Self-healing materials for flexible electronic devices

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**SELF-HEALING MATERIALS FOR FLEXIBLE ELECTRONIC
DEVICES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

SELF-HEALING MATERIALS FOR FLEXIBLE ELECTRONIC DEVICES

NAVEEN TIWARI

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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Naveen Tiwari

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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.

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31.07.2019

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.....
Nripan Mathews

Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals in which I am listed as a first author.

Chapter 4 is published as N. Tiwari, Ankit, M. Rajput, M.R. Kulkarni, R.A. John, and N. Mathews. “Healable and flexible transparent heaters”. *Nanoscale*, 9, **39**, 14990-14997 (2017). DOI: 10.1039/C7NR05748B.

The contributions of the co-authors are as follows:

- Prof N. Mathews provided the idea with guidance regarding the project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was edited by R.A. John.
- I performed all the laboratory work at the School of Materials Science and Engineering, NTU Singapore. I also analyzed and plotted the data.
- All microscopy analysis, including sample preparation, was conducted by me in the Facility for Analysis, Characterization and Testing of the prepared samples.
- Ankit and M. Rajput helped me in collecting the bending test data of the prepared samples. Ankit helped me in taking the videos of the transparent heaters.
- M.R. Kulkarni helped in calculating the sheet resistance of the fabricated transparent and healable heaters.

Chapter 5 is published as N. Tiwari, F. Ho, Ankit, and N. Mathews. “A rapid low temperature self-healable polymeric composite for flexible electronic devices”. *Journal of Materials Chemistry A*, 6, **43**, 21428-21434 (2018). DOI: 10.1039/C8TA08328B.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof. N. Mathews regarding the project direction and materials selection. Prof. N. Mathews revised the manuscript drafts.
- I wrote and prepared the draft of the manuscript. The manuscript was edited by Ankit in the area of mechanical properties of the polymeric composites.

- I performed all the materials synthesis and fabrication of devices, performed all the characterization and all microscopy analysis at the School of Materials Science and Engineering, NTU Singapore. Finally, I conducted the data evaluation.
- F. Ho helped me in the synthesis of polymeric composite with different compositions of the ionic liquid. She also helped in editing the manuscript.
- Ankit helped me in taking the videos of the fabricated EL devices.

Chapter 6 is currently being prepared as a manuscript- N. Tiwari, F. N. Rizki and N. Mathews. “Effect of the incorporation of ionic liquid on the self-healing behaviour of the polymeric composite”.

The contributions of the co-authors are as follows:

- Prof N. Mathews provided the idea with guidance regarding the project direction and the manuscript is under preparation.
- I am preparing the manuscript drafts and F. N. Rizki is also helping in that.
- I performed all the laboratory work at the School of Materials Science and Engineering, NTU Singapore. I also analyzed and plotted the data.
- All microscopy analysis, including sample preparation, was conducted by me in the Facility for Analysis, Characterization and Testing of the prepared samples.
- F.N. Rizki helped me in the synthesis of polymeric composite with different compositions of an ionic liquid.

31.07.2019

Date

Naveen Tiwari

Abstract

With the onset of flexible and wearable electronics, devices are now put on places like the human body and various curved surfaces which doesn't have any regular shape and sizes. Therefore, these devices need to be flexible, conformable and stretchable to fulfil all these applications. However, the continuous exposure of these devices is always subjected to higher mechanical stress, wear and tear when compared to conventional electronics. Hence the ability to recover and repair upon damage is a necessity and not a luxury for flexible electronic devices. These applications not only require good electrical conductivity but demand better mechanical properties like stretchability, flexibility and robustness where the conventional electrodes, for example, indium tin oxide (ITO) fail to perform. Hence, self-healing, flexible, transparent electrodes could transform the way of fabrication of electronic devices in future. Challenges associated with mechanical fracture of electrical conductors has hindered the realization of truly flexible, robust and high-performance wearable electronics. The remarkable achievements in transparent and flexible electrodes have raised widespread interest in research groups in flexible electronics, owing to their low-cost fabrication, easy scale-up, and unique properties. However, they still suffer from innate problems like mechanical rupture, scratching and bending torsion because of their “soft” and flexible nature related to their solid counterparts. Hence, self-healing capability would be highly desirable for these electrodes in flexible electronic devices.

In this dissertation, the demonstration of versatile transparent healable electrodes has been developed and examined to alleviate these problems. The composite electrode features a layer of interconnecting AgNWs network on a polyurethane film modified with Diels–Alder adducts (PU-DA). The PU based DA polymeric electrode can heal multiple times due to the presence of DA and retro-DA mechanism, which are based on thermo-reversibility. Surface modification using hydrophilic molecules improved adhesion of the AgNWs and resulted in mechanically robust flexible electrodes with a high figure of merit; showing low sheet resistance with good transmittance in the visible spectrum. Transparent and flexible healable heaters (TFHH) with good mechanical and thermal stability were

fabricated using these electrodes for potential applications in thermochromics, electrically driven displays and defrosters. The PU-DA based healable heaters exhibited high Joule heating temperatures with a low operation voltage, rapid thermal response and enhanced robustness to withstand large repeated mechanical strain for over 500 bending cycles with small variance in resistance. After deliberate damage by a knife cut, the electrodes healed and recovered back to its original conductivity via a simple heat treatment at 120 °C. Uniquely, the healing process can also be triggered by utilizing electrical power.

The self-healing polymer with the addition of ionic liquids (ILs) may have great potential for future electronic materials. ILs would make it possible to integrate functional excipients to recognize multifunctional electrical applications; owing to the intrinsic advantages of suppressed volatility, high ionic mobility, thermal stability, and a wide range of electrochemical window. Thermally-reversible Diels-Alder (DA) mechanism for self-healing are promising but have only been demonstrated healing at high temperatures (~120 °C). However, theoretically, the DA mechanism can be triggered at temperatures as low as 50 °C, indicating that the self-healing mechanism is limited by the thermal mobility of the polymeric chains. Next, the effect of ionic liquid as a plasticizer was investigated in PU-DA in order to minimize the healing temperature and increase the mechanical properties of the polymeric composite. The incorporation of ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITFS) alleviates this challenge, rapidly accelerating healing, while concomitantly improving the dielectric constant and the mechanical properties of a polyurethane derivative based on the DA chemistry for PU. For optimized compositions, the healing temperature reduced from 120 °C to 60 °C and the maximum strain to failure significantly increased from 17.1% to 102.1%. Owing to the ionic polarizability of EMITFS, the composite exhibited highly attractive dielectric properties with the dielectric constant enhanced from 2.7 to 12.9. Finally, a highly flexible, healable and fully solution-processed electroluminescent device was demonstrated.

To tailor specific multi-property materials, usually, sophisticated multi-step synthesis processes are employed and will affect the device fabrication method. With the increase in concentration of ionic liquid, the polymeric films have increased in mechanical, electrical

as well as healing properties as it was observed in the case of PU-DA. Taking that concept as a motivation, a composite system with healing behaviours in polymeric systems without DA recovery mechanism was investigated. The incorporation of ionic liquid (EMITFS) in amorphous polymer like PVP, rapidly accelerates the healing, while improving the mechanical properties. The PVP with ILs composite films were compared with IL composites with another amorphous polymer, PMMA, as well as semi-crystalline polymers like PVA and PVDF-HFP to mimic the healing behaviours and mechanical properties, while incorporating EMITFS in these polymers. The effect of cation and anion present in ionic liquids was investigated, on the best polymer system (PVP), in terms of healing behaviour and mechanical properties. The different ionic liquids (EMITFB and EMITFSI) was used as compared to EMITFS since these ionic liquids have the same cation but different anions. This chapter depicts the study of the influence of ionic liquids on the different class of polymer structure and its effects on the healing properties. In the end, a novel healing mechanism with ionic liquids was demonstrated in PVP polymer without DA recovery mechanisms.

Lay Summary

Polymers are fundamental materials in electronics, surface technologies and automobiles. The restoration of properties after environmental degradation or mechanically-induced damages has always been a huge challenge. Traditional repair methods become costly and unviable when dealing with delicate systems or inaccessible defects within materials. To address this, a new class of polymers that is intrinsically healable has been explored. These self-healing polymers have the ability to undergo restoration upon fracture, thereby reducing the need to engage in unfeasible material maintenance processes.

Various chemical approaches exist to achieve this self-healing functionality. One such approach is via formation of covalent bonds. The most prominent of which is through the Diels-Alder (DA) reaction. The DA reaction is a thermally reversible reaction which allows for repetitive reheating and hence multiple healing cycles. To employ this reaction, Diels-Alder adducts are incorporated within polymer networks. Upon mechanical damage, the covalent bonds within the adducts would be broken via the retro-DA reaction. After being exposed to a thermal stimulus, the reverse reaction (DA reaction) takes place and the bonds are restored. This DA based healing was attached with polyurethane polymer to fabricate a self-healable electrode, onto which a transparent flexible and healable heater was demonstrated.

While existing polyurethane-based DA networks are chemically robust in terms of healing, certain physical limitations remain inadequately addressed. These include the need for high healing temperatures of above 120 °C, as well as limited mechanical properties in terms of stretchability. To address these physical limitations, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITFS) ionic liquid was incorporated into a matrix of polyurethane with DA adducts (PU-DA). The ionic liquid molecules would disperse themselves into the regions between the PU-DA polymer chains. Likewise, EMITFS was chosen due to its compatibility as indicated by its dispersive behaviour within the PU-DA network. As such, there would be a plasticizing effect which also increases the free volume between the PU-DA chains, allowing for greater chain mobility and hence lowering its

glass transition temperature (T_g). The resultant composite would thus have more favourable mechanical properties in terms of increased flexibility, as well as vastly reduced healing temperatures to 60 °C due to increased flowability.

To tailor specific multi-property materials, usually, sophisticated multi-step synthesis processes are employed and will affect the device fabrication method. As it was noticed that with the increase in concentration of ionic liquid, the polymeric films have increased in mechanical, electrical as well as healing properties. Taking that concept as a motivation, we devise a composite system with healing behaviours in polymeric systems without DA recovery mechanism. It also depicts the study of the influence of ionic liquids on the different class of polymer structure and its effects on the healing properties. In the end, a novel healing mechanism with ionic liquids was demonstrated in PVP polymer without DA recovery mechanisms.

