typical elastic behaviour typical to elastomers.²¹ Stress strain curves provide useful information about the Young's modulus (modulus of elasticity) and ultimate strain (maximum strain at fracture) for both the material systems. Using Hooke's law, Young's modulus for VHB 4910 was calculated to be 0.04 MPa (40 kPa) at 10% strain and 0.07 MPa (70 kPa) at 50 % strain, and this increase in Young's modulus can be attributed to strain hardening caused by molecular chain alignment under applied stress.²² Similarly, Young's modulus for PDMS was calculated to be ~ 1 MPa at 10% strain and ~2 MPa at 50% strain, showing a similar strain hardening behaviour as acrylic tape. Young's modulus is a measure of mechanical stiffness and from comparison of both the material systems it is evident that VHB 4910 is a much softer material matrix with respect to PDMS. VHB 4910 possesses a Young's modulus 25 times smaller than PDMS. Additionally, the ultimate strain for VHB was measured to be 955%, 10 times higher than that of PDMS (95%) showing the superior stretchability of VHB 4910 (acrylates) compared to

the PDMS (silicones) matrix. The maximum stress at fracture is higher for PDMS (0.68 MPa) than that for VHB 4910 (0.195 MPa).

4.2.2 Compliant electrode systems

Carbon-based electrodes

Figure 4.3 Sheet resistance versus strain for carbon-based electrodes. Sheet resistance versus linear strain for carbon powder electrodes (A) and carbon paste electrodes (B).

As mentioned previously, carbon-based electrodes are the preferred material as compliant electrodes for DEAs owing to their cheap cost and easy availability. It is important to understand the conductive behavior of the carbon-based electrodes, carbon powder and carbon paste, by doing the sheet resistance measurements and measuring the variation in this sheet resistance under applied linear strains. Figure 4.3 shows the sheet resistance versus strain measurements for both carbon powder and carbon paste electrodes. To begin with, since both the electrode systems are carbon particle based, they start from high sheet resistance values.²³ Sheet resistance of carbon powder electrode is measured at 67.8 kΩ/□ and 34.13 kΩ/□ for carbon paste electrode. The lower sheet resistance value of carbon paste can be attributed to better contact between particles owing to the presence of a dispersion medium. Whereas, for carbon powder electrodes, particles are loosely held together without any chemical binder and there are a lot of junction resistances contributing to the overall sheet resistance as well. As the electrodes are stretched linearly, sheet resistance increases expectedly for both the electrodes. For carbon powder electrode (Figure 4.3-A), the sheet resistance goes from 67.84 kΩ/□ for 0% strain to 360 kΩ/□ for 10% strain and increasing further to 458.44 kΩ/□ and 3421.38 kΩ/□ for 20% and 30% strain, respectively. Carbon powder

electrodes show an increase of nearly 5 times in the sheet resistance at 10% stretch and it increases by 50 times at 30% stretch. For carbon paste electrodes (Figure 4.3-B), sheet resistance is measured at 34.12 k Ω /□, 40.71 k Ω /□, 50.23 k Ω /□ and 129.66 k Ω /□ for 0%, 10%, 20% and 30% strain, respectively. Only 1.2 times increase in the sheet resistance is observed at 10% strain, eventually leading to 3.8 times increase in the sheet resistance at 30% strain.

Figure 4.4 Optical micrographs of carbon-based electrodes under stretch. Carbon powder electrodes (A) and carbon paste electrodes (B) at 0% strain (left images) and 30% strain (right images) measured in reflectance mode. (Scale bar – 100 μ m)

Effect of stretching on the carbon powder and the carbon paste network can be understood clearly by observing the stretched networks under the microscope (Figure 4.4). Both the networks, carbon powder (Figure 4.4-A, left image) and carbon paste (Figure 4.4-B, left image), look sufficiently uniform. As the networks are put under linear stretch, discontinuities start to appear in the carbon powder network and can be observed by dark (black) spots in the optical microscope images (highlighted with black box in Figure 4.4-A, right image). On the other hand, although we observe the stretch marks in the direction of applied stretch in carbon paste electrodes, there are no visible

signs of discontinuity of the network (Figure 4.4-B, right image). Number of dark spots that appear under applied stretch and point towards discontinuity of the network, explains the tremendous increase in sheet resistance of the carbon powder electrodes. Absence of huge discontinuities leads to acceptable changes in the sheet resistance values of carbon paste electrodes.

Figure 4.5 Actuation behaviour of carbon-based electrodes. (A) Lateral strain and areal strain measured for carbon powder electrodes at different applied voltages. Digital image of the DEA with carbon powder electrodes at no voltage (B) and at 6 kV (C). (D) Lateral strain and areal strain measured for carbon paste electrodes at different applied voltages. Digital image of the DEA with carbon paste electrodes at no voltage (E) and at 6 kV (F).

As mentioned previously, carbon-based electrodes are the commonly used compliant electrode systems for DEAs. Hence, it is important to quantify the actuation

performance of these carbon-based electrode systems in terms of strains produced for benchmarking other compliant electrode systems. Figure 4.5-A and 4.5-D shows the plot of actuation strains produced by carbon powder and carbon paste electrodes at different applied voltages. Expectedly, as the applied voltage is increased, the electric field increases resulting in increase in the actuation strains produced. The quadratic dependence of Maxwell stress on the applied electric field explains the shape of the curve. For carbon powder electrodes, lateral strain (change in diameter of the circular electrode pattern) at applied voltage of 2 kV, 4 kV and 6 kV were measured at 2%, 10% and 19% respectively, and areal strain values (change in area of the circular electrode pattern) at 2kV, 4kV and 6kV were measured at 4%, 21% and 43% respectively. For carbon paste electrodes, lateral strain at applied voltage of 2 kV, 4 kV and 6 kV were measured at 1.5%, 8.5% and 28.5% respectively, and areal strain at 2kV, 4kV and 6kV were measured at 3%, 17.5% and 65.5% respectively. These results agree well with the actuation strains mentioned in the literature.¹³ Carbon paste electrodes produce higher actuation strains at higher electric fields (6 kV) compared to the carbon powder electrodes. This can be attributed to the fact that carbon paste electrodes maintain their conductivity at large strains without consequential changes in the conductance values (as seen in the Figure 4.3-B), whereas there was a significant change in the conductivity of carbon powder electrodes with stretch. Figure 4.5-B shows the image of the DEA with carbon powder electrodes at no applied voltage, and Figure 4.5-C shows the image at 6 kV. Figure 4.5-E shows the image of the DEA with carbon paste electrodes at no applied voltage, and Figure 4.5-F shows the image at 6 kV. The large actuation strains produced on the application of electric field can be observed clearly from the images.

4.2.3 Spray coated AgNW network²⁴⁻²⁵

A dense AgNW network is essential to form the compliant electrodes as they experience high strains and need to stretch out while remaining conductive at the same time. Higher densities will ensure sufficient overlap between the AgNWs even under high strain. Figure 4.6 shows the scanning electron micrographs for different concentrations of AgNW. A uniform coverage of the substrate was achieved for all the concentrations of AgNW by spray deposition method as seen in Figure 4.6.²⁶⁻²⁷ At smaller concentrations of AgNW of 14 mg/cm² (Figure 4.6-A) and 21 mg/cm² (Figure 4.6-B), even though the network is observably uniform, but the densities appear to be sparse. At AgNW concentration of 28 mg/cm² (Figure 4.6-C) and 35 mg/cm² (Figure 4.6-D), the density

of the AgNW network was dense on the surface ensuring proper interconnectivity of the nanowires. At lower nanowire densities, the stretching of the network is limited by the interruption of the electrically percolative network. Compliancy is compromised when the percolative network is disrupted and efficient distribution of charge homogeneously cannot take place. This leads to local discontinuities and premature failure due to high localized electric fields by electrical breakdown.

Figure 4.6 SEM images of AgNW networks. Coverage and density of AgNW network of substrate at different concentrations of AgNWs. (A) 14 mg/cm² (B) 21 mg/cm² (C) 28 mg/cm² (D) 35 mg/cm².

Optical transmission spectrum for varying concentrations of AgNWs in the visible light region is shown in Figure 4.7-A. As expected, the transparency of the nanowire coating decreases with increasing nanowire concentration. The optical transmittance in the visible region (at 550 nm) drops from approximately 85 % (for 14 mg/cm²) to 68 % (for 35 mg/cm²). This decrease in transparency as the concentration of AgNW increases can be attributed to increased light scattering.²⁶ Transparency (at 550 nm) for nanowire concentration of 21 mg/cm² and 28 mg/cm² was measured at 80% and 78.5%

respectively. Intuitively, the sheet resistance of the network also decreases with the increasing concentration of silver nanowires (Figure 4.7-B).²⁸ For 35 mg/cm², the sheet resistance is lowest at 11 $\Omega/\square$ whereas the concentration of 14 mg/cm² gives the highest sheet resistance of 367 $\Omega/\square$. Sheet resistance for 21 mg/cm² and 28 mg/cm² was measured as 212 $\Omega/\square$ and 15 $\Omega/\square$ respectively. Hence, for further studies and device fabrication, we have used concentration of AgNWs as 28 mg/cm², which provides a dense nanowire network required for the intended device performance with a high transparency.

Figure 4.7 Transparency, sheet resistance and stretchability. (A) UV-Vis measurements for different concentrations of AgNW network. (B) Sheet resistance of the spray coated AgNW network at different concentrations. Both sheet resistance and transparency decrease with increasing concentration of AgNW. (C) Variation in sheet resistance of a 28 mg/cm² AgNW network under different linear stretches.

It was also observed that although the sheet resistance varied with stretching, the patterned AgNW electrodes remained very conductive even at high strains, in agreement with previous reported works. Figure 4.7-C shows the plot for the variation in sheet resistance of AgNWs with stretching, and it can be observed that the sheet

resistance varies from $13.8 \Omega/\square$ to $45.6 \Omega/\square$ for 20 % stretching (linear strain) and proves the continuity of the network at high strains as well. Although the change in sheet resistance was observably high, the final conductance value was much higher than for carbon-based electrode systems.²⁹

To evaluate the performance of these spray coated AgNW networks in a DEA configuration and compare with that of conventional carbon-based electrodes, actuation performance of AgNW electrodes at different applied voltages was measured (Figure 4.8-A). Lateral strain at applied voltage of 2 kV, 4 kV and 6 kV were measured at 3.4%, 10.5% and 23% respectively, and areal strain at 2kV, 4kV and 6kV were measured at 7%, 22% and 50.5% respectively. It is evident that compliant electrodes formed by AgNW network produce similar actuation strains compared to the carbon-based electrodes for DEA device configuration. This can be attributed to the fact that AgNW electrodes exist as a network of nanowires and owing to their form factor, are able to stretch out with the elastomeric membrane. Additionally, they have shown to maintain high conductivities at large strains, even though they have changes in the conductance values. Figure 4.8-B shows the image of the DEA with AgNW electrode at no applied voltage, and Figure 4.8-C shows the image at 6 kV.

Figure 4.8 Actuation behaviour of AgNW electrodes. (A) Lateral strain and areal strain measured for AgNW electrodes at different applied voltages. Digital image of the DEA with AgNW electrodes at no voltage (B) and at 6 kV (C).

4.2.4 Conductive hydrogels

Figure 4.9 Conductive hydrogels. Images of conductive hydrogel cured directly on the substrates and given desirable form factor by designing the boundaries accordingly.

Another stretchable and conducting electrode introduced recently for DEAs was conducting hydrogels with superior transparency nearing 100% in the visible region of the spectrum.¹⁵ These conducting hydrogels work on the principle of ionic conductivity and owe its stretchability to covalently crosslinked networks and have enabled applications like transparent loudspeakers.¹⁵ The procedure for synthesis of conductive hydrogels has been explained the experimental section of the dissertation. Using our fabrication technique described there (Figure 3.2), conducting hydrogels with different form factors (Figure 4.9) can be fabricated without the need for expensive machining technologies like laser cutting. As seen from the image, hydrogels are completely transparent, except for the edges of the film, where light scattering becomes dominant.

The mechanical properties of the hydrogel are determined by the constituent polymer and water content. Molarity of acrylamide (AaM) is varied by keeping the polymer concentration constant and varying the content of water. Different stress-strain curves measured for these hydrogels (Figure 4.10) provide information about the effect of polymer to water ratio on the resulting hydrogel's mechanical properties. It can be observed that increase in the water to polymer ratio on the hydrogel network leads to softer and stretchable matrices. Gradient of the stress-strain curves change from steep to gradual as the amount of water increases and the concentration of AaM monomers decreases. Young's modulus is observed to decrease from 0.21 MPa to 0.6 kPa as the water concentration increases from 2.5 ml to 30 ml (and molarity of AaM decreases from 13.2 M to 2.2 M). This decrease in Young's modulus is also accompanied with an increase in the stretchability of the matrix; with an ultimate strain measured at ~400% for 13.2 M AaM hydrogel and ~2100% for 2.2 M AaM hydrogel. It is important to note

that the curve of 2.65 M AaM and 2.2 M AaM hydrogel nearly overlap and does not show any significant difference. Hence, this indicates the presence of a threshold whereby adding more water does not significantly change the elastic property of hydrogels. Based on the measured mechanical properties, 2.2 M AaM is chosen for conductive hydrogel synthesis.

Figure 4.10 Mechanical properties of PAAM hydrogels. Stress against strain for six different concentrations (molarities) of acrylamide (AaM) monomer in the hydrogel network. A ratio of higher water content to lower monomer concentration leads to lower elastic modulus and higher ultimate strain in the resulting hydrogel.

As mentioned in the synthesis section, sodium chloride (NaCl) is added to the polyacrylamide hydrogel network to provide ionic conductivity to the stretchable network. Conductivity measurement for these hydrogels is done by measuring the resistance and not the sheet resistance (since these electrodes are bulk conductors) and voltages above the redox potential of water to prevent electrochemical reactions. An additional precaution to prevent electrochemical reactions is done by maintaining the contact between hydrogel and contact electrode less than 1% the area of the hydrogel. Varying the molarity of sodium chloride leads to a significant decrease in the measured resistance value initially, followed by a small change in the resistance; with resistance

measured at $1587\ \Omega$ for 1M NaCl reducing to $1157\ \Omega$ for 3M NaCl, further reducing to $1050.5\ \Omega$ for 5M NaCl (Figure 4.11-A). For studying the effect of linear strain on the resistance, 3M NaCl hydrogel is chosen. Owing to their ionic conductivity, these hydrogels show insignificant change ($\sim 6\%$) in their resistance values under applied linear stretch. The resistance increases from $1157\ \Omega$ at no stretch to $1176\ \Omega$ at 10% strain, increasing further to $1200\ \Omega$ and $1228\ \Omega$ for 20% and 30% strain, respectively (Figure 4.11-B). This is because ionic conductors, unlike their electronic counterparts, relies on mobility of ions and not the movement of electrons.¹⁵ It is also important to note that the hydrogels have higher resistance values as compared to electronic conductors like silver nanowires.

Figure 4.11 Variation in resistance of conducting hydrogels. (A) Change in the resistance of conducting hydrogels with different molarity of the ionic species (NaCl). (B) Variation in resistance of a 3 M conducting hydrogel under different linear stretches.

Figure 4.12-A shows the plot of actuation strains produced by conductive hydrogel electrodes at different applied voltages. Lateral strain at applied voltage of 2 kV, 4 kV and 6 kV were measured at 2.1%, 9.6% and 14.8%, respectively. Areal strain at 2kV, 4kV and 6kV were measured at 4.3%, 20.15% and 30.15%, respectively. Figure 4.12-B shows the image of the DEA with conductive hydrogel electrode at no applied voltage, and Figure 4.12-C shows the image at 6 kV. Conductive hydrogel electrode devices produce similar actuation strains as compared to the previously mentioned compliant electrode systems. This can be attributed to the ability of the hydrogels to accommodate large strains while remaining conductive and their low mechanical stiffness, which compensates for high resistances to begin with.

Figure 4.12 Actuation behaviour of conductive hydrogel electrodes. (A) Lateral strain and areal strain measured for conductive hydrogel electrodes at different applied voltages. Digital image of the DEA with conductive hydrogel electrodes at no voltage (B) and at 6 kV (C).