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Figure 3.3 a) Device architecture of ACEL device. b) ZnS:Cu-PU-DA mixture after mixing in a planetary mixer. c) Samples spin-coated ZnS:Cu-PU-DA over the PU-DA/EMITFS film. © Reproduced from “Tiwari, Naveen, Fanny Ho, and Nripan Mathews. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434” with permission from The Royal Society of Chemistry.

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Figure 4.8 AFM images in 2D and 3D with and without APTES treatment. The RMS value of unmodified and modified sample was 4.8 nm and 4.3 nm respectively. (a) & (c) were the images of the sample without APTES treatment and (b) & (d) were the images of the sample with 15mM APTES treatment. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Figure 4.9 Optical photograph of the prepared polymer (a) & (c) and polymer with AgNWs (b) with 2.5*2.5 cm² area. d) Transmittance spectra of polymer with and without AgNWs (1-PU-DA; 2-PU-DA+AgNWs ($R_s=72.15$ ohm/sq); 3-PU-DA+AgNWs ($R_s=29.71$ ohm/sq); 4-PU-DA+AgNWs ($R_s=13.3$ ohm/sq); 5-PU-DA+AgNWs ($R_s=7.26$ ohm/sq). e) Haze factor of the PU-DA polymer with and without silver nanowires. f) The sheet resistance change of the sample with the cycle/times of peeling and adhesion with scotch transparent tape. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Figure 4.10 Sheet resistance change of the sample with the number of bending and unbending cycle/times. The image inset in the bending-unbending graph shows the sample was wrapped around a 20 mm (a) and 6 mm (b) diameter cylinder. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

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Figure 4.12 Surface roughness of the transparent electrode (TE) before and after healing. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Figure 4.13 Electrical power induced healing illustrated by optical images of the electrode (2 minutes apart). © Reproduced from Tiwari, Naveen, et al. "Healable and flexible

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Figure 4.16 a) Peak temperature versus power density for the transparent electrode (Sheet resistance $13.3 \Omega/\square$). b) Variation in sheet resistance at the different voltage for different transparent healable heater based on AgNWs. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Figure 4.17 Optical image of the goggle after the transparent healable heater had been applied to one of the sides. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Figure 5.1 a) ^{13}C solid-state NMR spectra of PU-DA/ 50 wt% EMITFS. b) ^1H solid-state

NMR spectra of PU-DA/ 50 wt% EMITFS © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." Journal of Materials Chemistry A 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.2 a) ^1H liquid-state NMR spectra of EMITFS (IL). b) ^1H liquid-state NMR spectra of PU-DA/ 50 wt% EMITFS © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." Journal of Materials Chemistry A 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.3 FTIR spectrum of PU-DA, 16.7 wt % EMITFS in PU-DA, 25 wt % EMITFS in PU-DA, 33.3 wt % EMITFS in PU-DA, 41.7 wt % EMITFS in PU-DA, 50 wt % EMITFS in PU-DA, 58.3 wt % EMITFS in PU-DA and EMITFS (IL). © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." Journal of Materials Chemistry A 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.4 FTIR spectrum of PU-DA/ 50 wt% EMITFS. FTIR spectrum of the film at range from a) $3500\text{-}2000\text{ cm}^{-1}$ and b) $2000\text{-}1000\text{ cm}^{-1}$. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." Journal of Materials Chemistry A 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.5 The optical microscopy images of PU-DA and PU-DA/ 50 wt% EMITFS. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." Journal of Materials Chemistry A 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.6 a) TGA curve of PU-DA and PU-DA/50 wt% EMITFS film. b) TGA curves of PU-DA, 16.7 wt % EMITFS in PU-DA, 25 wt % EMITFS in PU-DA, 33.3 wt % EMITFS

in PU-DA, 41.7 wt % EMITFS in PU-DA, 50 wt % EMITFS in PU-DA and 58.3 wt % EMITFS in PU-DA. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.7 Effect of Ionic liquid (EMITFS) on healable polymer (PU-DA). DSC curves of a) PU-DA film and b) PU-DA/50 wt% EMITFS film. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.8 DSC curves of 16.7 wt % EMITFS in PU-DA, 25 wt % EMITFS in PU-DA, 33.3 wt % EMITFS in PU-DA, 41.7 wt % EMITFS in PU-DA and 58.3 wt % EMITFS in PU-DA. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

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Figure 5.11 Healing behaviour of PU-DA/50 wt% EMITFS film. a) As a prepared film. b) Before heating. c) After healing at 60 °C for 10 min. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.12 a) Stress-strain curves of PU-DA/50% EMITFS; pristine, cut and healed samples. b) Image of the fracture of the damaged sample and the healed sample. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.13 Dielectric constant of PU-DA/EMITFS film with various concentrations of EMITFS added. a) From 1 Hz-100 kHz. b) From 100 Hz-10 kHz. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.14 Comparison of Surface Uniformity between PU-DA + 50.0% EMITFS with different concentration of EMITFS in PU-DA. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission The Royal Society of Chemistry.

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Figure 5.16 Schematics of the overview of the design concept for a self-healable polymeric composite film based on ILs. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from and The Royal Society of Chemistry.

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Abbreviations

1D	One dimensional
2D	Two dimensional
3D	Three dimensional
ACEL device	Alternating current electroluminescent device
AFM	Atomic force microscopy
Ag	Silver
AgNO ₃	Silver nitrate
AgNWs	Silver nanowires
APTES	(3-Aminopropyl)triethoxysilane
BaTiO ₃	Barium titanate
BMI	1,1'-(methylenedi-4,1-phenylene)-bismaleimide
CNT	Carbon nanotubes
CuCl ₂	Copper chloride
DA	Diels-Alder
DBDL	Dibutyltin dilaurate
DMF	Dimethylformamide
DPP	Diketopyrrolopyrrole
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetric
EDOT	3,4-Ethylenedioxythiophene
EG	Ethylene glycol
EMITFB	1-Ethyl-3-methylimidazolium trifluoroborate
EMITFS	1-Ethyl-3-methylimidazolium trifluoromethanesulfonate
EMITFSI	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
E-skin	Electronic skin
FESEM	Field-emission scanning electron microscopy
FET	Field-effect transistors
FTIR	Fourier transform infrared spectroscopy
GO	Graphene oxide
GPC	Gel-permeation chromatography

ILs	Ionic liquids
IPA	Isopropyl alcohol
IPDI	Isophorone diisocyanate
ITO	Indium tin oxide
kHz	Kilo hertz
LED	Light emitting diode
MEK	Methyl ethyl ketone
MPa	Mega Pascal
MWCNTs	Multi-walled carbon nanotubes
NMR	Nuclear magnetic resonance
NR	Natural rubber
OLEDs	Organic light emitting diodes
PDMS	Polydimethyl siloxane
PEDOT: PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PEI	Poly(ethyleneimine) solution
PET	Polyethylene terephthalate
PHPMA	Poly(N-(2-hydroxypropyl)methacrylamide)
PI	Polyimide
PLECs	Polymer light emitting chemical cells
PMMA	Poly(methyl methacrylate)
PMMA10	Poly(methyl methacrylate) with 10% IL
PMMA20	Poly(methyl methacrylate) with 20% IL
PMMA5	Poly(methyl methacrylate) with 5% IL
PU	Polyurethane
PU-DA	Polyurethane based Diels-Alder adduct
PU-F	Furyl modified polyurethane
PVA	Polyvinyl alcohol
PVA10	Polyvinyl alcohol with 10% IL
PVA20	Polyvinyl alcohol with 20% IL
PVA5	Polyvinyl alcohol with 5% IL
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)

PVDF-HFP20	Poly(vinylidene fluoride-co-hexafluoropropylene) with 20% IL
PVDF-HFP30	Poly(vinylidene fluoride-co-hexafluoropropylene) with 30% IL
PVDF-HFP40	Poly(vinylidene fluoride-co-hexafluoropropylene) with 40% IL
PVDF-HFP50	Poly(vinylidene fluoride-co-hexafluoropropylene) with 50% IL
PVP	Polyvinylpyrrolidone
PVP10	Polyvinylpyrrolidone with 10% IL
PVP20	Polyvinylpyrrolidone with 20% IL
PVP5	Polyvinylpyrrolidone with 5% IL
RB	Round bottom flask
S/D	Source and drain
SEM	Scanning Electron Microscopy
SH	Self-healing
SrTiO ₃	Strontium titanium oxide
STM	Scanning tunneling microscope
SWCNTs	Single-walled carbon nanotubes
T _d	Degradation temperature
TEs	Transparent electrodes
TFHH	Transparent flexible healable heater
TFT	Thin film transistor
T _g	Glass transition temperature
TGA	Thermogravimetric analysis
T _m	Melting temperature
UPy	Ureidopyrimidinone
X-RD	X-ray diffraction
ZDMA	Zinc dimethacrylate
ZnS:Cu	Zinc sulfide copper

Chapter 1

Introduction

This chapter introduces the field of self-healable polymers in the context of flexible electronic devices mainly focusing on the exploration of materials and device configurations. In short, it is identified that self-healing materials are in great demand for advanced technologies like flexible and stretchable electronics, where the devices are constantly subject to mechanical stress and torture. The factors which limit the performance of current implementations are identified. General schemes to realize low temperature healing while maintaining the high electrical conductivity are discussed, followed by the research motivation and objectives. The research objective of this dissertation is to investigate and examine new material sets and device configurations that couple the properties of healing and high electrical conductivity in order to realize self-healable flexible electronic devices with robust mechanical and functional tolerance to heal the damage in a more efficient manner without altering the polymer functionality. The motivation is to demonstrate the advantage of this low-temperature self-healing materials or composites in a flexible electronic device configuration. Subsequently, the research hypotheses and approaches are detailed. The last portion of this chapter provides an overview of the thesis organization with a brief introduction to each chapter and the major findings and outcomes.

1.1 Overview

Next generation electronics like wearable devices, electroluminescent displays and transparent electronics need novel polymer material systems with enhanced functionalities, robustness and shelf-life for widespread applications. However, the continuous exposure of these polymeric materials towards abrasion, impact, different mechanical, chemical and thermal stresses lead to the deterioration of their physical as well as the chemical properties, eventually leading to the mechanical failure of the material [1, 2]. Owing to this, there is a great demand for polymeric, transparent, and conducting active materials that can heal themselves upon damage. In order to avert the failure of active material, functional polymers with self-healing properties are promising candidates for designing next-generation technologies like flexible and conformable electronics where in the devices are constantly subject to mechanical stress and torture. These self-healable polymers can repair themselves when damaged, and regain the original properties of the parent polymer which in general upgrade the endurance and lifetime of the polymers in real-life applications (Figure 1.1). This would further increase the life span of materials. Recently there is a growing interest towards such self-healable materials for realizing robust electronic devices. Many approaches have been pursued for the preparation of self-healing materials- including reversible as well as an irreversible system of reactions. Despite significant advancements, it still remains challenging to achieve a transparent and healable polymer because of the limited availability of material systems that can meet all the requirements. To address this it is required to design new materials that are more mechanically robust and are reinforced with various unique functionalities like transparency and healability.

Figure 1.1[3, 4] Self-healability of electronic systems uniquely enables the fabrication of self-repairable electronics and modular and reconfigurable electronics. © Reproduced from Bartlett, Michael D., Michael D. Dickey, and Carmel Majidi. "Self-healing materials for soft-matter machines and electronics." *NPG Asia Materials* 11.1 (2019): 21. Jiheong Kang, Jeffrey B.-H. Tok & Zhenan Bao, "Self-healing soft electronics", *Nature Electronics* 2, 144–150 (2019).

Self-healing materials: The design of such self-healing materials often requires researchers to carefully control the molecular design, polymerization chemistry and chemical kinetics. Research over the past few years has revealed few families of reactions that follow the self-healing behaviour of polymers which include covalent bonding [5], supramolecular interactions [6, 7], hydrogen bonding [8], π - π stacking interactions [9], and ionic interactions [10]. These healing reactions are typically triggered by temperature, pH, light and solvent swelling. These external stimuli allow control over the transient effects of bond reformation and physical reconnection of the polymeric chains inside the polymer matrix, which in turn is responsible for the healing mechanism.

Covalent bonding based self-healing mechanism was first examined, since it is a single component reaction without the generation of byproducts upon materials synthesis. Under the class of covalent bonding induced healable materials, Diel's-Alder (DA) reaction has attracted interest as a cross-linker on account of its thermo-reversibility. [11]. The polymers produced via this mode demonstrate good mechanical properties as compared to epoxy resins for engineering applications. The Diel's-Alder adduct is formed by the cycloaddition of dienes and dienophiles that split when the temperature is increased. However, these healable polymeric systems do not intrinsically have the advantage of conductivity and transparency, both of which are critical for the flexible electronic devices. Incorporating such DA adducts into a highly transparent and flexible polymer such as polyurethane (PU) [12] capped with a conductive layer would create a highly transparent healable electrode. This would be superior to conventional rigid expensive ITO electrodes that are incapable of self-repairing which suffer from upon damage.

Flexible electrodes are of particular interest owing to their excellent conductivity and optical transmittance in conjunction with superior mechanical properties. They are

critical for a wide range of optoelectronic, electronic and energy devices (Figure 1.2).

Figure 1.2[13] Applications of flexible electrodes in the area of flexible electronics. © Reproduced from Gupta, Shoubhik, et al. "Ultra-thin chips for high-performance flexible electronics." *NPJ Flexible Electronics* 2.1 (2018): 8.

These applications not only require good electrical conductivity but demand better mechanical properties like stretchability, flexibility and robustness where conventional materials such as indium tin oxide (ITO) fail to perform [14, 15]. Additionally, the processing of ITO requires costly vacuum-deposition techniques and also suffers from high raw material cost [16]. Therefore, alternative materials and approaches for indium-free transparent electrodes are needed. Among flexible electrodes, silver nanowires (AgNWs), carbon nanotubes and graphene based electrodes have attracted attention because of their high electrical conductivity as well as optical transmittance. This is relevant for next generation flexible optoelectronic devices and wearable electronics. Although these electrodes have been deposited on technologically relevant substrates such as polyethylene terephthalate (PET) [17], polydimethylsiloxane (PDMS) [18], and polyimide (PI) [19], to form hybrid flexible electrodes, poor adhesion between the electrodes and the substrate remains a challenge [17]. Additional challenges for flexible

electrodes include innate problems like mechanical rupture, scratching and bending torsion induced failures because of their “soft” and flexible nature with respect to their solid counterparts. Hence, the self-healing capability of the electrodes is highly desirable for flexible electronic devices (Table 1.1).

Table 1.1 Comparison of the properties of self-healing electrodes over conventional electrodes

<u>Conventional electrodes (ITO glass)</u>	<u>Self-healing electrodes</u>
<ul style="list-style-type: none"> ➤ Transparent ➤ Brittle ➤ Robust ➤ Cannot be healed once cracked ➤ Fails to regain the property after failure ➤ Unsuitable for next generation flexible electronics. 	<ul style="list-style-type: none"> ➤ Transparent ➤ Mechanically flexible and stretchable ➤ Heals completely after cut at RT ➤ Regains the properties of the materials after failure ➤ Robust ➤ Wide range of application in next generation technologies (E-skin)

The focus of the proposed study is to explore the preparation of transparent and self-healing polymer with enhanced mechanical properties. The factors that modulate the self-healing properties are examined and efforts to induce healing property into a wide variety of polymers through appropriate fillers are made. Since the major application of these self-healing materials is in the area of flexible transparent electrodes and electronic devices, challenges which determine electrical performance are also examined. These efforts contribute to the development of robust transparent and flexible electronics.

1.2 Research significance

Electrodes are the backbone of electronic devices, interconnecting several elements to form an integrated circuit. The ability to make electrodes that can self-heal upon damage without compromising its electrical conductivity, is a new area of research for next-generation wearable and optoelectronic devices. Such applications often put the devices under constant mechanical stress, inducing cracks within the polymer that result in the loss of electrical conduction. Conventional electrodes like indium tin oxide (ITO) fail to perform, entailing significant research efforts in this direction. Polyurethane-based DA healable polymer is a single component reaction system that does not

generate any byproducts during the reaction. The presence of Diel's-Alder (DA) adducts in PU allows multiple healing cycles on account of its thermo-reversibility. Therefore, the self-healing polymer based on PU-DA can overcome these sorts of challenges and help to regain the material properties of the system. This PU-DA-based polymers can be used as self-healing electrodes with a capping layer of interconnecting AgNW network. These composite-based electrodes can be useful in making electronic devices such as transparent heaters and alternating electroluminescent devices for self-healing.

The project aims to investigate the underlying effect of ionic liquids as plasticizers on the mechanism of self-healing and in altering the healing temperature of the self-healing polymer. Low temperature healing of the polymers would enable facile realization of devices that can self-repair upon damage, thereby empowering the vision of transparent and flexible electronics. The project also aims to develop a novel healing mechanism and investigate the properties via incorporation of ionic liquid in various polymeric systems without DA recovery mechanism of healing. Addition of ILs would increase the plasticizing effects inside the polymer matrix which in turn makes the polymer soft and allows the polymer chains to flow under mild temperature condition. The inclusion of ionic fluid in amorphous polymers such as PVP can speed up the healing process, which could enhance the mechanical characteristics due to the plasticizing nature of ionic liquids. This healing mode can be employed with different polymer structures, such as the semi-crystalline polymers, to create new healable systems.

1.3 Objectives and scope

The primary objective of this dissertation is to investigate novel polymer material systems that can self-heal upon damage, restoring its full electronic functionality. This is expected to lead to high-performance healable electronic devices, immune to mechanical damage. This finds applications in advanced technologies like flexible and stretchable electronics, where in the devices are constantly subject to mechanical stress and torture.

The following are the objectives of this dissertation:

1. To design and fabricate healable electrodes based on processable transparent polyurethane by introducing Diels-Alder adducts. Subsequently, evaluate the

performance of healable electrodes based on various factors that affect conductivity, robustness and transparency in a Diels-Alder based healable system. To realize heaters as a demonstration of the utility of this healable electrode system.

2. Evaluate the effect of ionic liquids like 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITFS)-as plasticizers in PU-DA based self-healable polymers for self-contained polymeric composite fabrication based on the nature of the interaction. Investigate the stability of these composites. Characterize the healing, electrical and mechanical properties of the fabricated composite and compare with the pristine polymer system. Demonstrate the application of the polymeric composite as flexible alternating current electroluminescent devices.

3. Investigation of healing behaviours in polymeric systems without DA recovery mechanism based on the incorporation of ionic liquids. Study the influence of ionic liquid with different of polymer hosts like polyvinylpyrrolidone (PVP), poly(methyl methacrylate) (PMMA) (amorphous polymers) and polyvinyl alcohol (PVA), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) (semi-crystalline polymers). Evaluate the performances of these polymeric composites in terms of stability with ionic liquids. Investigate the healing and mechanical properties of the fabricated composites based on above-mentioned polymer systems.

1.4 Hypothesis and approaches

1.4.1 Transparent, flexible and self-healable electrode

Hypothesis: Incorporating DA-adducts into an intrinsically non-healing polymer housing like PU may induce healing of the resultant polymer matrix. Employing nanowire networks of conductive wires as a capping layer over this healable polymer may result in a healable electrode via fusion of the nanowires mediated via the DA reaction, which can result in homogeneous self-healable electrodes with attractive conductivity, flexibility and transparency properties, resulting in enhanced flexible self-healable electronic devices.

Approach: Here, a PU-DA based self-healable polymer was synthesized in ambient conditions with a low-temperature ($\sim 60\text{ }^{\circ}\text{C}$) synthesizing procedure. In order to do so,

a series of depositions and treatments were done to form a flexible and self-healable polymer system that is easy to fabricate without using high temperature processes and vacuum environment. Among flexible electrodes, silver nanowires (AgNWs) electrodes have been used because of their high electrical conductivity as well as optical transmittance, which depicts better compatibility with the polyurethane-based DA polymer. Since, silver nanowires demonstrated good physical properties (electrical, optical and mechanical), a self-healable electrode based on PU-DA was fabricated, showing healability even after multiple cuts. Finally, this self-healable electrode based on AGNWs was utilized to demonstrate a flexible, healable and transparent heater.

1.4.2 Low temperature self-healable polymeric composite for flexible electronic devices

Hypothesis: Lowering the healing temperature of self-healing polymers could lead to facile demonstrations on thermally-fragile substrates employed for flexible electronic applications. Appropriate choice of plasticizers could bring down the glass transition temperature (T_g) for these self-healing systems and hence reduce the minimum critical temperature at which the self-healing process gets triggered. Plasticizers such as ionic liquid could be a good option to reduce the healing temperatures. An appropriate choice of plasticizers, having favourable compatibility with the polymer matrix, can result in a homogeneous polymer composite with desirable healing and mechanical properties for high-performance flexible electronic devices.