4.3 Discussion

Different reports have mentioned varying material parameters (dielectric constant and Young's modulus) for acrylates and silicones, the two extensively used elastomeric matrices as active layer in the dielectric elastomer actuators. This hints towards the effect of environmental conditions and characterization techniques on the measured material parameters. Hence, an investigation of the underlying electrical and mechanical properties, using dielectric spectroscopy and uniaxial tensile test, was done. Acrylic tape (VHB 4910) has a much lower measured Young's modulus of 0.04 MPa compared to the 1 MPa for silicone (PDMS, Sylgard 184) elastomer. Also, the measured dielectric constant for acrylic elastomer (~ 5.2) is high compared to that of silicone elastomer (~ 3.7). Hence, acrylic elastomer is used for further benchmarking of compliant electrode systems. However, it is worth mentioning that acrylic elastomer is a propriety material from 3M corporation and further modifications are not possible. On the other hand, processing of silicone elastomers (Sylgard 184) is facile, allowing for further modifications. Additionally, they are transparent as well, similar to the acrylic elastomer, which is not the case with other variants of silicones like Ecoflex and BJB enterprises. Measurement of the material parameters for these systems allows for benchmarking the characteristic properties of novel material systems for active layer, which are discussed in following chapters.

Sheet resistance measurements are done for carbon-based electrodes in its powder and paste form, which are the commonly utilized compliant electrodes in DEAs. Since they are based on carbonaceous particles, they have a high sheet resistance to begin with (tens of $\text{k}\Omega/\square$). Study of variation in sheet resistance with linear stretch reveals drastic conductivity changes for carbon powder electrodes compared to the carbon paste electrodes. This is attributed to the absence of chemical binders and inability of the carbon particles to remain in contact. Both the carbon-based electrode systems are characterized for their actuation performance, which serves as a yardstick for evaluating performance of novel compliant electrode systems. Owing to their ability to maintain their conductivity over large strains, carbon paste electrodes produce higher actuation strains at higher voltages.

Finally, spray coated AgNW (silver nanowire) network and conductive hydrogels, which are novel transparent compliant electrodes for DEAs, are evaluated for their resistance, compliancy, actuation performance and other physical attributes. Silver nanowires have very low sheet resistance values ($15 \Omega/\square$ for a concentration of $28 \text{ mg}/\text{cm}^2$) to begin with owing to their electronic conductivity. Although there are notable changes in their resistance upon stretching, they are still able to maintain high conductivities. Even at such high conductivities, they maintain a high transparency (78.5%). Novel conducting hydrogels are fabricated successfully and have a very high transparency, nearing 100%. Effect of the ratio of water content to polymer concentration is studied and it is shown that increasing the ratio makes the hydrogel softer (0.6 kPa) and more stretchable ($\sim 2100\%$ ultimate strain). Owing to their ionic conductivity, they have high resistance values (1157Ω) but maintain their conductivity over large strains, showing only $\sim 6\%$ change in resistance values at 30% linear stretch. These transparent compliant electrodes show similar actuation behavior compared to their carbon-based counterparts and enable transparent DEA devices to be fabricated.

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Chapter 5

Synergetic effect on electro-mechanical properties by liquid-filler approach*

Performance of dielectric elastomer actuators (DEAs) depends on intrinsic material properties like dielectric constant and Young's modulus. Conventional approaches of using solid fillers, chemical additives and modifications to the polymer backbone to manipulate these material properties are limited and produce undesirable effects on other material properties. Here, a novel approach of using liquid fillers to fabricate a self-contained liquid-polymer functional composite is demonstrated based on theoretical predictions of the material properties. Nature of interaction between liquid filler and polymer matrix and its effect on the resulting composite is studied. Synergetic effects on electrical and mechanical properties of the resulting matrix are observed, with an increase of ~2 times in the dielectric constant and 100 times decrease in the Young's modulus compared to the pristine polymer. Calculated figure of merit for electro-mechanical performance stands at an impressive value of 187. These ultra-soft high-k composites have been demonstrated in an isotonic DEA configuration showing 5 times and 8 times better performance in terms of longitudinal strain areal strain produced, respectively, over the conventional DE material. Additionally, these composites show superior thermal stability, resistance to moisture uptake and excellent transparency (82% @ 550 nm).

*This chapter is currently being prepared as a manuscript.

5.1 Motivation

Traditional robots suffer from limited degrees of freedom, finite adaptability and mismatch in mechanical moduli make them unsuitable for interaction with humans. Soft robots can bridge this gap, providing the possibility of a continuously deformable structure capable of combining programmable actuation with biological compliance.¹⁻² These soft robotic systems have demonstrated the ability to manoeuvre in constrained spaces and enabled autonomous actuation, have been utilized as artificial muscles and versatile soft grippers, and have even found applications in adaptive infrared-reflecting systems and tunable meta-lenses.³⁻¹⁴ Electrically powered dielectric elastomer actuators (DEAs) made of elastomers are known for their high efficiencies, light weight design and superior structural compliance.^{4, 15} The integrability and versatility of DEAs have allowed them to be utilized in specific applications such as thin film speakers, haptic surfaces, mechanically active cardiac tissue analysis and biomimetic fish robots, apart from their usage for aforementioned applications like artificial muscles and soft grippers.^{3-4, 8, 10, 12-13, 16-21} These systems managed to demonstrate high energy densities (0.5–19.8J/kg) and significant actuation performance (2.5–70% actuation strain).¹⁷ However, these demonstrations still require very high voltages (3.5–13kV) corresponding to high electric fields for actuation (30–100V/μm), attributable to the polymeric acrylates and silicones, which comprise the active elastomeric layer.¹⁷ These popular materials systems suffer from high mechanical stiffness (0.1–1MPa) and low dielectric constants (2.8–4.8) which are crucial factors in determining the actuation strains produced and electric field needed by a DEA; driving researchers to target reduction in mechanical stiffness and increased dielectric constant.²² Attempts to reduce mechanical stiffness through plasticizers, chemical modification and cross-linking degree have only resulted in modest actuation improvements while suffering from undesirable changes in the viscoelastic properties and volatility.²³⁻²⁶ Strategies for improving the dielectric constant of the elastomeric matrix by addition of conductive fillers below percolation threshold and high-k ceramic fillers, as well as chemical modification of the polymer backbone, have been unfortunately accompanied by deterioration in electrical breakdown strength and increased mechanical stiffness (in some cases leading to twenty-fold increase in Young's modulus).²⁷⁻³¹ Thus, present approaches are unidimensional in their advent, improving only upon on either of the material properties, and more often than not, having detrimental effects on the other.

5.2 Inspiration from nature

In order to break this deadlock, we look to nature for inspiration. Biological materials such as human skin and muscles are solid matrices with distributed liquid phases, and the observed macroscopic mechanical properties like stretchability and stiffness are due to its components, structural organization and mutual interactions between the constituents.³²⁻³⁴ For instance, our human skin (epidermis) has a layered structure and the various layers are shown in the schematic in Figure 5.1-A.³⁵⁻³⁶ These layers, as shown in Figure 5.1-B have different compositional structures with varying concentration of fluids amongst them, leading not only to different functionalities but different mechanical properties as well.^{32, 37} Stratum Granulosum (Figure 5.1-C) has nearly 70% water content and exists similar to a gel-like phase, compared to 15–30% water content in Stratum Corneum, which is the outermost layer of skin.^{32, 37-38} Change in water concentration in these layers has been found to be an important reason for increased stiffness and reduced extensibility of human skin, with increasing age.³² The fluids exist in phases and flow into any form that the cellular membranes can tolerate, enabling the softness and stretchability of the biological materials.^{32, 37} Hence, drawing inspiration from biological material systems, a new class of composite materials can be fabricated following an approach of incorporating liquid fillers in a polymer matrix. An appropriate choice of liquid filler with properties such as high dielectric constant and thermal stability can help in improving the dielectric constant of the polymer matrix with no change in thermal degradation behavior, and mitigating issues like mechanical stiffening and reduced stretchability at the same time, generally observed in composites with solid fillers.

Herein, an ionic liquid 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) Imide (EMIMTFSI) as a novel liquid filler for polydimethylsiloxane (PDMS) polymer matrix is reported; resulting in synergetic effects on the dielectric and mechanical properties of the resulting composite (fabrication details provided section 3.2.4). An unprecedented decrease of 100 times in the Young's modulus and a striking increase of 360% in the stretchability (ultimate strain) indicate the substantial role of the liquid fillers in the composite. Remarkably, addition of liquid filler to the polymer matrix also leads to an improvement of 1.9 times in the dielectric constant of the composite. Owing to the synergistic improvement in dielectric constant and mechanical properties, DEAs fabricated from the composite displays a 2.5 times improvement in longitudinal strains

produced and 5 times improvement in areal strains at half of the applied electric field compared to acrylic films (VHB 4910, 3M), in a non-pre-stretched isotonic configuration. Owing to the thermal stability and non-volatile nature of the ionic liquid fillers, the composites show an excellent stability even at elevated temperatures. High transparency levels of 82–90 % make these soft composites a suitable candidate for other optoelectronic applications as well.

Figure 5.1 Schematic of human skin. (A) Different layers in epidermis are labelled by numbers. (1- Stratum Corneum, 2- Stratum Lucidium, 3- Stratum Granulosum, 4- Stratum Spinosum, 5- Stratum Basale). These layers have different compositional structures with varying concentration of fluids amongst them, leading not only to different functionalities but different mechanical properties as well. (B) An enlarged schematic of epidermis showing the different layers. (C) Schematic of the stratum granulosum, made of cells and lipids filling the intracellular spaces.

5.3 Results

5.3.1 Principles of design and choice of materials

As indicated previously, for field driven soft actuators, we desire a stable soft elastomeric material with enhanced dielectric constant and reduced mechanical stiffness. PDMS is chosen as the host elastomer owing to factors such as cost effectiveness, biocompatibility, good viscoelastic properties and facile fabrication suited for large scale manufacturing.²² Inclusion of high k fillers are necessitated by effective medium approximations which indicate that the composite's dielectric

constant lies between that of the individual constituents. Ionic liquids (ILs) are essentially a disparate group of salts which are liquid at ambient temperatures.³⁹ Aprotic ionic liquids like EMIMTFSI possess high dielectric constants (in the range of 10-12), have a big electrochemical window and very high decomposition temperatures which make them attractive for applications such as electronic recycling and electrolytes for batteries.³⁹⁻⁴²

Maxwell-Garnett approximation is one of the earliest and preferred effective medium theories for effective permittivity approximations.⁴³ The model assumes a two-phase isotropic dielectric component with spherical inclusions ideally dispersed, and defines the effective relative permittivity as given by equation (1).⁴³ ϵ_c is the effective dielectric constant of the composite, ϵ_1 is the dielectric constant of the matrix, ϵ_2 is the dielectric constant of the filler material and v_2 is the loading of the filler particle.

$$\epsilon_c = \epsilon_1 \left[1 + \frac{3v_2(\epsilon_2 - \epsilon_1)}{2\epsilon_1 + \epsilon_2 - v_2(\epsilon_2 - \epsilon_1)} \right] \quad (1)$$

However, the model is not accurate for accommodating drastic difference in dielectric constants and provides anomalous results for highly polarizable inclusions. Bruggeman's model is an extension of the Maxwell-Garnett approximation.^{28, 43} This model allows the computation of the overall electrical response of the composite at high loading contents of the high-k fillers, with the assumptions that the dispersed fillers are spherical in shape and the dispersions do not create a percolative path through the medium. The model encompasses the polarizability of the inclusions in the calculation and is given by the following mathematical expression in equation (2).^{28, 43}

$$\epsilon_c = \epsilon_2 \left[\frac{3\epsilon_1 + 2v_2(\epsilon_2 - \epsilon_1)}{3\epsilon_2 - v_2(\epsilon_2 - \epsilon_1)} \right] \quad (2)$$

Yamada's model, a more accurate approximation model, is based on the assumption that the polymer dielectric characteristics are quite distinct from the dielectric characteristics of the filler.⁴⁴ The model also introduces a shape parameter "n" for non-spherical inclusions in the polymer matrix. "n" is a geometry factor and is given a value of 3 for spherical particles. "n" < 3 corresponds to oblate particles, whereas n > 3 corresponds to prolate particles in the applied electric field (equation (3)).⁴⁴

$$\epsilon_c = \epsilon_1 \left[1 + \frac{nv_2(\epsilon_2 - \epsilon_1)}{n\epsilon_1 + (1 - v_2)(\epsilon_2 - \epsilon_1)} \right] \quad (3)$$

Figure 5.2 Effective medium theories for dielectric approximation. Approximated dielectric constant values of the EMIMTFSI-PDMS composites using Bruggeman's model and Yamada's model at different frequencies. Dielectric constant of PDMS matrix at different frequencies as measured by dielectric spectroscopy.

Figure 5.2 shows the plot of dielectric constant values of our EMIMTFSI-PDMS system approximated from the Bruggeman's model and the Yamada's model at different frequencies. The dielectric constant values for baseline matrix were measured by dielectric spectroscopy of PDMS. The static dielectric constant value of EMIMTFSI (12.25) was taken from literature for the approximations. For Yamada's model, the value of n was allotted as 3, for spherical particles of IL were observed in the PDMS matrix. This was later confirmed by optical microscopy images as well. The values were approximated at a 20% filler loading by volume.

The mechanical stiffness of dilute (small filler loadings) solid composites with liquid fillers could be predicted by extending Eshelby's theory which lays down the foundation for predicting the response of isolated inclusions in a composite, to applied stress.⁴⁵ It helps to predict the stiffness of solid composites consisting of low volume fraction of inclusions. According to Eshelby's result, liquid inclusions with zero

Young's modulus should lower the resulting stiffness of the solid composites. Mathematical expression for Eshelby's theory for dilute composites is given by equation (4).⁴⁶ Y_c represents the effective moduli of the composite, Y stands for the Young's modulus of the matrix and $\emptyset$ is the volume loading of the inclusions.

$$Y_c = Y / \left(1 + \frac{5}{3} \emptyset\right) \quad (4)$$

However, it neglects the contribution of interfacial stress, which can play an important role at small filler sizes and soft solid matrices. Additionally, the theory is relevant primarily for very small filler loadings with inclusions widely spaced apart from each other. Mori-Tanaka multiphase approximation framework extends Eshelby's theory for non-dilute concentrations but still neglects the effect of surface tension and interfacial stress.⁴⁷ And as is the case, when the inclusions become very small, the surface energy becomes important compared to the bulk strain energy and the interfacial effects cannot be ignored.⁴⁶ Surface tension (γ), which typically acts to smooth our interfaces, plays an important role when the inclusions become small and keeps liquid inclusions from deforming against applied stretch. Style et. al. considered the crucial role of surface tension and interfacial stress in their model. Style et. al. included the interfacial effects into their model for effective modulus approximations; and is given by equation (5) as extension of Mori-Tanaka approximation scheme and equation (6) as extension of Eshelby's theory.⁴⁶ It is important to note that the model is developed based on the assumption that surface tension is independent of surface strain, which does not hold true in general. Additionally, it is worthwhile to mention that the experimental validation of all the models has been done by force-indentation measurements and not uniaxial tensile tests. Y_c represents the effective moduli of the composite, Y stands for the Young's modulus of the matrix, $\emptyset$ is the volume loading of the inclusions, R is the radius of the liquid inclusion, L denotes the elastocapillary length (given by $L = \gamma/Y$), γ is the surface tension, and Y_i denotes the approximated moduli of the liquid inclusions (given by $Y_i = 12\gamma/5R$).

$$Y_c/Y = \frac{15 + 9\emptyset + (R/L)(6 - 6\emptyset)}{15 - 6\emptyset + (R/L)(6 + 4\emptyset)} \quad (5)$$

$$Y_c/Y = \frac{1 + (2/3)(Y_i/Y)}{(2/3 - 5/3 \emptyset) Y_i/Y + (1 + 5/3 \emptyset)} \quad (6)$$

Figure 5.3 Prediction of mechanical properties. Prediction of elastic modulus of the composite by Style et. al.'s extension of the Eshelby's theory within Mori-Tanaka multiphase approximation.