Approach: Here, a self-healing polymeric composite material was synthesized in an ambient condition with a low temperature synthesizing procedure, based on PU-DA and imidazolium based IL (EMITFS). The governing factor for the choosing EMITFS imidazolium-based ILs over the other ILs was its thermal stability. This is because of the presence of divalent cation and anion in the EMITFS, which comes into play in resisting high temperature. Addition of EMITFS-based ionic liquid into the polymeric backbone of the self-healing polymer (PU-DA) led to softening of the polymer matrix, resulting in a transition from plastic to quasi-rubber-like state. As a result, the polymeric composite based on EMITFS depict enhanced mechanical properties and heals at 60 °C compared to the 120 °C reported in chapter 4, without losing the self-healing behaviour of the composite, was demonstrated in the second result section of this dissertation.

1.4.3 Ionic liquids based polymeric composites

Hypothesis: Incorporation of ionic liquids as a plasticizer may also induce healing behaviour in amorphous polymer systems that are not based on the DA healing mechanism. In the case of semi-crystalline polymers, these ILs may hinder the orderly arrangements of the polymeric chains. Due to which there might be deformation in healing and mechanical properties for these types of composite materials.

Approach: Herein, the incorporation of ionic liquids via chemical grafting route has improved the mechanical and healing properties of self-healing polymers and enable a robust, superior self-healing polymeric composite based on PVP and EMITFS. This IL directly enters into the polymeric chain backbone and reduces the entanglements of the polymer matrix, hence making the composite soft. Due to the softness, the polymeric matrix has a tendency to flow under the application of heat, which allows the composite to recover back from the damage. However, such grafting methodologies hinder the self-healing mechanism in crystalline polymers like PVA and PVDF-HFP by restricting the motion of the polymer chains. Hence, periodical arrangements of the polymer matrix which leads to the crystallinity of these polymers hinder the healing as well as mechanical properties of the polymeric composites. In this section, a comparison was done in which ionic liquids were added in amorphous based polymers and semi-crystalline polymers to verify the above hypothesis. Investigations were carried out on linear or amorphous polymers (PVP and PMMA) and on semi-crystalline polymers (PVA and PVDF-HFP) and the effect on glass transition temperature was examined. The mechanical and self-healing behaviour of these composites were also investigated comprehensively.

1.5 Dissertation Overview

- *Chapter 1* provides a short introduction to the motivation and the problem statement for this work. The hypotheses and approaches are put forth. A brief architecture of the rest part of the thesis is provided and finally, the major findings and novelties are listed.
- *Chapter 2* reviews the literature concerning recent advances in the realization of self-healable polymers. The relevant advantages and disadvantages of these devices are addressed and strategies for achieving robust characteristics are discussed. The different mechanisms of healing and their application in self-healing electronics are discussed.

The importance of ionic liquid as plasticizers are discussed next. The research gap entailing the need for novel materials and devices with self-healing properties is finally provided to highlight the motivation of this research.

- *Chapter 3* outlines the rationale behind the choice of materials and device configurations and emphasize the various fabrication procedures and characterization techniques employed.
- *Chapter 4* details the fabrications and characterization of a low-temperature PU-based self-healable polymer which combines the properties of flexibility and transparency. A standard method of spray coating was used to deposit AgNWs as an electrode over the PU-DA substrate to fabricate self-healable electrodes. Performance of silver nanowire network-based flexible electrodes is measured and compared in terms of the transparency versus conductivity function. The healing mechanism was investigated in detail using scanning electron microscopy and optical microscopy instruments. A transparent and self-healable heater is finally realized as a goggle defogger to demonstrate the application of these AgNWs based electrodes.
- *Chapter 5* investigates the effect of ionic liquid (EMITFS) on the covalently bonded self-healable polymer. An increase in ionic liquid concentration helps to increase in chain mobility of the polymer, which leads to a decrease in glass transition temperature of that polymer composite. This change in glass transition temperature makes the polymeric composite soft and hence, increases the healing, electrical as well as mechanical properties of the composite. To demonstrate an application, this polymeric composite was utilized for the fabrication of a self-healable alternating current electroluminescent device. This work solves the high temperature healing problem as mentioned in the previous report, without hampering the healing, electrical as well as mechanical properties of the polymeric composite.
- *Chapter 6* examines the effect of ionic liquids as healing agents when housed in different classes of polymers. The amorphous/ semi-crystalline nature of the polymer housing is observed to affect the healing mechanism. This type of chemistry can be applied in designing new class of materials for flexible electronic devices. A detailed study was also conducted about the interaction of the ionic liquid with the polymers.

- *Chapter 7* finally summarizes and draws conclusions that prove the hypotheses as mentioned. A brief perspective on the future directions is stated with insights into the potential applications with these self-healable material systems.

1.6 Findings and Outcomes/Originality

This research addresses the chemistry and important issues related to flexible and self-healable polymers, electrodes and electronic devices, yielding novel and fundamental insights.

They include (chapter-wise):

1. *Polyurethane based DA mechanism for healable electrodes* [20]: In this chapter, a low temperature procedure was employed to synthesize a PU-based self-healable polymer which has the properties of flexibility and transparency. This synthesis process was employed without the use of an inert atmosphere or vacuum. A standard method of spray coating was used to deposit AgNWs as conducting capping layer over the PU-DA substrate to fabricate self-healable electrodes with better conductivity and transparency values when compared to state-of-the-art. By triggering this reaction via passage of electric currents, a novel method of healing these electrodes was also demonstrated. This healable electrode was utilized to demonstrate a healable transparent and flexible heater. **To the best of our knowledge, this is the first healable, transparent and flexible heater reported.**

2. *Polyurethane based ionic liquid composite for low temperature self-healable electrodes* [21]: In this chapter, the incorporation of ionic liquid in the polymer was investigated. The reason was to incorporate low molecular weight fillers like ionic liquid to the polymer that helps in decreasing the healing temperature by decreasing the glass transition temperature of the system. The decrease in glass transition temperature explains that the polymer composite has become soft. This softness property helps to stretch the polymeric composite beyond its normal limit. Hence, the mechanical property of that composite increases. Herein, a low temperature synthesis procedure was employed to develop the self-healable polymeric composite. This polymeric composite depicted a lower healing temperature of 60 °C as compared to the previous report of 120 °C, and also enhanced the mechanical property. **This chapter reports the first low-temperature self-healable polymeric composite for alternating current**

electroluminescent (ACEL) devices, to the best of our knowledge.

3. *Ionic liquid as a global additive to induce self-healing*: The performances of ionic liquid as plasticizers in the polymeric matrix depicted in the previous chapter provided us with another interesting research topics to be exploited. The incorporation of the ionic liquid tends to increase the healing behaviour and mechanical properties for PVP, as shown in chapter 5, which clearly opens a unique window for a new class of materials. These class of materials can be widely applicable in self-healable flexible electronic devices. The other polymeric composites (PVA, PMMA and PVDF-HP) with ILs did not show the desired enhancement in healing and mechanical properties as PVP. In this chapter different class of polymers were used to study in detail about the interactions of ionic liquid, which clearly defines the use of ionic liquid in the polymer matrix to enhance the healing mechanism without DA healing functionalities in the polymer matrix. **This chapter depicts a novel mechanism of healing without DA recovery mechanism.**

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Chapter 2

Literature Review

This chapter critically reviews the literature concerning self-healing materials with a focus on underlying chemistry and their recent advances in the field of flexible electronic devices. A brief overview of the various underlying mechanisms of self-healing process are first provided with a focus on thermal reversible process with self-healing electrodes. Next, the incorporation of fillers (ionic liquids) to form a polymer composite is surveyed. The effects of fillers in the polymers and how they can contribute to improve self-healing properties is well discussed. The pertinent merits and demerits of these approaches are evaluated in detail with focus on the fabrication of the polymer composite and device variability. Finally, the research gap entailing development of novel materials and device configurations with self-healing properties is provided to justify the motivation of this work-the need for self-healing materials for flexible electronics. The following chapters embark on the hypotheses and objectives to fill the research gaps identified in this chapter.

2.1 Overview

Polymers are fundamental materials in electronics, surface technologies and automobiles. However, the continuous exposure of these polymeric materials towards abrasion, impact, and different mechanical, chemical and thermal stresses lead to the deterioration of their physical as well as the chemical properties, eventually leading to the mechanical failure of the material. The restoration of properties after environmental degradation or mechanically-induced damages has always been a huge challenge. In order to avert failure of active material, functional polymers with self-healing properties are essential for the next generation technologies. Polymers which can repair themselves when damaged, and would regain the original property as the parent polymer; will in general upgrade the property of endurance and lifetime of the polymers in real-life applications. Traditional repair methods become costly and unviable when dealing with delicate systems or inaccessible defects within materials [1]. To address this, a new class of polymers that is intrinsically healable has been explored. These self-healing polymers have the ability to undergo restoration upon fracture [2], thereby reducing the need to engage in unfeasible material maintenance processes. Figure 2.1, depicts in general the role of self-healing materials in next generation electronics.

Figure 2.1[3] A schematic diagram depicting the evolution of an ideal damage–repair cycle in polymeric materials. © “Reproduced from Yang, Ying, and Marek W. Urban, Chemical Society Reviews 42.17, 2013, 7446-7467 with permission from The Royal Society of Chemistry.

Many approaches have been discovered for the preparation of self-healing materials, including reversible as well as irreversible system of reactions. In spite of all these

reactions, it remains challenging to achieve a transparent, healable, conducting polymer because of futile availability of material systems which can meet the expectations.

Self-healing functionalized polymeric materials: Self-healing materials have been extensively explored in the past few years, whereby the process of healing was generally focused on the recovery of the properties related from the mechanical point of view, after being damage. Therefore, self-healing functionalized polymeric materials are emerging as one of the most important materials for research. Now-a-days, the focus of the research groups is to fabricate a multifunctional self-healing system in the field of healable optoelectronic and wearable technologies. The scheme of self-healing mechanism of materials has frequently inspired nature. Inspired from nature, where materials rebuild their parent behaviour after damage such as a restoration of sense of touch after cut on finger is healed, or trees that itself initiates the mechanism of self-healing to protect their bark which consist of vascular cambium [3-5]. In comparison, the man-made materials are limited in terms of damage prevention and self-recovery. This has led to inspiration for material scientists to direct their attention to fabricate a new class of materials that can restore themselves back to their original state after chemical or mechanical damage. The driving force behind the fabrication of self-healing materials is the need of materials that are consistent, functional and robust over long time.

The process of self-healing is basically based on the combinatorial approach of detecting the damage and repairing the damage. The material must have a sensor which detects the damage inside the materials and must initiates the self-healing mechanism of the damaged portion in the material with help of chemical reaction or by regulating the movable phase to the place where crack is present. In most cases, damage itself acts as a sensor. Lastly, the material which are healed should follow the similar trait as the parent material, even after many repeated healing cycles [6] (Figure 2.2). It was clearly depicted from the Figure 2.2 that the self-healing materials has the better performances over time as compared to the traditional materials or chemically modified materials. Not only the performance but also service lifetime extension for the self-healing materials is better without the degradation of the materials properties even after repeated cyclic use of materials itself.

Figure 2.2[6] Shows the performances of conventional and different class of self-healing (SH) materials w.r.t time. © “Reproduced from Garcia, Santiago J. "Effect of polymer architecture on the intrinsic self-healing character of polymers." *European Polymer Journal* 53, 2014, 118-125 with permission from the 2014 Elsevier Ltd.

2.2 Classification and mechanism of self-healing polymers/materials:

The mechanism of self-healing is primarily based on the initiation of a mobile phase, which is generated with the help of an external agent such as heat or precisely initiated from the position where damage or crack has taken place. The self-healing material could be classified into two distinct groups based on their mode of triggering and also the strategies involved through which the healing functionality is incorporated into the matrix of the bulk materials [7-10]. First one is extrinsic self-healing material, which requires external stimulus for triggering the healing mechanism.

2.2.1 Extrinsic self-healing materials: This class of materials do not have the self-healing potential of its own. They are integrated with external healing agents encapsulated in the forms of capsules or vascular network. Failure to these materials causes the rupture of capsules or vascular networks and releases the healing agent from it, which intern heals the bulk material and protect the damage propagation of the material. Figure 2.3 depicts the mechanism of extrinsic self-healing system [11]. White and co-workers have reported self-healing concept by embedding micro or nano capsules containing the healing agent inside the polymer matrix, which gets ruptured

by the crack and the healing agent inside the capsules gets triggered and heals the crack as shown in Figure 2.4 a and b [12]. The initiation of the crack inside the matrix releases

Figure 2.3[11] Schematics of extrinsic self-healing mechanism. Reprinted in part with permission from Jiheong Kang, Jeffrey B.-H. Tok & Zhenan Bao, 'Self-healing soft electronics', *Nature Electronics* 2, 144–150 (2019).

the dicyclopentadiene (DCPD) monomer (healing agent) which was encapsulated in microcapsules, into the crack through capillary action and prevent the propagation of the crack in bulk material. Later, the healing agent can also be triggered by the catalyst, during the polymerization process. As reported, ruthenium-based Grubbs' catalyst ingrained during the reaction initiated the ring opening metathesis polymerisation, which interact with the catalyst and thus helps to heal the crack. Continuous improvement has been made in the encapsulation process of healing agents in the form of micro capsules, such as in situ [13], interfacial [14] and melttable diffusion [15] for the capsule based self-healing materials. Besides, many other healing process and catalyst were been investigated, for example, isocyanates [16], polydimethylsiloxane (PDMS) [17] and epoxy resins [18]. The concept of capsule based healing agents has been frequently employed in fabrication of the self-healing materials, which is quite straight forward by incorporating the capsules containing healing agents inside the matrix of the bulk materials [19]. The limitations of capsule based healing mechanism was that they have a limited healing agents to heal the system.

To overcome the limitations of the capsule based healing mechanism, vascular self-healing mechanism plays a vital role in the chemistry of the self-healing materials were developed. In vascular self-healing system, the healing agents and the catalysts are insulated in the networks in the form of capillaries or hollow channels inside the materials. This mode of healing were found to be efficient of repeated healing of the damage parts. White et al. has demonstrated the coating and the design of the substrate

with the help of bioinspired microvascular networks (Figure 2.4 c, d) [20]. They have well explained about the large volume and repeated healing mechanism with their design and approach. Healing agents which were ingrained in the substrate were repeatedly transported to cracks via specially designed three dimensional (3D) microvascular network. However, the reduction of the incorporated catalysts and the necessity to refill the multiple healing agents within these material architecture would restrict the healing mechanism of the system. To tackle with this present limitation, White and co-workers further refined a healing chemistry in which they use an epoxy healing mechanism. This system contain a photo-lithographically patterned isolated region within the embedded microvascular networks, which enhance their fabrication with 3D biomimetic coating [21]. Afterwards, Williams et al. have also fabricated a self-healing sandwich composite configuration with fluidic networks [22]. These configurations are either one dimensional (1D) or two dimensional (2D). This vascular self-healing mechanism has significant benefits over the mechanism of microcapsules based healing agents. But, vascular healing process has a disadvantage that they demand for the complicated design and fabrication methods for the microvascular networks inside the matrix of the bulk materials, which restricts its use in future electronic devices.

Figure 2.4 [23] Examples of Extrinsic self-healing materials (a, b) shows self-healing materials based on capsule mechanism, (c, d) depicts vascular mode of self-healing materials. Reprinted in part with permission from Tan, Yu Jun, et al. "Self-healing electronic materials for a smart and sustainable future." *ACS Applied Materials & Interfaces* 10.18 (2018): 15331-15345.

2.2.2 Intrinsic self-healing materials: There is also a class of material which enables the self-healing methods via intrinsic mechanism. To achieve an intrinsic self-healing materials, no external stimulus/healing agents for triggering the healing mechanism is required. The major advantages of this healing system is that, they can undergo multiple and repeated healing of cracks present in the bulk materials. The intrinsic healing materials are more reliable as well as durable as compared to the extrinsic healing materials. Intrinsic healing mechanism can be achieved through inherent reversibility of molecular interactions of the polymer matrix, which solves the inherent problem of integration and compatibility with respect to micro capsules or vascular network healing agents [19]. General schematic of intrinsic self-healing system is shown in Figure 2.5 [11]. On the basis of recent literatures [7, 10, 19], the mechanism that have been developed are divided into two categories, one is the physical molecular diffusion and the other is defined as the chemical bond interaction. The healing mechanism based on physical molecular diffusion was demonstrated in different forms of polyelectrolytes complex. In this method, healing mechanism depends upon the salt concentration in the bulk material. This means that the higher concentration of salt in the material leads to the greater mobility of chain segments, which speeds up the diffusion and hence results in the faster healing of the material.

On the other hand, chemical bond interaction based healing mechanism can be subdivided into three groups; one is covalent bond and the other is noncovalent bond interaction based healing. The third one is healing based on intermolecular forces, which includes hydrogen bond, ionic interaction, dipole-dipole and van der Waal's interactions [3]. In the section of covalent bond based healing, reversible covalent based healing has attracted most of the researchers because of its unique advantages, such as Diels Alder reaction [24, 25]. Under the class of covalent bonding induced healable materials, Diels-Alder (DA) reaction has attracted enough concentration as a cross-linker in the polymers on account of its thermo-reversibility. For cross-linking of polymers, the reaction which is mediated by Diels-Alder mechanism is suitable route for synthesising the polymeric material. The advantage of DA reaction is the thermo-reversibility, which allows for repeated healing after damage. The DA based material system are best in class, can be thermally triggered and utilized in self-healing materials.

Figure 2.5[11] Schematic of intrinsic self-healing mechanism. Reprinted in part with permission from Jiheong Kang, Jeffrey B.-H. Tok & Zhenan Bao, 'Self-healing soft electronics', *Nature Electronics* 2, 144–150 (2019).

Diels-Alder based Healable Polymers: The study of healable polymer-based networks based on the DA mechanism was first pioneered by Stevens and Jenkins, in which they incorporated maleimide units into a polystyrene-based network [26]. This was made relevant by Wudl and co-workers, who developed a highly-cross-linked healable polymer network from tetra-furan groups (dienes) and tris-maleimide units (dienophiles) [27]. The resultant network, however, had low transparency and a less than ideal healing efficiency of 57% at extraneous healing conditions of 120 °C under an inert atmosphere. Upon which, Liu and Hsieh devised a hydroxyl-based resin based upon similar constituents [28]. They were able to repair a knife cut on the material after exposure to thermal treatment at 120 °C for 20 min. In response, certain modifications have been attempted. Zhang et al. proposed using bismaleimide instead to crosslink with a polyketone network consisting of furan groups [29]. Similarly, a moderate healing temperature of 120 °C was required for an exposure time of 10min, in addition to the poor transparency that was obtained. On a similar front, Postiglione et al. proposed incorporating benzyl alcohol into a DA-based polymer network synthesised from a bismaleimide and a mixture of furanized resins [30]. The as synthesised polymer network unfortunately was very brittle and achieved poor healing efficiency at a stipulated healing temperature of 100 °C due to the irreversible surface cracks. More recently, Pyo and co-workers developed a novel DA-based polymer network via the addition of bismaleimides into a polyurethane network consisting of furyl groups [31]. However, while the resultant healable polymer had high transparency, its mechanical properties were highly compromised. In addition, the healing conditions for a

microscale cut were highly undesirable (120 °C for 10 min). Figure 2.6 depicts the DA based self-healing mechanism.

Figure 2.6[32] Schematics of DA based self-healing system. Reprinted in part with permission from Sheng Wu, “Research Progress of Self-healing Polymer Materials”, *Morden Materials Science and Technology* 1, 1-7, 2018.

In comparison to the covalent bond based healing mechanism, the interaction of materials via non covalent bond can also self-heal with or without external stimuli. Researchers have demonstrated a class of supramolecular gels, which heals the materials via the reversible host-guest interaction based healing mechanism [31, 33]. Leibler and co-workers have demonstrated a self-healable rubbery polymeric material, which was obtained from fatty acids and urea [34]. Here, the material self-heal via the hydrogen bonding present in fatty acid and urea at room temperature. Similar to the Leibler’s supramolecular gels, Wang et al. has synthesised a self-healing polymeric composite which was transparent as well as stretchable [2]. The mechanism of healing was based on ion-dipole interaction as depicted in Figure 2.7.

Healable Polymers with Ionic Mechanisms: The exploitation of ionic interactions to achieve self-healability has been reported in literature. Cao et al. synthesised a self-healable ionic-based polymer by incorporating EMITFS ionic liquid into polyvinylidene fluoride-co-hexafluoropropylene-5545 (PVDF-co-HFP-5545) [2]. While an impressive strain of more than 5000% was achieved for the best performing composition, an extensive period of 24 hours at room temperature is required for healing for a micronscale cut. Madsen et al. synthesised an interpenetrating polymer network from silicone and ionic silicone species [35]. However, healing was only possible at 120 °C for a minimum of 4 hours and poor transparency was achieved. Next, Xu et al. devised a self-healable polymer based on ionic supramolecular principles by incorporating zinc dimethacrylate (ZDMA) in natural rubber (NR) [36]. While healing

was achievable at room temperature after 10 min, the polymer was fragile and prone to necking.