By applying this model to an EMIMTFSI-PDMS composite for different average radii (R) of liquid inclusions, the mechanical stiffness was estimated for varying filler loading (Figure 5.3). Surface tension (γ) value is taken as 44.14 mN/m from the literature for the modelling.⁴¹ Value of R was taken as 1 μm , which was the average radii of liquid inclusions. Reduction of Young's modulus with increased loading of liquid fillers compared to the measured modulus for PDMS film was evident from the plot. The equations predict a Young's modulus of ~ 0.747 MPa for 20% filler loading compared to the 1 MPa for pristine PDMS film. The transitions in mechanical stiffness is linked to the elastocapillary length (ratio of surface tension to the Young's modulus) which can be modulated by the choice of liquid filler and the bulk matrix. In the case considered here, for small radii of inclusion (~ 100 - 250 nm), the surface tension effects are significant, resisting the stretching of liquid inclusions to keep them spherical. This results in only slight reduction in the Young's modulus. At radii exceeding 1 micron, the surface tension is overwhelmed by bulk elasticity and we see highly diminished

Young's modulus values for the composite from the estimations, compared to the polymer matrix.

The dielectric and mechanical predictions clearly show the potential of an ionic liquid filler composite. However, the mixing of a liquid and a solid phase poses challenge in terms of phase segregation and processability. In order for the liquid to exist as self-contained inclusions in the polymer matrix, the nature of interaction between the liquid and the matrix needs to be examined. Non-compatibility between phases can be estimated from contact angle measurements, with a contact angle greater than 90° indicating lower interfacial tension. If the liquid filler has poor compatibility with the solid phase, the resulting matrix can have phase separation, phase segregation and improper filler size distribution. This in turn leads to undesirable effects on the material properties like high viscosities, poor dispersion and poor mechanical properties. The contact angle of water on PDMS was observed to be quite high (116°) due to the hydrophobicity of the PDMS matrix (Figure 5.4-A and Figure 5.4-B). The interaction between EMIMTFSI and PDMS was observed to be more favorable with a lower contact angle (~80°) (Figure 5.4-D and Figure 5.4-E). This in turn leads to uniform filler size distribution in the composite. The aim is to capitalize on the immiscibility of the two systems and favorable interaction between the phases to create self-contained globules of EMIMTFSI inside the PDMS matrix, resulting in fabrication of composites with higher dielectric constant and reduction of the mechanical stiffness of the overall matrix. Figure 5.4-C and Figure 5.4-F shows the scanning electron micrographs for Water-PDMS and EMIMTFSI-PDMS composites at 10% filler loading fabricated by shear mixing. In the EMIMTFSI-PDMS composite, the fillers are distributed more uniformly throughout the matrix, show a very uniform filler size distribution and are quite small (~1µm) in size in contrast to the Water-PDMS composite.

Figure 5.4 Contact angle measurements. (A) Image of a water droplet (with red dye) on a PDMS membrane, maintaining a strong spherical shape. (B) Bitmap image of contact angle measurement for water on PDMS membrane (116°). A large angle emphasizes low interfacial tension and non-compatibility of the materials. (C) Cross-sectional scanning electron micrographs of PDMS+Water (10%) showing the uneven filler distribution in the composite (Scale bar – 100 microns). (D) Image of an EMIMTFSI droplet on a PDMS membrane, spread out on the surface. (E) Bitmap image of contact angle measurement for EMIMTFSI on PDMS membrane (80°). Small angle signifies high interfacial tension and compatibility of the materials. (F) Cross-sectional scanning electron micrographs of PDMS+EMIMTFSI (10%) showing the uniform filler distribution in the composite (Scale bar – 10 microns). Liquid filler phases can be observed clearly as spherical inclusions inside the polymer matrix.

Optical microscopy (OM) images confirm the uniform distribution of the globular phases while FTIR measurements indicate that the ionic liquids maintain their chemical composition as shown in the Figure 5.5. As seen in Figure 5.5-A, the density of the globular phases, observable through the microscope, increases with the increase in the EMIMTFSI concentration. The size distribution appears observably uniform and fillers appear to be homogeneously distributed. As mentioned, FTIR spectrum (Figure 5.5-B) shows no significant peak change or shift caused by the addition of EMIMTFSI in the PDMS matrix.^{40, 48} The characteristic C-H stretch peaks of EMIMTFSI are observed in the zoomed in picture of the graph (Figure 5.5-C).⁴⁰

Figure 5.5 Optical microscopy and FTIR for EMIMTFSI-PDMS composites. (A) Optical microscopy image for pristine PDMS, PDMS+EMIMTFSI (5%), PDMS+EMIMTFSI (10%), PDMS+EMIMTFSI (15%) and PDMS+EMIMTFSI (20%). (B) FTIR spectroscopy of pristine PDMS and EMIMTFSI-PDMS composites with different filler concentrations. Different peaks originating in the infrared spectrum compared to the pristine PDMS matrix are characteristic peak of EMIMTFSI and cements the proof of presence on EMIMTFSI phases in the PDMS matrix.

5.3.2 Synergetic effects on dielectric constant and Young's modulus

Figure 5.6 Dielectric spectroscopy of EMIMTFSI-PDMS composites. Plot of (A) dielectric constant (real part of permittivity), (B) imaginary part and (C) conductivity against frequency with increase in EMIMTFSI concentration. Increase in energy storage capacity of the elastomer matrix can be observed with increasing EMIMTFSI concentration, with negligible changes in the loss behavior of the material.

Dielectric spectroscopy of the EMIMTFSI-PDMS matrices show an impressive increase of around 200% in the dielectric constant value for PDMS+EMIMTFSI (20%) over the pristine PDMS matrix. Figure 5.6-A shows the real part of the relative permittivity (ϵ'), against the frequency of the external electric field. The curves show an increase in the ϵ' with increasing concentration of EMIMTFSI, for all frequencies, showing an increased energy storage capacity, and hence an increased k-value. The PDMS+EMIMTFSI (20%) has dielectric constant of ~ 7 compared to the value of 3.7 for pristine PDMS matrix. The dielectric constant increases monotonously with the concentration of the ionic liquid, with values of 5, 5.5 and 6.45 obtained for 5%, 10% and 15% filler loading. High-k value for EMIMTFSI-PDMS composites is attributed to enhanced space charge polarization of ionic species self-contained in the heterogeneous composite material.⁴²⁻⁴³ The plot of imaginary part of relative permittivity (ϵ'') shows no relative increase in the loss factor with increasing concentration of EMIMTFSI (Figure 5.6-B). This is attributed to the fact that the EMIMTFSI phases exist separate from each other inside the PDMS matrix and are not connected to provide an ionic conduction path. Even when ionic conduction is prevalent at low frequencies, it is prevented to contribute to the loss behavior of the composite by discontinuous existence of EMIMTFSI phases. Complex conductivity versus the frequency for different concentration of EMITFSI-PDMS shows negligible change over the frequency range (Figure 5.6-C).

Figure 5.7-A shows the stress-strain curve measured by uniaxial extension for EMIMTFSI-PDMS composites for varying concentration of EMIMTFSI. Pristine PDMS and EMIMTFSI-PDMS composites, show highly elastic, Hookean behavior in stress-strain curves; typical to most elastomers. Enhanced softening of the matrix with increasing concentration of EMIMTFSI can be clearly observed. The slope of the stress-strain curves reduces with increasing concentration of EMIMTFSI and reaching a maximum at 15% EMIMTFSI concentration. The Young's modulus of the composites decreases to 10 kPa for PDMS+EMIMTFSI (20%) compared to initial 1 MPa for pristine PDMS (Figure 5.7-B) resembling soft, biological materials.¹ Maximum strain at break (ultimate strain) was also extracted from stress-strain curves for these composites and showed superior stretchability over the pristine elastomer. Figure 5.7-C shows the stretching of more than 400% for PDMS+EMIMTFSI (20%) sample. Whereas previous reports have showed reduction in stretchability of the composites

with solid filler addition, our unique liquid filler system shows an impressive improvement in the maximum strain at break for all concentrations of EMIMTFSI. Where pristine PDMS showed an ultimate strain of 95%, addition of 20% EMIMTFSI increased the ultimate strain by 4.6 times to 435%. The enhanced stretchability of the composites can be attributed to the favorable interaction between the liquid filler and the polymer matrix.

Figure 5.7 Mechanical properties of EMIMTFSI-PDMS composites. (A) Stress-strain curves obtained by Uniaxial tensile tests for composites with different EMIMTFSI concentrations. Softening of the matrix can be clearly observed from the curves. (B) Plot of Young's modulus (300 kPa, 50 kPa and 10 kPa at 5%, 10% and 15% filler loading respectively) and Maximum strain at break against filler concentration. Decrease in Young's modulus can be observed with increasing EMIMTFSI concentration; whereas the Maximum strain at break increases with increasing EMIMTFSI concentration, till it reaches a minimum value at 15% filler loading. (C) Image of PDMS+EMIMTFSI (20%) stretched more than 400% of its initial length using Uniaxial tensile testing apparatus.

It is also worthwhile to note that the filler loading reaches an optimum value at a concentration of 15%; with the ultimate strain value at 497% and stretchability of composite starts declining after that. Large hysteresis was observed between the loading

and the unloading curves for pristine PDMS (Figure 5.8-A) in the 1st cycle, indicating towards dominant viscoelastic behavior and can be attributed to molecular orientation.⁴⁹ The hysteresis reduces for the 2nd cycle of loading and unloading (Figure 5.8-A). Interestingly, very small hysteresis can be observed between the loading and unloading stress-strain curve for PDMS+EMIMTFSI (20%) samples (Figure 5.8-B), showing reduced viscoelastic behaviour.

Figure 5.8 Cyclic testing for mechanical hysteresis. (A) Loading and unloading stress-strain curves for pristine PDMS showing large hysteresis owing to dominant viscoelastic behavior caused by molecular reorientation under stress. (B) Loading and unloading stress-strain curves for PDMS+EMIMTFSI (20%) composite showing small hysteresis, pointing towards reduced viscoelastic behavior.

Composites developed for DEAs have been benchmarked by a figure of merit (FOM) for electro-mechanical performance and was calculated based on the measured dielectric constant and Young's modulus. Figure of merit was estimated using the equation (7) employed by Romasanta et. al. for composites.²⁸

$$FOM = Y_o \epsilon'_c / Y_c \epsilon'_o \quad (7)$$

Where Y_o and Y_c are the Young's modulus of the elastomer matrix and composite matrix respectively, and ϵ'_o and ϵ'_c are dielectric constants for the elastomer matrix and the composite matrix respectively. PDMS+EMIMTFSI (20%) composites show an impressive FOM of 187, orders of magnitude higher than previous reports. A comparison of FOM with other approaches for improving the electro-mechanical performance of active layer of DEA by composite approach is presented in Table 5.1.

Table 5.1 FOM comparison. Figure of merit calculated for PDMS+EMIMTFSI (20%) composite and comparison to solid filler systems from literature.

Composites		Young's Modulus, Y (MPa)	Dielectric Constant, ϵ' at 1kHz	F.O.M.	Ref.
Elastomer Matrix	Filler				
SEBS-g-MA (poly-styrene-co-ethylene-co-butylene-co-styrene-g-maleic anhydride)	Polyaniline (PANI)	3.986 (At 2.0 vol%) 4.535 (Pristine)	63.0 (At 2.1 vol%) 2 (Pristine)	35.8	Stoyanov et al. ⁵⁰
Polydimethylsiloxane (PDMS)	Calcium Copper Titanate (CCTO) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$	0.58	5.22	1.64	Romasanta et al. ²⁸
Acrylic rubber (ACM)	Barium titanate (BaTiO_3) and Carbon Black	2.62	40.5	1.60	Poikelispää et al. ⁵¹
		0.85 (Pristine)	8.4 (Pristine)		
Polydimethylsiloxane (PDMS)	EMIMTFSI	0.01	6.93	187	Current work
		1 (Pristine)	3.7 (Pristine)		

5.3.3 Effect of type of filler and filler size distribution

As mentioned previously, if the liquid filler has poor compatibility with the solid phase, the resulting matrix can have phase separation, phase segregation and improper filler size distribution. This in turn leads to undesirable effects on the material properties like high viscosities, poor dispersion and poor mechanical properties. This results in observable phase segregation and filler size variation in the composite, leading to unpredictable and undesirable stress-strain behavior for the composites. This can be

observed from the measured stress-strain curves for water-PDMS composites shown in Figure 5.9.

Figure 5.9 Stress-strain curves for water-PDMS composites for different volume loading of water. PHR stands for parts of water (by volume) per hundred parts of the PDMS (by volume). Unpredictable mechanical properties are observed and can be attributed to non-compatibility between the filler and the matrices.

Our emphasis on filler size and distribution, which motivated the choice of liquid filler, is also borne out in the choice of the fabrication process. The fabrication technique affects the filler size distribution in the matrix, in turn affecting the electromechanical properties. The increase in dielectric constant with filler loading is observed for both uniform and non-uniform filler size distribution, however uniform filler size distribution, achieved by the shear mixing process (planetary mixing), results in higher dielectric constant at lower EMIMTFSI concentration (Figure 5.10-A) as compared to manual mixing. The positive effect of uniform filler size distribution is also observed on the mechanical properties of the matrix. With even filler size distribution, a Young's modulus of 10 kPa is achieved at 15% filler loading itself; compared to the Young's modulus of 20 kPa obtained for 25% filler loading for uneven filler size distribution

(Figure 5.10-B). It should be noted that even filler size distribution also contributes to better F.O.M. compared to the F.O.M. achieved by uneven filler size distribution (84.7).

Figure 5.10 Effect of filler size distribution on electro-mechanical properties of the EMIMTFSI-PDMS composites. (A) Effect of filler size distribution on the real part of the permittivity (dielectric constant, @1kHz) of EMIMTFSI-PDMS composites with different filler concentrations. (B) Effect of filler size distribution on the Young's modulus of the resulting composite matrix with varying filler loadings.

5.3.4 Stability and transparency

Ionic liquids have high decomposition temperatures and insignificant vapor pressures (30).⁴¹ Figure 5.11-A shows the isothermal TGA (Thermogravimetric Analysis) plot for pristine PDMS and PDMS+EMIMTFSI (20%) at 200°C. The plots for both pristine PDMS and PDMS+EMIMTFSI (20%) overlap and show superior stability for duration of 1 hour at 200°C, with no change in the weight of both the matrices. TGA for different EMIMTFSI ratios from 50°C to 600°C was also done to understand the effect of fillers on the onset temperature and decomposition mechanism (Figure 5.11-B). Very small change in the onset temperature was noticed with addition of EMIMTFSI fillers testifying to its thermal stability. Samples kept in the ambient (60% RH) for 12 days showed no weight change indicating no moisture uptake and non-volatility of fillers (Figure 5.11-C).

Figure 5.11 Stability of EMIMTFSI-PDMS composites. (A) Isothermal TGA @200°C of pristine PDMS and PDMS+EMIMTFSI (20%) samples. No weight change is observed for a duration of 1 hour. (B) Plot of TGA for different EMIMTFSI-PDMS composites from 50°C to 600°C. Negligible change in the onset temperature. (C) Plot of % weight change of samples with number of days kept in ambient conditions (R.H. – 60%). No change in the measured weight showing that there are no volatile losses and moisture uptake by the samples.

Optical absorption measurements for 200-micron thick films showed relatively high transparency in the visible region (Figure 5.12-A). Transparency @ 550 nm is measured ~95% for PDMS+EMIMTFSI (5%) and decreases gradually to ~90% for PDMS+EMIMTFSI (10%) & ~84% for PDMS+EMIMTFSI (15%); eventually dropping to ~ 82% for PDMS+EMIMTFSI (20%) (Figure 5.12-B). Difference in refractive index of the medium and the filler particle is a critical factor in determining the optical properties of a composite.⁵² Additionally, the size and shape of the filler particles also determine the extent of light scattering by the filler particles inside the matrix.⁵² While other solid fillers like TiO₂ and MWCNT's significantly decrease the transparency, EMIMTFSI-PDMS composites display an impressive 82% transparency at 20% filler loading. This can be attributed to two factors; first, the refractive indices

for PDMS and EMIMTFSI are 1.4118 and 1.4272 respectively and are actually very close to each other, and; second, the smaller filler particle size which scatters less light because of the sharper angular distribution of light.^{41, 53}

Figure 5.12 Transparency of EMIMTFSI-PDMS composites. (A) PDMS+EMIMTFSI (20%) sample in a petri dish kept in front of an image highlighting the transparency of the films. (B) Transmittance versus wavelength plot from the UV-Vis measurements. Plot shows the transparency of the pristine PDMS and EMIMTFSI-PDMS composites with different filler concentrations in the visible spectra.

5.3.5 Actuation performance of EMIMTFSI-PDMS composites

Skeletal muscles contracts either by shortening (concentrically) or lengthening (eccentrically), in isometric and isotonic configurations, and differs in terms of mechanism of force generation, maximum force production and energy cost.⁵⁴ Isotonic configurations are known to generate greater force than isometric and concentric contractions, at a lower metabolic cost.⁵⁴ Hence, the actuation performance of the PDMS+EMIMTFSI (20%) composite was characterized in a non-prestretched pure shear isotonic configuration (Figure 5.13-A) with a fixed load of 50 grams (0.4903 N~500 mN) and compared to the conventionally used DEA material (Acrylic tape, 3M VHB 4910) in the same configuration (32).⁵⁵ Figure 5.13-B shows the typical curves for longitudinal strain produced against the applied voltage, with PDMS+EMIMTFSI (20%) composite (3.32%) showing ~2.5 times better performance than the VHB 4910 (1.35%) in terms of actuation strain produced, at 8kV. This is attributed to higher dielectric constant and reduced mechanical stiffness of the PDMS+EMIMTFSI (20%) composite. Since the thickness of the two films are quite different, 1 mm for VHB 4910 and 2.25 mm for PDMS+EMIMTFSI (20%), a better understanding of the change in

terms of actuation performance can be seen by the plot of longitudinal strain against the nominal electric field (Figure 5.13-C). We observe an increase of ~ 2.5 times in the strain produced at nearly $1/2$ the applied nominal electric field, thus, making the effective improvement of 5 times in the actuation performance. 4 times improvement in areal strain produced by PDMS+EMIMTFSI (20%) composite (6.27%) and VHB 4910 (1.58%) was measured for similar applied voltages (8kV), with film thicknesses of 2.25 mm and 1 mm respectively, making the effective improvement 8 times in the areal strain (Figure 5.13-D and Figure 5.13-E).

Figure 5.13 Actuation performance of EMIMTFSI-PDMS composite. (A) Schematic of Pure-shear, Isotonic configuration of DEAs. (B) Longitudinal strain produced versus applied voltage. PDMS+EMIMTFSI (20%) shows ~ 2.5 times better actuation performance compared to commercially available acrylics (VHB 4910) at same voltage. (C) PDMS+EMIMTFSI (20%) shows better performance only $1/2$ the nominal electric field, making the effective improvement in longitudinal strain as 5%. (D) Areal strain produced versus applied voltage. PDMS+EMIMTFSI (20%) show 4 times better actuation performance compared to commercially available acrylics (VHB 4910) at same voltage. PDMS+EMIMTFSI (20%) shows better performance only $1/2$ the nominal electric field, making the effective improvement in areal strain as 8%.

Reduction in actuation strain with increasing load was also observed, which is a characteristic of mammalian muscle.³ At a fixed load of ~ 300 mN PDMS+EMIMTFSI

(20%) composite showed 2 times increased longitudinal strain compared to the strain produced with a fixed a load of 500 mN hanging from it (Figure 5.14).

Figure 5.14 Actuation in different loading conditions. Variation in longitudinal strain with applied voltage at 2 different loading conditions, showing a reduction in actuation strain with increasing load.

Image of PDMS+EMIMTFSI (20%) composite device (Figure 5.15-A) and VHB 4910 acrylic device (Figure 5.15-B), actuated at 8 kV. In absolute terms, actuation stroke of more than 5 mm (0.5 cm) was achieved by PDMS+EMIMTFSI (20%), as shown in the zoomed in picture. EMIMTFSI-PDMS composite show an enhanced performance compared to the conventionally used acrylates (3M VHB) in terms of actuation strains achieved for applied electric field; and the results are comparable to the non-prestretch modified material systems, standing in good stead against other chemical and filler modifications of polymer backbones.

Figure 5.15 Demonstration of isotonic actuation. Digital image of (A) PDMS+EMIMTFSI (20%) and (B) VHB 4910 devices with 50 grams (~ 0.5 N) load hanging from it. Digital image of the actuated devices under applied voltage (8 kV) are shown next to them.

5.3.6 Electrical breakdown of EMIMTFSI-PDMS composites

One of the major drawback on fabricating composites with any conductive or ceramic filler is that it affects the electrical breakdown strength of the matrix.⁵⁶ Increase in the dielectric constant value leads to reduction in the breakdown strength owing to interfacial (Maxwell-Wagner) polarization phenomena. Although there are no general expressions relating dielectric constant and Young's modulus of a material with its electrical breakdown strength; an empirical relation based on Maxwell-stress actuation suggests a reduction in electrical breakdown strength with increase in dielectric constant and reduction in Young's modulus.⁵⁶ Electrical breakdown measurements (Figure 5.16-A) were done for 13 different samples of the fabricated EMIMTFSI-PDMS composite (PDMS+EMIMTFSI (20%)) and it yielded an average breakdown strength of ~ 15 V/ μm . Even though this is comparable to the prescribed breakdown strength of 19 V/ μm from the manufacturers, the measured strength is considerably lower than the values mentioned in the literature. This can be attributed to highly polarizable species present in the matrix, leading to high localized fields around them.

Figure 5.16 Electrical breakdown of EMIMTFSI-PDMS composites. (A) Electrical breakdown measurements for 100 microns thick PDMS+EMIMTFSI (20%) composite showing a low breakdown strength. (B) SEM image of the top surface of a PDMS+EMIMTFSI (20%) composite film. SEM images ((C), (D) & (E)) showing the breakdown of the PDMS+EMIMTFSI (20%) composite under applied electric field.

5.4 Discussion

Drawing inspiration from soft biological materials in the nature, fabrication of a self-contained liquid filler-polymer composite using EMIMFTSI as the liquid filler and PDMS as the polymer matrix is demonstrated. The material composite is conceptualized using the theoretical predictions for the material properties from Style et. al.'s extension of Eshelby's theory under Mori-Tanaka approximation scheme and effective medium theories for dielectric constant approximations. The liquid fillers exist in globular phases, separated from each other, inside the polymer matrix. Addition of EMIMTFSI fillers leads to synergetic effect on the electrical and mechanical properties of the resulting composite; showing an increase of ~2 times in the dielectric constant from 3.4 to 6.3 with no change in the loss behavior of the base polymer and a decrease of 100 times in the Young's modulus of the composite from 1 MPa to 10 kPa. This is accompanied by an unprecedented 4.6 times increase in the maximum strain at break. A figure of merit of 187 is calculated for the electromechanical performance of the fabricated composite. These composites are actuated in a non-prestretch pure shear isotonic DEA configuration and showed superior performance compared to conventionally used 3M VHB 4910 acrylic tape. An effective improvement of 5 times and 8 times is demonstrated in terms of longitudinal strain and areal strain produced, respectively. Additionally, these composites show excellent stability against high temperatures and moisture uptake; and no change in the thermal degradation compared to the pristine matrix.

However, desirable changes in the Young's modulus and the dielectric constant is accompanied with undesirable reduction of the electrical breakdown strength. Nonetheless, the material system is capable of tremendous improvement in the actuation performance at low electric fields, making it an attractive option for new applications like adaptive surfaces and other low electric field applications.

Excellent optical, electrical and mechanical properties of the composite make them a suitable candidate for a variety of other applications, such as soft elastomeric layer in soft robotics powered by other actuation technologies such as pneumatics and magnetic fields, high-k dielectric for wearable electronic devices and high-k elastomeric layer for optoelectronic devices.

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Chapter 6¹⁻³

Electrically modulated adaptive surfaces for tactile feedback

Haptic technologies play crucial role at human-machine interfaces. Most of the current haptic technologies work to simulate the texture change without creating actual topographical transformations. This makes it challenging to provide localized feedback. Here, a new concept for on-demand surface texture augmentation that is capable of physically forming local topographic features in any pre-designed pattern is demonstrated. The transparent, flexible and integrable configuration of the device comprises of transparent system of electrodes (conductive hydrogel, silver nanowires and conductive polymers) with conventionally used acrylic elastomer as the dielectric layer. Desired surface textures can be controlled by pre-designed pattern of electrodes, which operates as independent or interconnected actuators. Surface features with up to a height of 0.16 mm and blocked force output of 47mN are demonstrated, with a transformation time of less than a second for a device area of 18 cm², and performance lying above perceptual threshold of receptors in human fingers. High transparency levels of 76% are achieved owing to the choice of the materials and novel device configuration. The capability of localized and controlled deformation, together with the high integrability to different substrates is demonstrated. A design approach of stacking of active layers is shown to improve the actuation performance; producing surface features of 0.3 mm height and blocked force output of 90mN.

¹⁻³ This chapter has been substantially published as Ankit et. al. “Highly transparent and Highly Transparent and Integrable Surface Texture Change Device for Localized Tactile Feedback”. *Small* (2018): 1702312; Ankit et. al. “Large-area, flexible, integrable and transparent DEAs for haptics”. *Proc. SPIE 10966, Electroactive Polymer Actuators and Devices (EAPAD) XXI*, 109661W (13 March 2019). and Ankit et. al. “Surface texture change on-demand and microfluidic devices based on thickness mode actuation of dielectric elastomer actuators (DEAs)”. *Proc. SPIE 10163, Electroactive Polymer Actuators and Devices (EAPAD) 2017*, 101632G (17 April 2017).

6. 1 Introduction

Surfaces communicate the information by targeting human senses like vision and touch. There are several instances in nature where surfaces modulate their shape and topographical features in response to changes in their local environment.⁴ Hence, surfaces are a very important interface between man and material, which can convey a lot of information via haptics. The field of adaptive surfaces and haptics has invariably enjoyed widespread attention from research groups and industry; attributed to a variety of factors like evolution of sense of touch in robotics, tactile perception in virtual and augmented reality, remote sensing and enhancing the quality of human-machine interaction for touch sensitive consumer products such as smartphones and touch-pads.⁵⁻⁶ Tactile feedback allows for superior identification and sorting, with the feel of touch being able to sort and resolve incoming data five times faster than visual sorting.⁶ Our sense of touch is remarkably adept at identifying different textures by swiping across a surface. Tactile interfaces can communicate information and recreate authentic sensations. These texture changes can be perceived from a range of physical attributes like variations in friction (moist to dry, sticky to slippery), hardness (soft and hard), temperature (cold and warm) and roughness (unevenness and smoothness).⁷ According to previous studies on human sense of touch, there are 4 different types of mechanoreceptors in our fingertips: Merkel disk (slow adapting type I, SA I), Meissner's corpuscles (fast adapting type I, FA I), Ruffini endings (slow adapting type II, SA II), and Pacinian corpuscles (fast adapting type II, FA II). SA I and FA I receptor units are located closer to the surface of the skin than the SA II and FA II units, as shown in Figure 6.1-A, and hence receive most of the tactile feedback.⁸⁻⁹ Additionally, SA I and FA I receptor units are more densely distributed in our fingertips compared to their type II counterparts, imparting outstanding spatial discrimination capability to our fingertips (Figure 6.1-B).⁸⁻⁹ Our fingertips are able to distinguish surface deformations of micron-sized features at low frequencies, and few recent studies even suggest that human fingers can detect nanometre-scale irregularities on surfaces of soft materials.⁵ Force perceptual threshold for our fingertips lies within a range of 32-43 mN.⁹ These thresholds help us in determining the performance of our haptic devices and decide on design modifications effectively.

Figure 6.1 Mechanoreceptors in human fingers. (A) Schematic of the depth of mechanoreceptors from the epidermis. It is important to note that SA I (Merkel disk) and FA I (Meissner's corpuscles) are in the proximity of epidermis.⁹ (B) Schematic showing the spatial distribution of mechanoreceptors in our fingertips. The density of SA I and FA I receptors is quite high compared to SA II (Ruffini endings) and FA II (Pacinian corpuscles) receptors.⁹

Several existing technologies such as electrostatic, piezoelectric, Peltier elements, surface acoustic waves, air jets and pneumatic valves aim to simulate the perception of texture change via sensory manipulation for tactile feedback.¹⁰⁻¹⁶ On the other hand new technologies like microfluidics and electroactive polymers create actual topographical changes on the surface for haptics.^{3, 17-20} Among these, actuators based on electroactive polymers (EAPs), and dielectric elastomer actuators (DEAs) in particular, provide an attractive alternative as they can directly induce topographical changes on the surface that can be felt by touch and are electrically controllable.^{3, 18, 20-21} DEAs have been investigated for applications in tactile and vibrotactile feedback devices via different approaches.²¹⁻²⁵ Since the deformation produced in the active DEA layer can be small, appropriate coupling is required for out-of-plane deformation. Hydrostatic coupling utilising an incompressible fluid in conjunction with a DEA has been shown for refreshable braille displays.²¹ Coupling DEAs with rigid mechanical components allows for an amplification of fine deformations.²⁴ Other approaches to “amplify” tactile feedback included coupling DEAs with vibrational simulation via variations in amplitude, frequency or pulse-time combinations.²²⁻²³ These systems are single, discrete actuators and need to be arranged in an array for conveying multiple information. Additionally, these systems still suffer from the issue of fabrication complexity, rigid frames for free standing films and opaqueness. Assembling large

arrays of discrete actuators is prohibitive in terms of cost, actuator density and fabrication complexity. This problem can be addressed by making use of the thickness mode actuation of dielectric elastomers, in which a soft passive layer is integrated on the DEA and capture the changes in the underlying active layer to produce desirable surface patterns.^{3, 18, 20} Specific topographical changes can be achieved by straightforward patterning of electrodes, resulting in deformations as desired.

The thickness mode actuation of DEAs for obtaining out-of-plane deformations on a soft passive layer under the application of the electric field is illustrated in Figure 6.2.^{1-3, 18, 20} On the application of an electric field, the elastomer in the active region experiences electrostatic attracting forces, squeezing the elastomer (Figure 6.2-A). Thus, there is a reduction in the thickness of the elastomer in the active area. At the same time, the elastomer in the non-active region experiences a shear stress caused by the expansion of the active area (Figure 6.2-B). The soft passive layer integrated atop the DEA captures these strains produced in the active layer and displays out-of-plane deformation (Figure 6.2-C). Due to the strong interaction between the PDMS and the underlying layers, the PDMS over the active region experiences a reduction in thickness whereas the PDMS over the non-active region bulges out of the plane. The net effect of reduction in thickness at certain locations and increase in thickness at different locations creates a texture change on a flat smooth surface. The thickness mode actuation of DEAs is more suitable for tactile applications as the soft insulating layer on top of the electrically active layer provides the user with additional safety.

Figure 6.2 Thickness mode actuation of DEAs. (A) Elastomer (in the active region) gets squeezed between compliant electrodes upon application of voltage. (B) Elastomer region between the adjacent active regions experiences shear stress, at the same time. (c) Stresses produced in the underlying active layer leads to deformation of the soft passive layer on the top of the DEA device.

6.2 Results

6.2.1 Device architecture for transparent devices

Figure 6.3 Device architecture. (A) Cross-sectional schematic of the overall device architecture. (B) The coverage of bottom blank electrode (conducting hydrogel) demarcated by the red box and the overall area of the top patterned electrodes shown bounded by the blue box. Transparency of the device on text on display screen (C) and on video on display screen (D) (Device inside the red square).