Figure 2.7 [23] Examples of intrinsic self-healing materials. Reproduced with permission from Tan, Yu Jun, et al. "Self-healing electronic materials for a smart and sustainable future." *ACS Applied Materials & Interfaces* 10.18 (2018): 15331-15345.

Many recent reports have also mentioned a different type of approach for the self-healing of the materials, which need a pre heating of the damaged part present in the bulk materials. The heating was based on the temperature above its glass transition temperature or melting temperature or revealing the materials to a plasticizing fillers or solvents [7, 37]. The self-healing mechanism could also be farther differentiated based on the employed external force. These external impetus can be mechanical [12], photochemical [38], electrochemical [39], chemical [40], electricity [41, 42], electromagnetic forces [43], ballistic impact [44, 45] and as well as light [46, 47].

Self-healing via electrically driven process: The process of self-healing of electrodes propose the feasibility for the introduction of electrically driven healing process which, therefore, represents a novel procedure with superior cost effective as well as rapid control over the healable materials [48]. The state of art for different approaches for self-healing conductive materials are classified into three main classes as stated below:

1. By introducing dynamic reversible bond into the conducting polymer for generating a self-healing polymer [41].
2. By embedding conducting material into the polymer matrix for producing self-healing conductors [49, 50].
3. By incorporating additives in conducting ionic liquids [51].

Self-healable materials in recent times have been developed in various ways to meet the present challenges, one is mechanical properties which includes the strength, stretchability as well as flexibility, two is the faster way of self-healing of materials and third is the optical property like transparency for different applications. Self-healing materials has also been progressed in the biocompatibility with different materials systems. The next portion of this review is committed to the self-healable polymeric composites based on ionic liquids, which can come-up with a different class of self-healing materials with interesting materials properties like mechanical and electrical. The intrinsic mode of healing can be utilised to heal small cracks and can be used to heal the materials at the molecular scale. Whereas, vascular healing method can be applicable to heal large crack and can effectively boost the upper limits of self-healing mechanism. But, the capsule based healing method lie somewhere in between the intrinsic and the vascular self-healing mechanism.

2.3 Ionic liquids and Ionic liquid polymeric composites

Advanced polymeric materials are the cutting edge for tackling the major challenges around the globe such as environmental protection, conversion and storage of energy and cost efficiency in transportation field. Researchers are exploring new methods and platforms for advanced materials based on the concept of ‘functions through structural designs’. In this concept, Ionic liquids play an important part and act as a functional building block in synthesizing and designing new polymeric materials for the next generation smart materials [52]. Ionic liquids, by definition, are salts consisting of bulky or asymmetric organic cation and inorganic or organic anion, having melting point below 100 °C [53]. Figure 2.8 shows examples of ionic liquid used in the research for various applications. Ionic liquids are thermally stable and have a large electrochemical window which makes them to be applicable in thermal as well as electrochemical

applications [54]. Incorporation of filler particles as a plasticizer of nanometre sized in polymer composites have been developed recently, which tends to improve the mechanical, chemical resistance and thermal properties to polymers. This kind of approaches can be also effective step to enhance the properties of the polymer electrolytes. This strategy could become a productive way of counterbalancing the plasticizing effect of higher loading of ionic liquids in the polymer-ionic liquid composites. The challenges associated with the polymer-ionic liquids (ILs) composites such as the issues of compatibility between polymers matrix and fillers (plasticizers). Next is the re-aggregation of the nano-fillers to form an agglomerated particles, while synthesising the polymer-ILs composites and finally the orientation and leaching out of the ionic liquids from the composites.

Figure 2.8 [55] Examples of ionic liquids in which different cations and anions used, together with the properties of hydrophilic–hydrophobic correlated with the anions involved in ionic liquids. Reprinted in part with permission from Ye, Yun-Sheng, et al. "Ionic liquid polymer electrolytes." *Journal of Materials Chemistry A* 1.8 (2013): 2719-2743.

Recent reports suggests two types of processes which can be implemented to synthesise polymer-IL composites as depicted in Figure 2.9. The two approaches include the design of polymeric composites composed of polymer matrices and ILs. In the first approach, it depicts that the polymer electrolytes were physically blended with the

desired inorganic materials [56-60] with ionic liquid and the monomers of polymers in suitable solvents. The highlights of this approach is the importance of expanding a detailed understanding of the specific physical interactions between supported polymer matrices and ILs, in which the ILs are compatible to the polymer matrix. The only point of concern in this approach is the compatibility between the individual components in the polymer matrix. In the second method, ionic liquids are reacted with modified polymer in desired solvents in presence of acid or base catalyst [61, 62]. Because of the high solubility of a large amount of monomers in ionic liquids, which helps to form direct fabrication of polymeric composites with ILs. By this approach, it also allows to have an empirical control over the physical and chemical nature of such polymer based IL-composites.

Figure 2.9[23] Schematic for the preparation process for non-covalent and covalent, organic–inorganic polymer–ionic liquid composite. Reprinted in part with permission from Fuller, J., A. C. Breda, and R. T. Carlin. "Ionic liquid-polymer gel electrolytes." *Journal of the Electrochemical Society* 144.4 (1997): L67-L70.

From the application point of view, doping functional materials into ILs broaden the electronic devices for more potential. Essentially, nanomaterials are tried to trigger the electrical response of ILs by converting the external responses into thermal energy. Wang et al. reported a self-healing sensor by combining acid-modified CNT with the ability to perform as a photo-thermal transformation in the ionic liquid [63]. Polymers with ionic liquid as gate dielectrics for the polymer based thin film transistors have been reported recently. Bubel and his team members were the first group to demonstrate

a self-healable ionic-gated transistor [51]. The polymer was used as a dielectric layer which displays a good self-healing property, which can be demonstrated as a self-healing polymer which can be utilized as a dielectric for a high capacitance gate insulator. Recent reports shows that researchers are paying much attentions on ionic conductivity as well. Unlike electrical conductivity via metals electrodes, it was investigated that the ions present in a polymer composites are also excellent medium for the self-healing mechanism due to generation of electrostatic interaction evolved between the anions and cations. Hence, the resulting polymer composite with ionic liquid have both the capabilities of self-healing as well as ionic conductivity [64-68]. Scientist have reported earlier the reduction of healing temperature by the addition of plasticizers [69]. They had used the derivate of PMMA polymer i.e. PHPMA which has self-healing ability due to the presence of dynamic bonding (H- bonding) but had Tg above 100 °C, and to overcome this problem the more flexible polymer additive PEI was added which interacts with PHPMA through dynamic bonding. The Tg of the resulting blend is reduced to less than 40 °C. Even people have reported ionic liquid as a plasticizer in PMMA [70]. In this ionic liquid was based on imidazolium salts which act as a plasticizer. This also open an extra window for my research to utilize the ionic liquid as a plasticizer as well as the formation of thin film with good mechanical properties to form a self-healable polymer with sufficient conductivity.

The next portion of this review is committed to the transparent and flexible electrodes, which are the backbone of any electronic devices. The electrodes are also responsible for the self-healing electronic devices because the entire device should heal including the electrode and the polymer substrate.

2.4 Transparent, Healable and Flexible electrodes

Transparent and flexible electrodes draw equal attention from many technological area, including optoelectronic devices, transparent flexible film heater, photovoltaics and display applications. The key properties expected from next generation transparent electrodes are to have high transparency, to show high electrical conductivity and be mechanically robust, stretchable and flexible. Among the best and most efficient transparent electrode is the indium tin oxide (ITO). However, ITO fails to meet the property of flexibility and fairly high fabrication costs have provoked the researchers to find an alternative materials. Figure 2.10 shows the examples of healable electrodes utilised for electronic devices.

Figure 2.10[23] Examples of self-healing conductors. a) & b) self-healing polymeric composite conductors using μNi particles. c) & d) self-healing conductors based on AgNWs/(PEI/PAAHA). Reprinted in part with permission from Tan, Yu Jun, et al. "Self-healing electronic materials for a smart and sustainable future." ACS Applied Materials & Interfaces 10.18 (2018): 15331-15345.

In the electronic devices background, nanostructured transparent electrodes [71-75] including CNT, PEDOT: PSS, Graphene and especially metallic nanowires have been studied thoroughly and have attracted the attention of the scientist in past years because of their promising properties and applications [73, 76, 77].

Metal nanowires: Among the metal nanowires, silver (Ag) is the largest and extensively studied metal in its 1D form (nanowires), having an outstanding electrical conductivity among the various different metals [78]. Silver nanowires (AgNWs) can be manufactured by using different technical process which include hydrothermal process, polyol process, electro chemical technique and microwave-assisted method [73]. Many studies have reported that the surface roughness of as prepared AgNWs network on substrates are not favourable for optoelectronic applications, and hence to improve the roughness several methods have been looked into, such as coating a layer

of PEDOT:PSS above the percolation network of the AgNWs and also by embedding the silver nanowires into the substrate [79, 80]. Researchers have also employed sufficient amount of worked to improve the electrical performances of AgNWs films by decreasing the resistance at the junction or by increasing the percolation path. This improvement in electrical performances has been accomplished by utilizing the process of welding or by doping an additional material into the percolation network of the nanowires [81-86]. Owing to their better optoelectronic and mechanical properties and facile fabrication process, flexible and transparent electrodes which are based on AgNWs have been demonstrated in flexible and stretchable devices [87-89]. Groups have reported AgNW electrodes having excellent conductivity with high transparency on different polymer substrate with an unchanged conductivity upon elongation [88, 90]. These electrodes been utilized for making actuators based on flexible substrate and polymer light emitting chemical cells (PLECs). The limitations of silver nanowire networks includes inter-nanowire junction resistance, chemical oxidation and lack of success because of the electrical breakdown. Therefore, hybrid electrode structure formation with graphene, CNT and graphene oxide (GO) has been demonstrated to overcome the limitations [90-94]. Figure 2.11 shows the transparent electrodes based on silver nanowires (AgNWs).