The cross-sectional schematic of the complete device architecture with all the layers in the device is shown in Figure 6.3-A. For generating predetermined surface texture changes in thickness mode actuation, patterning of the compliant electrodes is essential.^{3, 18} The patterning of electrodes on both the top and bottom sides makes it challenging for DEAs to be integrated onto hard substrates. This is because the non-active region adheres to the substrate constraining the deformation of the elastomer in the active region and limiting the compliancy of the electrodes, resulting in no actuation under applied voltage. Hence, a novel strategy has been developed which does not require the patterning of the electrodes on both sides. The bottom electrode covers the predetermined area of the elastomer and is not patterned. The predetermined area of the bottom blank electrode is designed to be greater than the overall coverage of the top patterned electrodes. This provides the active region of the elastomer freedom to stretch under application of electric field. Figure 6.3-B shows the area of bottom blank electrodes highlighted in red and the region of top patterned electrodes demarcated in

blue. Since most of the metallic and non-metallic transparent electrodes exist in the form of nanoparticles and nanowires, they cannot be used for bottom blank electrodes as they will render regions of the elastomer uncovered, susceptible to sticking to the underlying substrate (Figure 6.4). We can clearly see regions of elastomer uncovered by the nanowire network susceptible to adhesion with the substrate. Using conductive nanostructures on both the sides of elastomer will also compromise the transparency of the device. Thus, a conducting hydrogel layer was utilised for the bottom electrodes, rendering the elastomeric layer free to stretch in the active region and enabling high transparency. The overall high transparency of the device is also visible from the images of the device taken on top of text and video on a computer display screen in Figure 6.3-C and Figure 6.3-D respectively.

Figure 6.4 Rationale for non-selection of AgNW as bottom electrodes. Scanning electron micrograph of AgNW network on stretched out acrylic elastomer, rendering (rectangular regions highlighted in blue) regions where AgNW networks do not cover the sticky acrylic film and pose the risk of the film getting adhered to the substrate.

Although the use of conducting hydrogels as top patterned electrodes would be attractive, it is impractical for scalability due to the cumbersome laser patterning processes required to pattern them to small dimensions. Additionally, use of very thin hydrogel layers, suitable as top patterned electrodes, will pose more fabrication complexity in terms of handling. Patterned uniform AgNW networks have been shown to be facilely fabricated by spray coating of AgNWs over physical masks.²⁶⁻²⁸ For our

device fabrication, we utilized AgNW concentration of 28 mg/cm^2 , which provides a dense nanowire network required for the intended device performance. However high junction resistances at AgNW-AgNW junctions can create high localized electric fields leading to electrical breakdown.²⁹ One approach to homogenise the electric fields is to coat it with a transparent conducting polymer, which also improves the surface roughness of the nanowire network. Hence, sprayed PEDOT: PSS (poly-(4,3-ethylene dioxythiophene): poly(styrene-sulfonate)) is used as the transparent conducting polymer on the AgNW network.³⁰ The conducting polymer layer functions as a filler within the AgNW network to give a uniform conductivity over the elastomer surface and prevent electrical breakdown while also potentially improving mechanical properties.³¹⁻³²

Commercially available acrylic tapes (VHB 4910) consisting of mixtures of aliphatic acrylates have excellent transparency and have been known to produce largest actuation strains in the family of elastomeric matrices in DEA configurations.³³⁻³⁴ Prestretching the film biaxially reduces the thickness; which in turn leads to reduction of the required electric field for actuation.³³⁻³⁴ Biaxial prestretching has also been known to increase the breakdown electric field and improve the actuation performance, however necessitates the use of rigid frames to retain the pre-stretch. For the scope of this transparent surface texture device, VHB 4910 was used as the active elastomeric layer. Polydimethylsiloxane (PDMS) elastomer serves as the soft top layer on the top of the active DEA layer due to its low elastic modulus. Tactile systems necessitate the need for the users to touch the naked conducting electrodes, which poses a risk of high electrical shock in case of electrical breakdown.³⁴ It additionally serves as a protective layer against atmospheric oxidation of top patterned AgNW electrodes.³⁵

The assembled DEA device primarily suffers from transparency losses due to the top patterned electrodes, made up of sprayed AgNW network and PEDOT:PSS. Figure 6.5 shows the transparency measured for AgNW and PEDOT:PSS network and compared to the AgNW network. The diluted PEDOT: PSS layer adds minimally to the transparency losses. Compared to the 78.5% transparency (@ 550 nm) measured for the AgNW network, the transparency for the AgNW and PEDOT:PSS network was measured at 76% @ 550 nm.

Figure 6.5 Overall device transparency. Diluted PEDOT: PSS layer adds minimally to the transparency losses of the device.

6.2.2 Actuation performance of thickness mode DEAs

Carbon powder-based devices can be considered as a standard in the field of DEAs owing to the extensive use of carbon powder in fabrication of actuators and generators. We compare the performance of transparent electrode devices and carbon powder electrode devices at 3 different applied electric field values, with the thickness of the soft layer maintained at 1 mm for both the devices. The change in thickness of the soft passive under the application of applied electric field depends directly on the magnitude of the applied electric field.^{3, 18} Hence, we observe an increase in the change in thickness of the top layer with increase in the applied electric field in both the transparent electrode devices and carbon powder electrode devices as shown in Figure 6.6-A. The device performance for transparent electrodes is comparable with carbon powder electrodes at all the 3 applied electric fields; with the maximum attainable surface deformation being 155 microns for transparent electrodes and 160 microns for carbon powder electrodes at an applied electric field of 21.4 V/ μm . Peer-reviewed reports mention the threshold displacement detection values as 30 – 100 microns for slow adapting receptors (Merkel cells) and 17 microns for fast adapting receptors

(Meissner's corpuscles), which are distributed closer to the skin and contribute to the feel of touch.²⁴ The deformations achieved by our device (up to 0.16 mm out-of-the plane deformations) are significant enough to be easily detected by fingers; as they are much higher than the threshold values for the spatial recognition by receptors in the fingertips.^{9, 16, 24} At higher applied electric fields, the Maxwell stresses are higher, consequently leading to higher shear strains and reduced thickness of active elastomer layer and electrical breakdown. At lower electric fields, similar magnitudes of surface deformation were measured for both the devices. Transparent electrode devices showed a deformation of 78 microns and 106 microns compared to the 80 microns and 119 microns in the carbon powder electrode devices at an applied field of 14.3 V/ μ m and 17.9 V/ μ m respectively. The passive soft layer has no electric field applied to it and all the active properties of the laminate are derived from the underlying elastomer layer.^{3,}

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Figure 6.6 Out-of-plane deformations and blocked force. (A) Plot and comparison of out-of-plane surface deformations produced on the soft passive layer with varying electric field in transparent electrode devices and carbon powder electrode devices. (B) Blocked force from

transparent electrode devices against applied electric fields (DC). (C) Profile of surface change upon application of electric field (Transparent electrode-based surface texture device, applied electric field – 17.9 V/ μm).

The blocked force measurement for the transparent electrode devices revealed a maximum of 47 mN at 21.4 V/ μm and the force output reduced with lowering the applied electric field as shown in Figure 6.6-B. These forces are large enough to be detected by the slow adapting and fast adapting receptors in our fingers.²⁴ It is important to note that the profile of these surface deformations is parabolic in nature, as seen from Figure 6.6-C. Corresponding voltages and power consumption for the applied electric fields have been mentioned in Table 6.1; and although the voltages seem high (4kV – 6kV), the current drawn (1.2 μA – 11 μA) and the peak power consumption (4.8mW – 66mW) remains very low.

Table 6.1 Electric field vs voltage and power. Power consumed is calculated from the voltage applied across the device and measuring the current (in series) drawn by the device.

Applied Electric Field (V/ μm)	Voltage (kV)	Current (μA)	Peak power consumption (mWatts)
4.3	4	1.2	4.8
17.9	5	3.1	15.5
21.4	6	11	66

These transparent electrode devices also show a consistent performance when tested over several cycles. It can be seen from Figure 6.7-A that the device performance remains nearly the same; with the device retaining 91 % of surface deformation after 250 cycles of operation (within 20 minutes) at an applied electric field of 17.9 V/ μm . To measure the response time and frequency bandwidth of the device, blocked force was measured as a function of frequency at 21.4 V/ μm . As seen in Figure 6.7-B, the device retains its performance at lower frequencies, but the performance starts to reduce at higher frequencies. Frequency profile of the device performance in terms of blocked force can be seen at 10 Hz in Figure 6.7-C. At 20 Hz frequency, the device provides a force output of 43 mN as compared to 47 mN at static fields. The force output starts decreasing, reaching 22 mN at 1000 Hz frequency and the device is not functional at

even higher frequencies. Device maintains 50 % of the maximum force output over the frequency range of 0 Hz to 1000 Hz. The bandwidth of the actuator may be limited by several factors.³⁶ It may be attributed to the latency in the electronic circuit, electrode materials, and most importantly, the viscoelastic nature of acrylic tape.³⁶ Transparent electrode based tactile devices have similar amplitude of blocked force till the frequency of 20 Hz; and it decreases and reaches 50 % of its maximum performance at 1000 Hz, from which the response time of these devices can be said to be as low as 1 milli-second.³⁷

Figure 6.7 Cyclic performance and frequency bandwidth. (A) Device actuation performance in terms of vertical deformation produced over 250 cycles of operation. (B) Blocked force from transparent electrode devices against applied electric field at different frequencies (Square waveform). (C) Blocked force from transparent electrode device at 21.4 V/μm and 10 Hz frequency.

The estimated RC time constant for the circuit was in the range of microseconds (μs); significantly lower than the current limit of actuation frequency of the device (kilohertz, millisecond range). Thus, the viscoelasticity of the dielectric polymer is suggested to be the primary reason for the bandwidth limitations of the device. As already

mentioned, DEAs are variable capacitors and the equivalent circuit model is shown in Figure 6.8.³⁶ The resistance can be derived from the leakage current through the elastomer and is represented by a parallel resistor R_C to the capacitor C (measured for the device). R_C values were estimated in the range of mega-ohms. Resistance of the compliant electrodes represented by R_{SR} were calculated in the range of kilo-ohms as shown in Table 6.2. Silver nanowire network has much lower resistance than the conducting hydrogel layer, hence can be neglected from R_{SR} calculations. Time constant (τ) of the device is estimated by formula (equation (1)) and results are shown in Table 7.2.

$$\tau = (R_{SR} \times R_C \times C) / (R_{SR} + R_C) \quad (1)$$

Figure 6.8 Modeling a DEA as a variable capacitor. C represents the energy storage part of the insulating material, R_C represents the internal losses in the dielectric material and R_{SR} represents the sheet resistance of the electrodes.

Table 6.2 Estimation of RC time constant of the device. Measured values of R_{SR} , R_C and C to calculate the time constant of the device, for understanding the frequency limitation.

R_{SR} (Ohms)	R_C (Ohms)	C (F)	τ (sec)
23.3×10^3	5.4×10^5	2.9×10^{-10}	6.6×10^{-6}

When an electric field is applied by switching on the voltage, opposite charges build up on the facing sides of the sandwiched elastomer layer creating Maxwell stresses and causing in-plane deformation of the elastomer. This in-plane actuation for transparent hybrid system of electrodes and carbon powder electrodes devices are worthwhile to be examined to understand the strains being produced in active layer. The images of the

transparent and carbon powder electrode devices used for comparison are shown in Figure 6.9-A and Figure 6.9-B, respectively. The dimension of the active and the non-active areas have been kept nearly the same for comparison of the lateral and areal strain. The width of the patterned electrodes can be used for lateral strain comparison. Transparent electrode devices produced an areal strain of 8.3 % compared to 15.87 % in carbon powder electrode devices (Figure 6.9-C). The difference in the lateral strains produced is significantly lower with the transparent electrode devices showing a lateral strain of 9.5 % in comparison to 13.5 % observed in carbon powder electrode devices. Although there is a difference between the lateral and areal strains between the transparent and carbon powder electrode devices, there is no significant difference in the intended actuation performance, which is shown in later sections (out-of-the-plane surface deformations). It can also be inferred that the stress on the nanowire networks is relatively small for producing a similar kind of vertical deformation, which in turn helps in better cyclability of the device.

Figure 6.9 In-plane strains produced. (A) Image of hybrid transparent electrode DEA with dimensions of the active and the non-active region. (B) Image of carbon powder-based DEA showing the dimensions taken for device fabrication. (C) Comparison of areal strain and lateral strain for the transparent electrode devices and carbon powder electrode devices. The applied electric field for all the measurements was 21.4 V/ μ m.

The surface deformations and blocked force produced from these thickness mode actuation devices can be augmented by adopting a multi-active-layer approach. The

DEA devices were stacked before putting the final top soft layer. By stacking 3 active layers, the surface deformation can be increased to nearly 300 microns (0.3 mm, 30% strain) from 160 microns (0.16 mm, 16% strain) (Figure 6.10-A). This can be attributed to increased stresses produced in the stacked active layers. Intuitively, the blocked force from the device also increased with stacking of active layers. A blocked force of 90 mN was measured for 3 active layers compared to 35 mN for the single active layer and 65 mN for the 2 active layers (Figure 6.10-B). These values are significantly higher than the perceptual force threshold and detectable deformation threshold for the mechanoreceptors in our fingertips. Hence, the force feedback can be augmented significantly by stacking multiple active layers, accompanied with a significant increase in the surface deformation as well.

Figure 6.10 Augmentation of surface deformation. (A) Comparison of surface deformations produced by a single active layer device and a triple active layer device. (B) Blocked force output measurements for stacking of active layers. A triple active layer device doubles the performance of these devices.

6.2.3 Localized, patterned and flexible tactile feedback on surfaces

A unique advantage enabled by our patterned DEA device is the ability to provide localized feedback. Typically, conventional tactile feedback devices transmit the information to the users through vibration produced on the whole surface of the device. This limits the detectability of the exact location on the interaction surface and hinders localized differentiation of the information. However, with our thickness mode actuation DEA devices, localized feedback on the surface through actual topographical changes has been demonstrated, as shown in Figure 6.11-A. Although these changes are easily observable by our human eye, capturing them on a still image by a camera is

a difficult task. These sub-millimetre level deformations can be easily detected by our fingers through touch. Under no applied electric field, the surface remains completely smooth. Upon first actuation, the surface texture changes on the left side of the device while the right side remains smooth. The vice versa holds true as well. These changes in the actuation of a particular part of the device can be linked to user interfaces and could be used to convey more meaningful information than simple location information. Unprotected fingers can probe the surface under the actuated condition indicating that the surfaces are electrically insulating and safe to touch (Figure 6.11-B). 1mm thick soft insulating layer on the top provides insulation from direct contact of fingers with electrodes.

Figure 6.11 Localized tactile feedback, probing by naked finger. (A) Localized surface deformations produced on the surface for imparting the location information along with other information as well. (B) Image showing the safe operation of devices and can be touched by naked hand.

The ability of the device to produce deformations at desired locations was demonstrated further with fabricating a multilayer device containing 4 active regions that can be controlled individually. These 4 active regions create four pixels on the surface and can be activated separately or together. The device had no deformations and its surface was smooth when no input was given (Figure 6.12-A). When a particular region on the surface was chosen to be activated, high voltage electrical signal was sent to the corresponding device. Figure 6.12 shows the actuation for 4 different possibilities of actuation of pixels on the surface. Figure 6.12-B shows the activation of only one pixel (top left) of the device; Figure 6.12-C shows the activation of two pixels at the same time, top left and bottom left; Figure 6.12-D shows the activation of 3 pixels together, top left, top right and bottom right; Figure 6.12-E shows the activation of all the 4 pixels

at the same time. In this manner, different combinations of pixels can allow us to communicate different information to the user.

Figure 6.12 Multiple devices on single surface. A 4 region-multilayer device where individual regions correspond to pixels and can be activated individually or together. (A) Smooth surface. (B) One pixel activated. (C) 2 pixels activated together. (D) 3 pixels activated together. (E) All pixels activated.

Blocked force output from the different pixels were measured at 6 kV applied voltage to check the uniformity of actuation from individual pixels of such a large area device. The different pixels were located at the junction of demarcated rows and columns, as shown in Figure 6.13-A. As observed from Figure 6.13-B, all the 4 pixels have force

output of more than 90 mN, well above the perceptual force threshold for mechanoreceptors in human fingers. There is slight observable difference between the different pixels, with the range of force output varying between 90 mN and 110 mN. This can be attributed to non-automated fabrication of the devices leading to slight design non-uniformity at individual pixels. A more automated fabrication process is believed to provide more uniform force feedback.

Figure 6.13 Uniformity of the individual pixels on a large area device. (A) Location of the 4 individual pixels on the device demarcated at the junction of rows and columns. (B) Blocked force output from individual pixels.

Another advantage that the thickness mode actuation provides is the patternability of the surface deformations. This is attributable to the fact that the top electrodes can be

patterned by designing of appropriate mask, which in turn defines the shape of the non-active region as well. Figure 6.14-A shows the actuation of these patterned deformations. This lends the advantage of producing complex surface modulations for improved sorting of information. Flexibility of these devices was also demonstrated by fabricating the device onto a flexible substrate as shown in Figure 6.14-B. This is possible owing to the unique architecture of the device. Working of flexible devices has been demonstrated in Figure 6.14-C where the surface deformation could be clearly observed. DEAs conventionally require rigid frames to retain the pre-stretched state of the elastomer, critical for device performance. Hence, a concept that does not require such rigid frames has been demonstrated which can enable facile integration.

Figure 6.14 Patternability and flexibility. (A) The surface deformations are not limited to straight ridges and difficult patterns can be generated on the surface. (B) Device fabrication on a flexible substrate. (C) Surface transformation from a smooth state to a deformed state for the device fabricated on a flexible substrate upon application of electric voltage.

6.3 Discussion

A novel device architecture, first of its kind, which lends DEAs much more practicability and applicability, allowing the lamination and integration with surfaces without the need of rigid frames has been demonstrated. A transparent surface texture change device for tactile feedback making use of this architecture has been demonstrated. The transparency of the system (76% @ 550 nm) is excellent; achieved by making use of hybrid system of electrodes – conducting hydrogel as bottom electrodes and silver nanowire – PEDOT: PSS as top electrodes, transparent acrylic elastomer as active layer and transparent PDMS as soft passive layer. The device produces physical surface deformations of 0.16 mm, which are easily detectable by touch. It is observed that the actuation performance in terms of surface deformation for transparent electrode devices agrees well with the well-established carbon-based electrode surface texture change devices. The device produces blocked force output of 47 mN, which lies above the perceptual force thresholds of receptors in our fingertips. The devices also show superior cyclability and frequency bandwidth; with device providing similar performance till 20 Hz and half of the maximum performance till 1000 Hz. A simplistic approach of stacking of active layers is demonstrated to improve the performance of devices in this configuration, with a triple active layer device doubling the actuation performance (0.3 mm surface deformations and 90 mN blocked force output). Owing to its unique architecture, patterning of the deformations has been demonstrated, along with the flexibility and the reliability of operation. Localized tactile feedback demonstrated using these devices, opens up applications in tactile touchpads, braille displays and on-demand buttons.

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Chapter 7

Enabling reversible rigidity using biphasic material as active matrix*

One of the important attributes missing in the current generation of soft actuators is the ability to reversibly modulate its mechanical properties upon demand. Current approaches focus on augmentation of a reversible stiffness component on the existing actuator. This creates a need for an intimate integration which provides reversible modulation of mechanical properties and contributes directly to the actuation behavior as well. Thermal perturbation is chosen for the modulation control owing to its lightweight design and scalability. Two low-temperature phase change materials, polyethylene glycol (PEG) and paraffin wax, are evaluated for their thermal behaviour, mechanical strength and dielectric properties and PEG emerges as a suitable choice owing to the measured characteristic properties like low melting point ($\sim 56^{\circ}\text{C}$), significant gap between melting and solidification (around 35°C), superior thermal stability (onset temperature $\sim 345^{\circ}\text{C}$), high mechanical strength (failure @ 244 N for 0.58 mm compression) and high dielectric constant (10@1kHz). Fabricated composites show 700 times change in Young's modulus, 100 times change in the flexural modulus and 10 times change in hardness. These reversible rigidity composites also show the ability to regain their structural integrity and mechanical strength. Phase change behavior is demonstrated by integration of the composite with a flexible joule heater and the performance of the joule heater is characterized.

*This chapter is currently being prepared as a manuscript.

7.1 Introduction

Biological appendages, consisting of natural muscles and tissues, make perfect exemplars of actuators that we aspire to replicate. Not only can they lift and push weights, they can also adapt to different surface contours, handle objects of different rigidities, and manipulate things with great dexterity. Their remarkable versatility can be attributed to one of their unique properties: the ability to modulate stiffness. Variable rigidity is a key feature in achieving compliance matching under different circumstances; enabling the actuator to be highly conformable to irregular surfaces in its soft (flexible) state, and support load in its hard (rigid) state.¹⁻² Natural materials demonstrate remarkable variations in their stiffness under different surrounding conditions. These changes be very slow or fast and can be triggered by a variety of stimulus like temperature (transition of stiffness for byssal threads in mussels, Figure 7.1-A), moisture (abrupt loss of stiffness in basic constituents of plants, “hemicellulose”, Figure 7.1-B), mechanical forces, & chemical and electrical mechanisms (living tissues belonging to complex organisms like animals).³⁻⁷

Figure 7.1 Modulation of mechanical properties in nature. (A) Byssal threads in mussels demonstrate a change in mechanical stiffness owing to temperature variations. Dynamic analyses provide glass transition and an operational range of temperatures during which the mechanical stiffness remains constant.³ However, a lower temperature leads to sudden increase in the stiffness (almost by an order of magnitude).³ (B) Hemicellulose, one of the basic constituents of plants, shows a drastic reduction (3 orders of magnitude) of Young’s modulus upon increase in moisture content.⁵

Soft actuators, an emerging field of research, aims at mimicking these biological systems by making use of soft materials and has demonstrated greater mechanical compliance, ability to conform to irregular shapes, deliver large strains and manoeuvre within confined spaces.⁸ So far, a great deal of focus has been given to the actuation technologies like pneumatics, fluidics, magnetic fields, thermal transitions and electroactive polymers (EAPs) for driving these soft actuators.⁹⁻¹⁵ Electrically powered dielectric elastomer actuators (DEAs) made of elastomers are known for their high efficiencies, light weight design and superior structural compliance.^{9, 11, 16-19} And even though existing soft actuators have demonstrated the ability to produce different kinds of motion, they still lack the unique intrinsic ability to reversibly modulate rigidity; to be flexible, stretchable and bendable at one moment, whilst rigid, able to bear load and resist deformation at another moment. The inability of soft actuators to stiffen/strengthen when required not only necessitates the use of actuating/input signal to be applied for the whole duration of actuation, making them susceptible to failures and damages, but also limits the ability of soft actuators to grasp and support the load of an object, sustain its configuration in its active state while being exposed to forces from the surroundings, and impart forces to manipulate and push objects around.

Existing approaches to achieve variable stiffness in soft robots can be grouped into two broad categories – structural stiffening and material stiffening.^{2, 20} Structural stiffening techniques like particle jamming, cable tension method and electroadhesion involves the altering of degree of restriction or freedom of relative motion between components within the composite.²¹⁻²² Structural stiffening approaches necessitates the augmentation on the actuation mechanism and do not contribute to it. Material stiffening approaches like use of phase-change materials, electrorheological materials and magnetorheological materials, on the other hand, generally involves altering the mechanical properties of a component material in the composite, through application of external stimuli, such as heating or applying a force field.²³⁻²⁷ A material stiffening approach based on thermal transition has advantages in terms of scalability and lightweight.^{2, 20} Thermal transition enables devices to maintain high rigidity in load bearing state without energy consumption as compared to systems.^{2, 20}

Material stiffening approach with thermal perturbation has been investigated by employing thermoplastics and low melting point alloys (LMPAs).²⁴⁻²⁵ These materials possess either a lower melting temperature (T_m) or a lower glass transition temperature

(T_g). The change in the microscopic arrangement leads to a reduction in the Young's modulus and can enable rigidity modulation within temperature ranges above, below, or across either T_g or T_m . Even though some of these systems have been coupled with the soft actuators, it is notable that these existing rigidity modulation approaches are augmented on the actuator system and do not contribute directly in the actuation process.²⁵ Additionally, use of LMPAs such as Galinstan (EGaIn) & Field's metal raises cost concerns as they are very expensive metal eutectics, incorporating rare earth elements.

Herein, a novel material system for fabricating reversible rigidity composites is reported, which undergoes thermally triggered phase change to enable modulation of mechanical properties. Polyethylene glycol turns out to be a suitable choice as a phase-change material system owing to its characteristic properties like low melting point ($\sim 56^\circ\text{C}$), significant gap between melting and solidification (around 35°C), superior thermal stability (onset temperature $\sim 345^\circ\text{C}$), high mechanical strength (failure @ ~ 244 N for ~ 0.58 mm compression) and high dielectric constant ($10@ 1\text{kHz}$). Fabricated composites show modulation of mechanical properties between its rigid state and soft state, with 700 times change in Young's modulus, 100 times change in the Flexural modulus and 10 times change in the Shore hardness value. Owing to the ability to re-melt and re-solidify, it enables healing of the mechanical integrity of the composite. Furthermore, the reversible rigidity composite is integrated with a flexible joule heater. Joule heater produces a similar heating curve in its flexed and straight configurations and can reach a temperature greater than 160°C in less than 4 minutes (@2 V).

7.2 Our Approach

7.2.1 Principle of design

As mentioned in the earlier section, modulation of mechanical properties by thermal perturbation employs material with low glass transition temperature or low melting point. Where glass temperature is associated with a material phase change from a hard and brittle "glassy" to a viscous and rubbery state, melting point is associated with the material changing from a solid phase to a liquid phase.²⁸ Such a phase change from a solid to liquid state is associated with drastic changes in the mechanical properties of the material. Our approach (Figure 7.2) aims to make use of this phase transition for achieving modulation in mechanical properties. A low-temperature phase change

material is encapsulated in a polymer matrix, which maintains its structural integrity within the temperature range. Below the melting temperature, the phase change material remains in solid state and the composite shows a rigid behavior. Above the melting temperature, the material undergoes a phase transition to a liquid state and composite becomes flexible and stretchable. Providing control for heating and cooling of material enables reversible modulation of mechanical properties. It is more difficult to cool materials below room temperature on a small scale and in an untethered fashion compared to heating of materials, which can be done by a simple joule heater. Hence, it is desirable to pursue for a low-temperature phase-change material which maintains solid phase at room temperature and transitions to a liquid phase upon heating. Removal of the thermal perturbation will lead to eventual re-solidification.

Figure 7.2 Low temperature phase change material as active matrix. Schematic of melting point of a material as observed from a DSC curve. Before the melting point, material is in a solid state enabling rigidity in the composite. After the melting point, material transitions to a liquid state imparting stretchability and flexibility to the composite.

7.2.2 Choice of materials

Most frequent choice of researchers for a low-temperature phase change material are paraffin wax and low melting point alloys.²⁹⁻³⁰ Low melting point alloys are very expensive and consist of rare earth elements like indium. Additionally, they are highly conductive in nature, which will limit their utilization in a capacitor configuration, as

needed for a field driven DEA architecture. Polyethylene glycol (PEG) is primarily a polyether compound, hydrophilic in nature and has widespread applications in industrial, chemical, medical and biological applications.³¹ It is an established organic solid–liquid phase change material demonstrating varying values of enthalpies and phase-transition temperatures depending on its molecular weight.³¹ While lower molecular weight PEGs (like 300,400 & 600) are viscous liquid at room temperature, higher molecular weight PEGs (like 2000, 4000 & 6000) exist as flaky solids at room temperature. To establish the distinct advantages of using PEGs for reversible rigidity composites instead of the established paraffin wax material, a one to one comparison is done for specific material properties. Findings are presented in the following section.

7.3 Results

7.3.1 Material characterization

Thermal behavior

Since, the focus is on thermally assisted phase change, it is pertinent to start with thermal analysis of both the materials. Figure 7.3-A shows the DSC measurement for both PEG (MW–2000) and wax for 2 cycles under nitrogen environment. Melting temperature of both the materials are observed to be quite similar, with melting point observed at ~56°C for PEG and at ~59°C for wax. However, a drastic difference is found in the observed solidification (crystallization) temperature for individual material systems. Solidification temperature for PEG is observed at ~20°C whereas for wax it is observed at ~54°C. Hence, a bigger operating window (around 35°C) is obtained for PEG compared to wax for actuating the composite while it is in liquid state. On the other hand, the wax provides a very small window (around 4°C) between melting and solidification, which is highly impractical for real-life applications. It is important to even though the observed solidification of PEG in a nitrogen environment lies around 20°C, it is a solid at room temperature in ambient conditions. Additionally, repeated melting and solidification behavior for PEG is also demonstrated.

A noticeable additional phase change is observed in wax between 40°-45°C, which is also observed in higher molecular weight PEGs (MW–6000, Figure 7.3-B). This phenomenon is attributed to different crystal folding modifications during the solidification process.³²⁻³³ When these endothermic and exothermic phase-change peaks appear close to solidification and melting points, as in DSC curve of PEG (MW–

6000, Figure 7.3-B) they do not produce any significant effects. However, spaced out nature of these peaks, as observed for paraffin wax (Figure 7.3-A), could lead to variable nature of mechanical properties measured after cycle heating and re-solidification.

Figure 7.3 Thermal analysis of the phase change materials. (A) DSC curve (2 cycles) for PEG (MW–2000) and paraffin wax showing melting and solidification behavior of the material

systems. (B) DSC curve (3 cycles) for PEG (MW–6000) showing melting and solidification peaks, accompanied with adjacent endothermic and exothermic peaks, similar to wax.

Thermogravimetric analysis is also done for PEG (M.W.–2000) and wax to understand the thermal degradation behavior of both the materials (Figure 7.4). The samples were heated at a rate of 10°C/min from 30°C to 400°C in nitrogen environment to get the TGA curves. As seen from the Figure 7.4, paraffin wax has an onset temperature (characterized by a 2% weight loss) at 204°C and burns off completely by 345°C. On other hand, onset temperature for PEG is recorded at 342°C, a much higher temperature compared to paraffin wax. This shows much better thermal stability of PEG compared to wax.

Figure 7.4 Thermogravimetric analysis (TGA) for phase change materials. TGA curve for PEG (MW–2000) and paraffin wax from 30°C to 400°C showing the thermal degradation behavior for these materials.

Load bearing ability

Going back to the original intention of reversible rigidity modulation, it is imperative to compare the mechanical strengths of PEG (MW–2000) and paraffin wax in their solid states. Since liquids are considered to possess no mechanical strength, the magnitude of rigidity modulation in the composites will be determined by the mechanical strength of their constituent fillers in solid state.³⁴ A uniaxial compression

test is performed to understand the load bearing ability of both the materials and their ability to resist deformation under loading conditions. The tests are performed for the materials in their composite forms, with similar dimensions of the silicone based reversible rigidity composites as explained in the experimental section. A steeper curve (Figure 7.5) is observed for PEG compared to paraffin wax, showing a better load bearing ability and resist deformation under the loading conditions. Further observation points to a much higher load carrying capacity of PEG, with fracture for PEG occurring at ~ 244 N (~ 0.58 mm compression). Compared to PEG, the fracture for wax occurs at only ~ 40 N (0.36 mm compression), a difference of more than 6 times in terms of mechanical strength.

Figure 7.5 Load bearing ability of the phase change materials. Compressive load versus compressive extension (compression) for PEG (MW-2000) and paraffin wax showing much higher mechanical strength for PEG.

Dielectric behavior

Since our aspiration is to use the phase change filler as the active component in soft actuators contributing directly to the actuation process and owing to the advantages of employing a DEA configuration, the material is desired to have a high dielectric constant value.¹⁶⁻¹⁸ Dielectric spectroscopy reveals the dielectric constant of the PEG (MW-2000) and paraffin wax material and its frequency-dependent behavior (Figure

7.6-A). At lower frequencies, PEG has orders of magnitude higher dielectric constant than paraffin wax and remains greater than wax at higher frequencies. Dielectric constant value for PEG is measured to be 142 at 1 Hz, which reduces to ~52 at 10 Hz, ~22 at 100 Hz and ~10 at 1 kHz. On the other hand, dielectric constant for paraffin wax is measured between 4.3-4.2 for all the same frequencies. The high dielectric constant of PEG is attributed to the presence of end hydroxyl groups and the flexible oxyethylene chain of the molecule.³⁵⁻³⁶ The contribution of the oxyethylene chain to the dipole moment is significantly higher than the end hydroxyl groups.³⁶ It is also evident from the plot in Figure 7.6-A that PEG has a frequency dependent permittivity behavior, typically caused by orientation of ionic and dipole species present in the molecule.³⁷ Loss behaviour for both the material systems could be derived from the plot of imaginary part of permittivity against frequency (Figure 7.6-B). Both PEG and paraffin wax show similar values at 1 kHz. However, in the low frequency regime PEG shows high loss behaviour owing to its ionic nature.