Figure 2.11[95] Silver nanowire based transparent electrodes. (a) SEM image of AgNWs-PTBA/AA copolymer. (b) SEM image of AgNWs/composite electrode. (c) Photograph of PLECs. (d) SEM image of GO welded with AgNWs. (e) SEM images of AgNWs-CNT hybrid nanocomposite. Reprinted in part with permission from Kim, Kukjoo, et al. "Stretchable and transparent electrodes based on in-plane structures." *Nanoscale* 7.35 (2015): 14577-14594.

Carbon nanotubes (CNT): The most important allotropes of carbon is the carbon nanotubes which are divided into two main section according to their layers of graphitic carbon such as single-walled CNTs (SWCNTs), having a single layer of graphitic carbon or multi-walled CNTs (MWCNTs) which has multiple layers of graphitic carbon. These CNT exists in the shape of a cylindrical tube which are composed of one or multi layers of graphitic carbon. The cylindrical tube of carbon has outstanding properties including high aspect ratio, high thermal conductivity, good mechanical strength and electrical conductivity [96-100]. The initial approach of using CNTs as a transparent electrodes was to draw aligned CNT from the agglomerate of CNT. These transparent, stretchable and unidirectional CNTs were employed as electrodes for OLEDs [101], supercapacitors [102], touch panels [103] and loudspeakers [104]. Feng et al. reported the process of roll-to-roll fabrication to produce highly transparent and super-aligned CNT films by decreasing the height of CNT agglomerate and minimizing the residual big bundles of CNT with the help of laser and plasma trimming [103]. These films were highly stretchable along the diagonal direction with respect to stacking angle [105]. People have also reported stretchable transparent electrodes by embedding or direct deposition of CNT in PDMS [106, 107].

Other than CNT, graphene as well as PEDOT:PSS has also been demonstrated as a flexible stretchable and transparent electrodes for applications like of supercapacitors [108], artificial muscle actuators [109] and organic photovoltaics [110].

The final portion of this review is committed to the self-healable polymeric materials integrated in electronic use, which opens a new-window for the next-generation self-healable electronic devices with interesting electrical properties. Figure 2.12 depicts the carbon nanotube based electrodes.

Figure 2.12[95] CNT based transparent electrodes. (a) Photograph of MWCNT that has been drawn from the CNT forest. (b) Image of OLED from aligned MWCNT sheet. (c) Flexible and transparent touch panels based on super-aligned CNT. (d) Sheet resistance of multi layers along with the cross stacked film in three different directions. (e) Morphology of CNT films with stretching. (f) SEM image of the SWCNT film. (g) Fabrication of SWCNT-PU for elastic transparent electrode. Reprinted in part with permission from Kim, Kukjoo, et al. "Stretchable and transparent electrodes based on in-plane structures." *Nanoscale* 7.35 (2015): 14577-14594.

2.5 Self-healing devices

Recent literatures shows a remarkable evolution in the development of self-healing materials for electronic devices [23, 50, 111, 112], which shows their favourable integration into functional self-healing electronic devices, for example sensors, E-skin, dielectric actuators, field-effect transistors, solar cells and energy devices. Figure 2.13 [11] clearly analyse the development in self-healing electronic devices that will open the gate for the next generation flexible electronic devices.

Figure 2.13[11] Self-healing soft electronics. Schematic of a multifunctional self-healable soft electronic device on human skin. Self-healability of electronic systems uniquely enables the fabrication of self-repairable electronics and modular and reconfigurable electronics. Self-repairable electronics can autonomously restore their electrical and mechanical properties when they are mechanically damaged by scratching, poking, rubbing and tearing. Modular and reconfigurable electronics allow users to customize their own electronic devices with various two- or three-dimensional shapes and multiple functionalities by a simple mechanical cut and self-healing process. Reprinted in part with permission from Jiheong Kang, Jeffrey B.-H. Tok & Zhenan Bao, 'Self-healing soft electronics', *Nature Electronics* 2, 144–150 (2019).

Electroluminescent Devices: Self-healable electroluminescent devices have hardly been reported. However, there is one study that proposed the idea of an “add-on” self-healable component to an electroluminescent device. Kitai et al. synthesised a $\text{Zn}_2\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}_4\text{:Mn}$ -based ACEL device that contained a thin layer of self-healable strontium titanium oxide (SrTiO_3) [113]. The device is fully functional and exhibited luminance of 300 cd/m² at 50 V with a frequency of 60 Hz. Yet, while it has been packaged as a “self-healable”, the self-healing properties are merely contributed by a thin “add-on” layer. The active layer of the device is not self-healable. In fact, no conclusive healing tests were conducted to justify the authenticity of this self-healing behaviour. Furthermore, the device was fabricated on rigid, non-flexible ITO glass, which suggests that the device would be rigid in nature.

Sensors: Self-healable sensors are broadly explored in our regular lives to examine the physical (like, heat, light, pressure, humidity and strain) and chemical signals [114]. These sensors can effectively enhance the lifespan of these devices for both as sensing ability as well as aesthetic functions. Initially, Bao et al. demonstrated a self-healable sensors which was synthesised by mixing μNi particles with a self-healing polymer

[49]. In contrast to μNi microparticles, particles of carbon and graphene were utilised in pressure as well as flexion sensors [115, 116].

Transistors: In the area of field-effect transistors (FET), researchers have already demonstrated a self-healable dielectric layer, which is electrically stable and have been formulated by combining metal-ligand linkages in a polymer matrix [117]. The electrodes based on carbon nanotubes (CNT) and silver nanowires (AgNWs) have also been utilised for the fabrication of source, drain and gate element for transistors [118]. In spite of all these development, the fabrication of a fully self-healing FET is still a challenging work because of obstructions in the fabrication methods and of limited self-healable semiconductors and dielectrics in thick or thin films.

Energy devices: The real advantages of energy storage devices is required for the working of electronic devices. Initially, a self-healable based supercapacitors was made generally laminating CNT (acid treated) over the healable substrate [119]. Sun et al. has successively demonstrated a wire shaped healable supercapacitor, in which the electrode was fabricated by mixing silver nanowires, aligned graphene sheets and CNT in fibres [120]. The accomplishment of self-healing behaviour of the device at room temperature was determined by 92%. A perovskite solar cells was also fabricated by Zhao and co-workers, where they formed the device by incorporating polyethylene glycol in the active part of the device [121]. Figure 2.14, compile the recent progress in self-healing electronic active layers and devices.

Figure 2.14[11] Self-healing electronic devices. Recently reported self-healing electronic devices based on publication year and complexity of electronic devices. Red, self-healable active layer; blue, standalone self-healable electronic devices; purple, multifunctional self-healable stretchable system. Reprinted in part with permission from Jiheong Kang, Jeffrey B.-H. Tok & Zhenan Bao, 'Self-healing soft electronics', *Nature Electronics* 2, 144–150 (2019).

2.6 Outlook and research gap

Self-healable materials and devices have shown a promising future for the next generation electronic devices. Recent reports and literature have shown a progressive efforts in the field of self-healable electronic devices. Nevertheless, there are ample of challenges which is required to sort out before these devices can be integrated in our regular daily life.

Fabrication: Primarily, the most important step is the fabrication of self-healable materials, which are basically incompatible with the current electronic technologies. In particular, the patterning of healable materials with very specific characteristics and size needed for integrated electronic technologies remains tedious and contentious.

Properties: In spite of interesting advancement in the area of self-healing materials, the requirement of functionalised materials for the applications still remains inadequate. Moreover, the electronic properties of recent healable devices are not yet up to the level of non-healable electronic devices. Therefore, for the high performances of these self-healable devices, the self-healing polymers hybridised with inorganic nanomaterials will be an essential parameters for their enhancement in electronic properties.

Process: Regarding the processing of self-healing materials is that the healing process is quite slow and non-autonomous. Therefore, the improvement of an autonomous self-healable devices like a human body would be perfect. Further, in the expansion of self-healing materials, which permit the action of self-healing mechanism to the selective portion of the devices which will be an interesting in integrated electronic technologies.

Large area: Large area damages or crack are the most critical obstruction in the development of self-healing materials. It is challenging to figure out a powerful self-healing materials, when the size of crack or failure is bigger than the thickness of the active layers. Therefore, the self-healing materials is now limited to small area of crack or damages.

Thermal stability: Generally, it has been seen that the intrinsic self-healable materials are based on covalent and non-covalent bonds, in which their properties like mechanical and healing are sensitive to higher temperatures. Thus, the thermal stability of these

materials is likely to be poor. New strategies and process should be employed to fabricate a thermodynamically stable self-healing material system, which will make these materials more stable and reliable. In this aspect, self-healing chemistry will be a promising approach especially for the fabrication of self-healable electronics with the functionalities like configurability, modularity and robustness.

Research gap: All these self-healing process reviewed, opens a new-window for the next-generation transparent flexible electronic devices which will be attractive and advantageous in terms of low cost as well as with an outstanding lifetime. Thus, healing process of functionalized materials has become an emerging areas of research for regaining the properties of materials which can be utilized even after their mechanical or chemical damages. These behaviour of materials emphasizes on the reconstructing in terms of functionalities present inside the materials. The challenges of these materials come into play when they are required to fulfil the transparent based materials. For the optical appliances, these self-healable materials are keen to have a great interest for the future electronic devices.

Extensive literature is available on healable polymers based upon both DA and ionic mechanisms. For DA-based polymers, the key limitation lies in the high temperature requirement for healing due to the intrinsic kinetics of a DA reaction. While modifications have been attempted, the healing temperature was lowered to only a minimum of 100 °C. The high temperature limits the applicability of such polymers. Furthermore, existing unreinforced DA-based polymer networks have are highly brittle, which greatly compromises durability. On the other hand, while ionic-based healing mechanisms do have some system-dependent limitations such as extensive healing time, successful attempts of healing at room temperature have been demonstrated. Hence, by incorporating ionic-based healing mechanisms into DA-based polymers, the novel self-healing composite in this project is proposed to experience a synergistic effect. The co-workings of the DA reaction and ionic interactions would serve to address the healing limitations. Whereas, the mechanical limitations of existing DA-based polymer networks would be addressed by the plasticising effect contributed by the EMITFS ionic liquid.

Next, the literature review on the dielectric properties of existing stretchable, flexible, transparent and self-healable polymers provides a platform for comparison against the dielectric behaviour of the self-healing composite proposed in this project. The main issues of existing stretchable, flexible, transparent and self-healable dielectrics lie in their limited dielectric properties and non-robust healing mechanisms. Issues regarding low transparencies are also present in some existing self-healable materials, limiting applicability in optoelectronics. In comparison, owing to the highly polarisable imidazolium-based ionic liquid (EMITFS) component [122], the self-healing composite proposed in this project would have highly favourable dielectric properties. Its healing mechanism may also be sufficiently robust due to the ionic-DA co-working effect as explained previously. The self-healing composite proposed in this project also has good transparency, and is thus applicable to a wide range of optical devices.