Figure 7.6 Dielectric behavior of the phase change materials. (A) Plot of dielectric constant against the varying frequency for PEG (MW–2000) and paraffin wax, revealing higher dielectric constant values for PEG. (B) Plot of imaginary part of permittivity against the varying frequency for PEG (MW–2000) and paraffin wax.

7.3.2 Reversible rigidity

Based on the measured material properties, PEG emerges as a suitable choice for further investigations and fabrication of reversible rigidity composites. Rigidity encompasses the ability of the material to resist mechanical deformation homogeneously and isotropically.² On the other hand, stiffness often pertains to a singular loading direction whereas elasticity is related to stretching of material and recovery of the shape on

removal of load.^{2, 20} Rigidity modulation of PEG filled bulk composites (fabrication details in Section 3.2.5) are detailed in this section.

Stretching modulation

Figure 7.7 Stretching behavior in soft and rigid state. (A) Demonstration of the ability of the composite to resist stretching under applied load with filler in solid state and allowing stretching when filler is in liquid state. (B) Stress strain curve for composite in rigid state (filler in solid state) and soft state (filler in liquid state).

As mentioned above, one of the aspects of rigidity modulation is to vary the ability to stretch under the applied load. PEG based reversible rigidity composites demonstrate the capability to resist stretching under loading conditions (Figure 7.6-A) in their rigid state (PEG fillers in solid phase). On application of thermal stimulus, the fillers

transition to liquid phase, bringing the composite into a soft state where they can stretch with applied load (Figure 7.7-A). As seen in Figure 7.7-A, a 1 N (100 grams) load is applied to the composite in its rigid and soft state. Where the composite is able to resist any visible deformation under the 1 N load in its rigid state, there is a ~30 mm (>50% strain) deformation of the composite in its soft state, observable easily in the image. To quantify the applied load and stretching deformation, a temperature dependant uniaxial tensile testing was done. Figure 7.7-B shows the stress-strain curve for the reversible rigidity composite in its rigid state and soft state. The huge difference in the mechanical stiffness is apparent from the curve. While the composite maintains a steep stress-strain relation in its rigid state, it deforms without the application of any significant stress. Young's modulus in the soft state of the composite is calculated at 7.87 kPa while in rigid state, it is measured at 6.23 MPa. A dramatic change of >700 times in the Young's modulus of the composite is observed.

Figure 7.8 Comparison of soft state of reversible rigidity composite with pristine elastomeric matrix. Soft state of the composite (liquid phase of the filler) shows much reduced mechanical stiffness compared to the pristine elastomeric matrix.

The soft state of the composite is compared with the pristine elastomeric film (Acrylic 250 μm /0.25 mm thick), which has been utilized for the composite fabrication, to analyse the effect of liquid state of PEG filler in the composite. As seen from Figure

7.8, the slope for the stress-strain curve of the pristine elastomeric film is higher than the slope for the soft state of the composite. This can be attributed to no reportable mechanical stiffness of liquids which leads to their deformation without any significant applied stress. There is a significant difference between the measured Young's modulus for the individual systems; with a value of 92 kPa (@10% strain) calculated for pristine acrylic elastomer compared to 6.9 kPa (@10% strain) for the soft state of the reversible rigidity composite.

Flexural modulation

Figure 7.9 Flexing behavior in soft and rigid state. (A) Demonstration of the flexural modulation of the composite where it resists bending under applied load with filler in solid state and shows complete bending even with no applied load when the filler is in liquid state. (B) Load-deflection curve from 3-point flexural tests for composite in rigid state (filler in solid state) and soft state (filler in liquid state).

Another significant aspect of rigidity modulation is to vary the ability to flex (bend) under the applied load. The reversible rigidity composites show the ability to resist bending under loading conditions (Figure 7.9-A) in their rigid state (PEG fillers in solid phase). Upon heating of the fillers to transition them into liquid phase, the composite transforms into a soft state where it can bend completely even with no applied load (Figure 7.9-A). As shown in Figure 7.9-A, the composite is placed on two cylindrical glass rods and loads are placed on either side. Two 1.25 N (125 grams) loads are placed on the hanging part of the composite in its rigid. And the composite resists any visible deformation or deflection under the applied load in its rigid state. On the other hand, there is a complete bending of the composite in its soft state even when the load is not applied, as seen in the image.

To quantify the modulation in flexural strength and flexural modulus, a temperature dependant 3-point bending test is performed. Figure 7.9-B shows the load-deflection curve for the reversible rigidity composite in its rigid state and soft state, with the rigid state showing a very steep curve. In rigid state, flexural strength and flexural modulus of the composite are calculated as 1.46 MPa and 202.6 MPa, respectively. On the other hand, in soft state, the flexural strength and the flexural modulus are calculated as 0.025 MPa and 2.13 MPa, respectively, showing a reduction of ~100 times in the flexural strength of the composite in the soft state.

Hardness modulation

Adding on to the ability to modulate stretchability and flexibility, the reversible rigidity composites show a remarkable change in the hardness in its rigid and soft state. The hardness measurements are done using a Shore durometer, which provides Shore A hardness values for polymeric matrices. As shown in Figure 7.10, 4 individual pieces of 2 mm thick PDMS elastomer films are stacked together for control measurements of hardness of soft polymeric matrices. Stacking is done to prevent contribution of underlying surface on the measured hardness. For PDMS polymer sheet, the measured hardness value is ~35 Shore A. Hardness measurement of reversible rigidity composite in its rigid state shows a value of ~50 Shore A. This increase in the hardness value is not substantially high owing to brittle nature of PEG, as the test requires the needle of the equipment to be pressed in the surface. Presence of a lot of grain boundaries, due to uncontrolled grain growths during the solidification process, in the solidified PEG can

be attributed as the reason for the observed brittleness. Upon heating of the composite, the PEG filler melts and the composite reaches its soft state. Measurement in its soft state shows a value of ~5 Shore A hardness, which is 10 times lower than in its rigid state.

Figure 7.10 Hardness variation in soft and rigid state. Hardness measurement using a Shore durometer for rigid and soft state of the reversible rigidity composite; and comparison with hardness of pristine PDMS polymer films (4 stacked layers, each 2 mm thick).

7.3.3 Healing of structural integrity

As mentioned above, solidified PEG is brittle in nature and generally exist as solid flakes. Due to this, they are prone to fracture and damage from mechanical loading beyond ultimate strength and high impact forces, unavoidable in practical scenarios. However, owing to its ability to melt and solidify over several cycles, these low-temperature phase change fillers enable healing behavior in the composite, making them more robust. As seen from Figure 7.11-A, the composite loses its mechanical integrity owing to loading beyond its ultimate strength and a fracture line is clearly visible (Figure 7.11-A, top right). By applying thermal perturbation, the fillers are melted to a liquid phase and allowed to solidify. Upon re-solidification, the composite heals back, and the structural integrity is restored. It is important to mention here that

the composite not only restores the structural integrity, but the mechanical strength for the composite remains nearly the same. Flexural tests employing 3-point bending tests are performed for the fresh and healed sample, and load-deflection curve is presented in Figure 7.11-B. The composite maintains a very similar load-extension curve even after 2 cycles of healing with nearly identical slope for the curves. Flexural modulus is calculated to be 205 MPa for fresh sample, which reduces to 196 MPa after 1st cycle of healing and eventually increasing to 222 MPa after 2nd cycle of healing. The difference in flexural modulus can be attributed to the uncontrolled solidification process.

Figure 7.11 Healing behavior of reversible rigidity composite. (A) Reversible rigidity composites can restore their mechanical integrity upon healing of fractures inside the structure

by melting and re-solidification. (B) Quantification of healing efficiency by measuring flexural modulus after 2 cycles of healing.

7.3.4 Controlling phase change by joule heater

Figure 7.12 Characterization of joule heater. (A) Top surface SEM image of the printed silver joule heaters. (B) Temperature versus time curve at different voltages. (C) Heating and cooling curve of the joule heater at 6 V. (D) Temperature versus time in flexed and straight configuration.

To control the phase change behavior of the composite and modulate the mechanical properties on demand, the reversible rigidity composite is integrated with a joule heater. A low-resistance joule heater is fabricated by screen printing of silver ink on flexible polyimide substrates. Screen printing provides uniform coverage of the substrate without observable agglomeration (Figure 7.12-A). Before integration with the composite, flexible heater is characterized for its heating behavior. Temperature is recorded with time for different applied voltages, as shown in Figure 7.12-B. As expected, the temperature increases with the increase in applied voltage, as the current drawn by the heater also increases. Initially the rate of increase of temperature is high

for all applied voltages (Figure 7.12-B), as observed from the slope of temperature-time curve and it slowly reaches a steady state. After 4 minutes, the heater reaches a maximum of 37°C, 69°C, 114°C and 168°C for 0.5V (0.84A), 1V (1.58A), 1.5V (2.27A) and 2V (2.90A) respectively. The cooling down trend of the heater is observed with temperatures recorded at different time intervals after the power is switched off and the heater finally reaches the initial temperature (Figure 7.12-C). The cooling down process is a bit slow compared to the heating process, owing to the absence of any cooling mechanism. The lowering down of temperature only relies on the losses to the surrounding environment. Upon flexing on a glass beaker of 45 mm bending radius, the heater maintains a similar heating behavior with only a slight drop in the temperatures achieved owing to the heater maintaining high conductivity in flexed configuration (Figure 7.12-D). After 4 minutes, the heater reaches a maximum of 87°C compared to 90°C for straight configuration of the heater.

Figure 7.13 Phase change of the reversible rigidity composite by integrated joule heater.

Reference sample and sample with integrated joule heater (inside the red box) showing similar hardness values (50 Shore A). After heating for ~14 minutes, the phase change filler melts completely and there is huge change in the measured hardness values. While the reference sample gives the same hardness value as before, the sample with integrated heater shows a hardness of ~5 Shore A, showing a 10 times reduction in the hardness.

After characterization of the fabricated joule heater, it is integrated externally with the reversible rigidity composite. The setup for demonstrating the phase change and modulation of mechanical properties is shown in Figure 7.13. Image of the flexible joule heater is shown inside the red box (Figure 7.13). A reference sample of the reversible rigidity composite is placed next to the sample with integrated joule heater. Hardness measurements are done for both the samples before the start of the heating process and as expected the measurements return similar values for both the samples (50 Shore A hardness). Heating is done by switching on the power for the joule heater. Within 14 minutes, the PEG fillers inside the composite get completely melted. The observably significant time taken for the melting can be attributed to following reasons; heating done from one direction only, time taken for heater to reach steady state, large volume (6cm*2cm*0.5cm) of phase change filler inside the composite to undergo melting and losses to the surrounding environment not contributing to the melting process. After the phase change filler melts completely, there is a noticeable change in the measured hardness of the sample with integrated joule heater, with the measured hardness value ~5 Shore A. The reference sample with no integrated heater maintains the same hardness as measured at the start of the experiment.

7.4 Conclusion

Potential applications for the reversible rigidity composites are abound. They could be used in medical assistive co-robots that can accommodate free motion of the patient in flexible state and offer assistive mechanical work in rigid state. They could be used in exploratory robots capable of navigating a variety of terrains, like rocky terrain, easily deformable mud, or sandy beaches. In addition, reversible rigidity soft actuators would make more dextrous grippers that can handle delicate tasks and fragile objects.

Herein, a novel material system for fabricating reversible rigidity composites has been reported, which undergoes thermally triggered phase change to enable modulation of mechanical properties. Two phase change materials, Polyethylene glycol (PEG) and Paraffin wax, are evaluated for their specific material properties. The measured material parameters and properties for PEG, like low melting point (~56°C), significant gap between melting and solidification (around 35°C), superior thermal stability (onset temperature ~345°C), high mechanical strength (failure @ ~ 244 N for ~0.58 mm compression) and high dielectric constant (10@ 1kHz), makes PEG an appropriate

choice for the reversible rigidity composite. Fabricated composites show modulation of mechanical properties between its rigid state and soft state on applying thermal stimuli. The reversible rigidity composites show 700 times change in Young's modulus, 100 times change in the Flexural modulus and 10 times change in the Shore hardness value between their rigid and soft state. Initial trials of these reversible rigidity composites in an isotonic DEA configuration provided an actuation strain of ~5% (@ 10 kV, 100 gm load). However, these were just the initial trials and have not reached the maturity to be included in the thesis. Currently, more experiments are being conducted to get consistent sample preparation, high quality images and videos for characterizing the actuation performance.

Owing to its ability to re-melt and re-solidify, PEG as filler imparts reversible rigidity composite the ability to regain its structural integrity. Healing of the composite is accompanied with no significant change in the mechanical properties of the composite. Furthermore, the reversible rigidity composite is integrated with a flexible joule heater. These low resistance joule heaters can reach temperatures in excess of 160°C in less than 4 minutes (@2 V). The change in the mechanical properties is demonstrated by applying the thermal stimuli using these joule heaters and the complete phase transition takes around 14 minutes.

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Chapter 8

Discussion and Future work

This chapter summarizes the results and the extent to which these results addresses the hypotheses proposed at the beginning of this dissertation. The chapter also details the limitations and drawbacks with their implications. Finally, the new strategies and opportunities for future work are identified.

8.1 Summary

Soft robotics is an emerging field of research which draws inspiration from nature and makes use of soft materials for producing dexterous, fluidic motion. Different actuation strategies like embedded pneumatics and fluidics, varying magnetic fields, thermal transitions and electrical stimuli have been adopted for these soft actuators. Dielectric elastomer actuators (DEAs) within the family of electroactive polymers (EAPs) are of interest owing to the advantages of large actuation strains, facile fabrication, thin film configuration and simple architecture, which also makes them an attractive option for next generation haptic technologies. However, in their current form, DEAs suffer from material limitations like low dielectric constant, high mechanical stiffness, significant viscoelastic effects and opaque compliant electrodes; and design limitations like necessity of rigid frames and device architectures. This makes them unsuitable for many applications. Generally adopted strategies of chemical modification and addition of solid fillers for improving the actuation performance leads to undesirable changes on the associated material properties. Additionally, DEAs also lack the critical attribute of modulating their mechanical properties on demand, which is needed to mimic the biological systems at a closer level.

To begin with, an investigation of the electrical and mechanical properties of the conventionally used elastomeric matrices, Acrylic tape (VHB 4910) and Silicone elastomer (PDMS, Sylgard 184), in DEAs was performed. Measurement of the material parameters for these systems allowed for benchmarking and comparison of novel material systems for active layer. Carbon-based electrodes (powder and paste) were characterized for their compliancy, conductivity and actuation performance, which served as a yardstick for evaluating performance of novel compliant electrode systems. Novel transparent compliant electrodes, spray coated AgNW (silver nanowire) network and conductive hydrogels, were evaluated for DEAs and compared with carbon-based electrodes. These transparent compliant electrodes demonstrate similar actuation behavior and better conductivity together with high degree of compliance.

Next, drawing inspiration from soft biological materials in the nature, fabrication of a self-contained liquid filler-polymer composite using EMIMFTSI as the liquid filler and PDMS as the polymer matrix was successfully demonstrated. The material composite was conceptualized using the theoretical predictions for the material properties from

Style et. al.'s extension of Eshelby's theory under Mori-Tanaka approximation scheme and effective medium theories for dielectric constant approximations. Addition of EMIMTFSI fillers leads to synergetic effect on the electrical and mechanical properties of the resulting composite. These composites were actuated in a DEA configuration and showed superior actuation performance compared to the conventionally used elastomer. Additionally, these composites show excellent stability against high temperatures and moisture uptake; and no change in the thermal degradation compared to the pristine matrix. These composites also showed excellent transparency even at high filler loadings.

Moving ahead, a novel device architecture enabling transparency and integrability was demonstrated for DEAs allowing their lamination and integration with surfaces. A highly transparent surface texture change device for tactile feedback was shown making use of this architecture.¹⁻² The device produced physical surface deformations and blocked force well above the detectable thresholds for receptors in fingertips. The devices also showed superior cyclability and frequency bandwidth. An engineering approach of stacking of active layers was demonstrated to improve the performance of devices in this configuration. Owing to its unique architecture, successful demonstration of patterning of the deformations, flexibility and the reliability of the device, and localized tactile feedback on a single tactile device was done.

Finally, polyethylene glycol (PEG) was reported as a novel material system for fabricating reversible rigidity composites which undergoes thermally triggered phase change to enable modulation of mechanical properties. PEG has significant advantages over conventionally employed paraffin wax owing to desirable properties like low melting point, superior thermal stability, high mechanical strength and high dielectric constant. Fabricated reversible rigidity composites showed orders of magnitude change in Young's modulus, flexural modulus and hardness value between their rigid and soft state. Owing to its ability to re-melt and re-solidify, composites demonstrated the ability to regain its structural integrity. Phase change behaviour in the reversible rigidity composite was controlled by an integrated flexible joule heater.

To summarize, Table 8.1 provides an overall view of material properties for novel material composites developed within the scope of this thesis, compared against the conventional acrylates and silicones.

Table 8.1. Comparison of conventional material systems against novel composites.

Material	Dielectric constant (@1 kHz)	Young's modulus (@ 10% strain)
3M VHB 4910 acrylic tape	5.2	0.04 MPa
Polydimethylsiloxane (PDMS, Sylgard 184)	3.7	1 MPa
Ionic liquid polymer composite (PDMS+EMIMTFSI (20%))	6.93	0.01 MPa
Reversible rigidity composites (PEG-0.25 mm thick Acrylic composite)	10 (Solidified PEG)	6.23 MPa (rigid state) 7.87 kPa (soft state)

8.2 Conclusions

- Acrylic tape (VHB 4910) showed a much lower Young's modulus of 0.04 MPa compared to the 1 MPa for silicone (PDMS, Sylgard 184) elastomer, accompanied with a higher dielectric constant for acrylic elastomer (~5.2) compared to that of silicone elastomer (~3.7). Hence, acrylic elastomer was used for further benchmarking of compliant electrode systems. Silicone elastomers (Sylgard 184) were chosen for modifications owing to their facile fabrication and complete transparency to begin with. Carbon-based electrode systems (powder and paste) were characterized for their actuation performance, which serves as a yardstick for evaluating performance of novel compliant electrode systems. Novel transparent compliant electrodes, Silver nanowires (AgNWs) and Conductive hydrogels, compared well against the established carbon-based electrodes in terms of compliancy and actuation performance. AgNWs showed very low sheet resistance values and conductive hydrogels showed little changes in resistance over large strains. Additionally, both the electrode systems enabled high transparency, allowing for next generation of DEAs.
- Agreeing well with hypothesis, addition of EMIMTFSI (liquid filler) in the PDMS (polymer) matrix showed an increase of ~2 times in the dielectric constant and a

decrease of 100 times in the Young's modulus of the composite. This was accompanied by 4.6 times increase in the stretchability of the matrix. Owing to synergistic effects on electrical and mechanical properties, the composites demonstrated an effective improvement of 5 times in longitudinal strain and 8 times in areal strain produced. Adding on to excellent electrical and mechanical properties, the composites also showed excellent thermal stability and moisture stability and were resist degradation even at prolonged exposure to high temperature (200°C) for long durations (60 minutes). Due to form factor of fillers and refractive index matching, the composites demonstrated high transparency (82%) even at high filler loadings (20%). Excellent electrical, mechanical, optical and thermal properties of the composite make them a suitable candidate for a variety of other optoelectronic applications.

- Utilizing the thickness mode actuation of DEA devices, a novel device architecture enabling transparency and integrability was realized with the high overall transparency of the system (76% @ 550 nm), achieved by making use of hybrid system of electrodes – conducting hydrogel as bottom electrodes and silver nanowire – PEDOT: PSS as top electrodes, transparent acrylic elastomer as active layer and transparent PDMS as soft passive layer.¹⁻² The device produced surface deformations of 0.16 mm and a blocked force output of 47 mN, which lies above the perceptual force thresholds of receptors in our fingertips.¹⁻² With a triple active layer device achieved by stacking of layers, doubling of the actuation performance (0.3 mm surface deformations and 90 mN blocked force output) was demonstrated.³ Devices showed good performance over large frequency bandwidth, providing similar performance till 20 Hz and half of the maximum performance till 1000 Hz.¹⁻
² Flexibility, integrability, patterning of deformations and localized tactile feedback was demonstrated making use of this architecture.¹⁻³
- Utilization of polyethylene glycol (PEG) as a low-temperature phase change filler enabled fabrication of a reversible rigidity composite. PEG showed desirable properties for such a filler like low melting point (~56°C), significant gap between melting and solidification (around 35°C), superior thermal stability (onset temperature ~345°C), high mechanical strength (failure @ ~ 244 N for ~0.58 mm compression) and high dielectric constant (10@ 1kHz). These reversible rigidity composites showed modulation of mechanical properties between its rigid state and

soft state on application of thermal stimuli with 700 times change in Young's modulus, 100 times change in flexural modulus and 10 times change in the Shore hardness value. Healing of the composite was demonstrated with no significant change in the mechanical properties of the composite. Control on the modulation of mechanical properties was demonstrated by integrating low-resistance joule heaters, changing the phase of the filler completely in around 14 minutes.

8.3 Limitations and their implications

- Desirable changes in the Young's modulus and the dielectric constant of the self-contained liquid filler-polymer composite is accompanied with unwanted reduction of the electrical breakdown strength. This directly affects the maximum actuation strain produced and the figure of merit for electromechanical performance. Nonetheless, the material system still provides an attractive option for new applications like adaptive surfaces and other low electric field applications owing to the significant improvement in the actuation performance at low electric fields.
- Since conventional elastomeric matrix, acrylic (VHB 4910) has been utilized for demonstrating the novel device architecture for DEAs, the active film has to be still biaxially stretched. And the performance of these devices is hence limited by the active material system. Additionally, hydrogels face the issue of water loss in ambient conditions, making them unsuitable to some extent for practical usage. However, proper encapsulation strategies (demonstrated in our device architecture where hydrogel is enclosed by elastomer) could provide viable mitigations from this issue. Furthermore, novel material systems have been studied under the scope of this dissertation and it can significantly improve the performance of these device configurations.
- Although no time constraints are observed for modulation of mechanical properties in natural organisms, human designed systems are always put under the aspiration, unrealistic at times, of being fast. Thermal transition processes are always seen as a slow process, owing to the losses taking place to the environment. Hence, large volumes of phase change filler in the fabricated reversible rigidity composites necessitates the heating to be applied for a considerable time. However, the changes in the mechanical properties are very significant with changes observed in orders of magnitude.

8.4 Future Work

8.4.1 Tackling manufacturing constraints

During the course of this dissertation, difficulties associated with the fabrication of samples were realized like biaxial stretching of the acrylic membrane, application of compliant electrodes and providing electrical contacts for signal input. These processes are labour intensive and affect the performance of the actuators, and not only create complexity in the fabrication process, but also limit the adoption of soft actuators by industries.

Some research groups have already started to investigate the fabrication strategies like electrospraying followed with UV crosslinking and inkjet printing suited for large scale manufacturing of these field driven soft actuators.⁴⁻⁵ Currently, the focus is on the conventional material systems like silicones and carbon-based electrode systems (Figure 8.1), which provides limited actuation performance and versatility. However, the novel elastomeric matrices and compliant electrode systems developed within the scope of this dissertation can be investigated with these techniques. UV curable formulations of silicone elastomer matrix with these novel ionic liquid fillers could be suitable for on-demand printing. Similarly, UV curable conductive hydrogels could be deposited by these techniques. Silver-nanowire based ink formulations suited to printing processed could be developed for compliant electrode fabrication.

Figure 8.1 Novel fabrication strategies for DEAs. (A) Fast deposition technique for silicone elastomers has been demonstrated using electrospraying followed by UV irradiation, capable of producing 1 μm thick elastomer films.⁴ (B) Inkjet printing of carbon-based formulations as compliant electrodes for DEAs.⁵ (Scale bar – 125 μm)

8.4.2 Avenues of further material exploration

Owing to the nature of Maxwell stresses and intrinsic material properties of the conventional material systems like silicones and acrylates, generally high electric fields are required to produce actuation accompanied with design necessities like pre-stretching. A general strategy to augment the performance of such actuators without developing new material systems is to fabricate multilayer device architectures with multiple active layers stacked together. This approach can combine the performance of individual actuators to provide enhanced actuation performance (as demonstrated briefly in Figure 6.10 - Augmentation of surface deformation). Furthermore, design strategies to induce anisotropy in the conventional material systems like embedding of rigid fibres inside the soft elastomeric matrix could possibly be adopted to mitigate pre-stretching.⁶ Apart from these engineering and design approaches, detailed investigation into material approaches is needed.

Improvement of haptic feedback in novel device configuration

Figure 8.2 Material strategy to improve haptic feedback. (A) Enhancing dispersion of LM in polymer matrix by self-assembled surfactant molecules and optimized concentration, size of LM phases and mechanism of self-stiffening under compressive stress. (B) Schematic of a responsive haptic system with reversible control over stiffness and hardness.

To prevent the opposing effect of touch-pressure on top passive layer in thickness mode actuation, it will be advantageous if the modulus of the passive layer can be modulated

on demand. Such modulation of mechanical properties can be explored by innovative tailoring of material chemistry and smart integration of active and passive layer, such that the passive layer will become stiffer only under compression resulting from the actuation of the active layer. Development of a biphasic polymer-LM system that will self-stiffen under mechanical activation can be done. LM in liquid form will be directly added to the uncured polymer gel via shear mixing and will exist in form of small phases inside the polymer matrix. In general, the heavier LM phases may settle to the bottom and cause severe phase separation. To tackle this, utilization of amphiphilic molecules as surfactants and control of size distribution of LM phases can be done to enhance the dispersion in the polymer gel. Under compression, storage modulus of the composite system will increase due to the higher density of LM phases jammed into a reduced volume of the polymer matrix (Figure 8.2-A). Releasing the compression allows the system to return to the original compliant state. In the case of haptic feedback, the compressive actuation of the active DEA layer can provide a synergetic integration with the passive layer of bi-phasic system to result in self-stiffening and enhance tactility, while remaining highly compliant to allow strong deformation (Figure 8.2-B).

Investigations for other high-k liquid filler and suitable polymer matrices

Investigation undertaken within this dissertation have revealed design of new class of polymer composites employing liquid fillers that can be fabricated with desirable electrical and mechanical properties. The current study has been performed using only a select few material matrices and the concept can be translated to other polymers and liquid fillers. UV curable acrylates are an attractive option for polymeric matrices owing to their low mechanical modulus, tunable properties by varying chemical compositions and high stretchability added to their non-proprietary formulations and facile fabrication.⁷ Recent advent of healable systems like polyurethane and silicone based polymers also appear as an attractive option for this liquid filler approach, and would enable durable and reliable devices.⁸⁻¹⁰ Liquids like glycols, alcohols and carbonates have very high dielectric constant and can be explored as options for liquid fillers apart from other ionic liquids.¹¹⁻¹³

Improvement in electrical breakdown for fabricated liquid filler-polymer composites

As already mentioned, a significant loss in the electrical breakdown strength for the fabricated ionic liquid-silicone elastomer composite is observed. Although it remains

an attractive option for low-field applications and can produce significant actuation performance as compared to commonly utilized systems, an understanding of the electrical breakdown mechanism can prove useful in efficient material design. This is first of its kind of composite, employing an ionic liquid filler as opposed to conventionally used conductive and ceramic solid fillers. There is generally an increase in the loss factor of the matrix associated with addition of these solid fillers, which is not observed in the case of ionic liquid fillers. Hence conventional breakdown models cannot be used and a complete understanding of the breakdown behaviour is needed for these high-k composites, as phenomenon like electrical double layer come into play with introduction of ionic liquids.¹⁴⁻¹⁵ Understanding of the breakdown phenomenon can be developed based on localised field theories which suggests that addition of fillers leads to concentrated electric fields in the polymer and breakdown phenomenon originates in the polymer.¹⁵ So, changing to a polymer system (for instance acrylates) which have higher breakdown strength promises improvement in the electrical breakdown strength of these liquid filler-based composites.¹⁶

Material strategies for fast and contactless heating for phase modulation in reversible rigidity composites

One of the major drawbacks associated with thermal transition is that of longer cycle times. The major constituents of the cycle time are intrinsic material properties and employed technique of joule heating. Joule heating is accompanied with significant losses to environment and is a contact-based method. One of the ways to enable a contact-free heating mechanism is to make use of the lossy behaviour of PEG (polyethylene glycol) fillers, as observed from the imaginary part of the dielectric spectroscopy (Figure 7.6, Chapter 7) and employ capacitive heating using alternating current.¹⁷ Another approach which could also result in improvement of the response speed of these thermal transition systems can be addition of magnetic nanoparticles to the filler matrix and employ inductive heating by applying varying magnetic field.¹⁸ To further improve upon the cycle times, fast and efficient removal of heat from the system needs to be done. For this non-contact cooling techniques like magnetocaloric effect and thermoelectric effect can be employed.¹⁹⁻²⁰ Additionally, novel material and design approaches for electroadhesion and particle jamming technologies could be investigated to combine with DE actuators to enable faster rigidity modulation processes.

8.4.3 Potential for novel material systems in adaptive surface configurations

Specific advantages and the significant role of adaptive surfaces in enhancing the user experience at machine interfaces, enabling optical manipulation through metasurfaces and mimicking shape morphing behaviour found in nature has been indicated earlier. Soft actuators have definitive advantages over conventional rigid actuators owing to their inherent compliance. Research groups trying to realize adaptive surfaces have adopted different strategies such as small-scale deformations on organic coatings (Liquid crystal elastomers) via alternating electric field (Figure 8.4-A), coupling of patterned and segmented DEAs with metasurfaces for optical modulation (Figure 8.4-B), shape morphing by a multilayer DEA architecture and spatially varying electric field (Figure 8.4-C) and shape morphing by design of embedded pneumatic channels inside an elastomer (Figure 8.4-D).²¹⁻²⁴

Figure 8.3 Adaptive surfaces enabled by soft actuators. (A) Liquid crystal polymer networks coated on interdigitated electrodes protrude and create surface deformations at the application of alternating electric field.²² The deformations are quite small and lie in nanometre range. (B) Patterning of electrodes around Si-based metasurface lens for optical modulation through

electrical stimuli.²³ Prestretching of membranes necessitate the use of rigid frames. (C) Shape morphing to demonstrate Gaussian curvatures achieved by stacking of multiple devices and spatially varying electric fields.²¹ Careful integration of multiple layers is needed to prevent defects. (D) Shape morphing achieved by design on embedded pneumatic channels inside the elastomer.²⁴ Pneumatics requires source of pressurized air, making the whole system less mobile.

Electrical control of adaptive surfaces through DEAs lends advantage of superior control, easily detected deformations and untethered actuation. New material systems investigated under the scope of this dissertation can be utilized for adaptive surfaces applications. Low field actuation of EMIMTFSI-PDMS composites accompanied with softness and deformability makes it an attractive choice for shape morphing applications. PEG filler based reversible rigidity composites could be designed to enable a novel hardness varying surface mimicking nature at an intimate level. These systems in their current form still necessitate utilization of voltages in kV regime due to large thickness of active membrane, making them more suitable for applications such as adaptive optical modulators, varying reflectance surfaces and biomimetic shape morphing devices. In future, reducing the film thickness for device fabrication combined with design strategies like multilayer stacking could realistically bring down the operational voltages below kV regime. New device configuration achieved by thickness mode actuation could lay path for next generation transparent haptic devices and adaptive-informative surfaces.

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