While optoelectronic properties are highly pursued in existing studies, they often come at the compromise of flexibility. The inclusion of impurities to enhance optoelectronic properties may cause additional plasticising effect as shown in some of the aforementioned studies. While some researchers have been successful in developing highly flexible devices with decent optoelectronic performance, any form of plastic micro-fracture within the device is completely non-recoverable. This is where this project is relevant. The introduction of self-healing functionality would address the durability limits of ACEL devices, which is just an example to demonstrate the utility of these material systems. While other non-conventional functionalities like actuation properties have been proposed, they do not address the issue of durability of ACEL devices. On top self-healability, the ACEL device fabricated in this project is also concurrently flexible with moderate optoelectronic performance. While an existing study points to the possibility of the “self-healable” ACEL device, it is not entirely effective as only a segregated fraction of the device is truly self-healable.

2.7 PhD in the context of literature

Identifying the importance of self-healing polymers which are necessary for flexible electronic devices from the above literature. This dissertation focusses on the fabrication of self-healing devices and the importance of healing mechanism via ionic liquids.

First, the self-healable polymer via DA mechanism was utilised for the fabrication of self-healable electrode. The electrode was silver nanowires which shows the healability with the polymer matrix. The conductivity of the electrode with respect to transparency was similar as compared with the recent literatures reports. Here, the healing mechanism was triggered by heating the electrode at 120 °C for 10 min. A novel method of healing via electrical power was also demonstrated. Later on, this healable electrode was utilised for the fabrication of healable transparent heater. This study reports the first transparent healable and flexible heater having robust electrode based on AgNWs.

Secondly, the incorporation of ionic liquid was investigated to improve the healing temperature and mechanical properties of the polymers. The ionic liquid acts as a plasticizers which tends to improve the entanglement of the polymer chain and hence lowers the glass transition temperature of polymer composite film which in turn make the film soft. Here, it was observed that upon the incorporating of ILs helps to reduce the healing temperature to 60 °C from 120 °C as reported in the previous report. A novel healing mechanism was demonstrated via incorporating ionic liquid in the polymer matrix. Later on, the polymeric composite (PU-DA-IL/AgNWs) was utilised to demonstrated a self-healable alternating current electroluminescent devices (ACEL), which was first reported in this section.

Finally, ionic liquid based healing mechanism was investigated on different polymer matrix to understand clearly the effect of ionic liquids on healing. This novel method of healing in PVP was not clearly been studied by the researchers before. In this section, even the roles of cation and anions involved in the formation of ionic liquid was also investigated regarding the healing process of the polymeric composite. Here, the same IL (as used in the previous study) was utilised to understand the compatibility with PVP, PVA, PVDF-HPF and PMMA polymer matrix and further characterisation was done to prove the ionic liquid based healing concept.

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Chapter 3*

Experimental Methodology

This chapter covers the rationale behind the selection of materials and device configurations adopted for this study. The fabrication processes and characterization techniques employed to investigate the healing, physical, mechanical and electrical properties of these materials and devices are also covered. The demonstration of the device fabrication on self-healing materials is described in details. The basic principles of the techniques employed are described with analytical details of the data obtained from these equipment. The details of materials characterization techniques (FTIR, NMR, XRD, TGA and DSC), surface morphology characterization techniques (FESEM and AFM), electrical characterization techniques (dielectric spectrometer and Ocean optics QE pro spectrometer), mechanical characterizations techniques (MTS, C42/C43) and optical characterization techniques (UV-Vis spectrometer and polarizing microscope Olympus) are utilized to characterize the synthesized materials and the performances of the devices are well described in this chapter.

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3.1 Rationale for selection of materials and device fabrication:

Transparent and flexible electronic devices are now also materialized [1-3], which have potential applications in health monitoring, artificial skins and implantable bioelectronics. This could allow the recent phase of electronics to be smoothly integrated into our everyday life [1-8]. These flexible devices have been fabricated through various synthesis process of different materials and design approaches. However, the approaches are not resistant to unexpected mechanical damage caused by repeated wear and tear and accidental cutting or scratching, which are the limitations of device failure [6, 9]. As a result, researchers have looked to construct flexible electronic devices that can self-heal, minimize the electrical waste and thus, can repair the accidental internal or external damages with the regain of critical functionalities of the electronic devices, as like human skin [1].

In spite of the flexible materials, the flexible electrode is as crucial as it is. The critical properties expected from the transparent electrodes are to have high transparency, to show high electrical conductivity and be mechanically robust, stretchable, and flexible. Among the best and most efficient transparent electrode is the indium tin oxide (ITO). However, ITO fails to meet the property of flexibility, and relatively high fabrication costs have provoked the researchers to find alternative materials. In this background, nanostructured transparent electrodes, including CNT, PEDOT: PSS, Graphene and especially metallic nanowires have been studied thoroughly and have attracted the attention of the scientist in past years because of their promising properties and applications [10-16]. Among the various metal nanowires, silver nanowires (AgNWs) have received vast concentration by many researchers nowadays. Since AgNWs have excellent electrical conductivity and high optical transparency, they were intensively utilized as transparent electrodes and are now considered as robust electrode to replace indium tin oxide. Moreover, AgNWs is a noble metal, and it shows good mechanical strength [17] as well as high chemical stability in ambient conditions and high thermal conductivity for flexible and stretchable applications. Additionally, the high transparency of AgNWs provided an aesthetic appearance that was able to avoid the uncanny valley effect.

With the method employed in this report to prepare transparent, healable, and flexible polymer via Diels-Alder reaction, it is seen that the PU based polymer has repeated

healing at a specific location after the cut. This kind of reaction is a reversible system. These reversible systems include covalently bonded system (like Diels-Alder reaction). Advantages of the reversible system include the repeated healing at a particular location even after repeated damages and the single-component material systems, rather than the composite, which further reduces the system complexity.

Also, an appropriate choice of ionic liquid-like EMITFS, as plasticizers, having favorable compatibility with the polymer matrix, results in a homogeneous polymer composite with desirable healing and mechanical properties, resulting in enhanced polymeric composite electrodes for flexible electronic devices. Hence, a detailed study was done on the PU-DA based self-healing polymer with EMITFS. The increase in ionic liquid concentration helps to increase in chain mobility of the polymer, which leads to a decrease in glass transition temperature of that polymer composite. This change in glass transition temperature makes the polymeric composite soft and hence, increases the healing, electrical as well as mechanical properties of the composite. The ionic liquid (EMITFS) has better compatibility with PU-DA based healable polymers and has been utilized for the fabrication of polymeric composite based on ILs. Later this ionic liquid was incorporated in a different polymer matrix (like PVP, PVA, PVDF-HFP, and PMMA) to understand the healing mechanisms without the DA recovery mechanism.

3.2 Synthesis procedure and device fabrication:

3.2.1 Synthesis of silver nanowires as a transparent electrode

Materials: All chemicals used during the synthesis of silver nanowires include silver nitrate (AgNO_3), polyvinylpyrrolidone (PVP), ethylene glycol (EG) and copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) were purchased from Sigma-Aldrich, Singapore.

Fabrication of transparent electrodes over a different substrate: Silver nanowires were produced by the reduction of AgNO_3 in the presence of CuCl_2 in an ethylene glycol (EG) solution containing polyvinylpyrrolidone (PVP). In a typical synthesis [18], 10 mL of EG was added in a round bottom flask (RB) to which a stir bar was added; then the RB was suspended in an oil bath and heated for 1 hr at temperature 156°C under magnetic stirring (260 rpm). After 1 hr, 80 μL of 4 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ /EG

solution was added, and the solution was allowed to heat for an additional 15 min. 3 mL of 147 mM PVP/EG solution was added, followed by 3 mL of 94 mM AgNO_3 /EG solution to the heated EG. After the entire addition of the reagents, the solution mixture was heated for an additional 60 min. After 60 min, color of the solution mixture changes from clear and colorless to opaque gray with wispieness indicating the formation of long nanowires. The simultaneous and dropwise addition of PVP and AgNO_3 solutions was crucial to the formation of a silver product with wire-like morphologies. After the reaction, the solution is kept in a bottle to settle down the grey residue containing nanowires for 2 days. The residue containing nanowire is then washed with acetone to remove the organics. The obtained silver nanowire (AgNWs) is stored in ethanol for further characterization. The average diameter of the nanowires was 200 to 300 nm while the lengths were close 6 to 18 μm . Transparent electrodes using above AgNWs were formed by spraying over different substrate like glass, polymer (PET, PDMS), which shows good transparency, as shown in Figure 3.1.

Figure 3.1 Fabrication of transparent electrode using silver nanowires (AgNWs). **a)** Optical image of the silver nanowires solution after the complete reaction. **b)** Spray coated silver nanowires on the different substrate (glass, PET, PDMS).

3.2.2 Polyurethane based DA mechanism for healable electrodes [19]

Materials: All chemicals used in this study included poly(1,4-butylene adipate) commonly known as polyester diol or polyol (average molecular weight, $M_w \sim 12,000$ by GPC), Isophorone diisocyanate (IPDI), Furfurylamine, Dibutyltin dilaurate (DBDL), 1,1'-(methylenedi-4,1-phenylene)-bismaleimide (BMI), (3-Aminopropyl)triethoxysilane (APTES) and silver nanowire (AgNW) of diameter 115 nm and length 20-50 μm dispersed in Isopropyl alcohol (0.5% by weight) were

purchased from Sigma-Aldrich, Singapore. Methyl ethyl ketone (MEK) and glycerol 1, 2-carbonate were purchased from Tokyo Chemical Industry, Japan. All the chemicals were used as received without any purifications.

Experimental procedure

Synthesis of diol 1: Diol 1 was prepared by reacting glycerol 1, 2-carbonate and furfurylamine. A round bottom (RB) flask was charged with glycerol 1, 2-carbonate (4.28 mL, 50.8 mmol) and furfurylamine (4.46 mL, 50.8 mmol). This reaction mixture was heated at 60 °C for 3 h. The reaction mixture was maintained at 60 °C by continuous stirring at 260 rpm in an oil bath. The final product (diol 1) was used in the next step without any purification.

Synthesis of furyl modified polyurethane (PU-F): To prepare furyl modified polyurethane, polyester diol (5.1 g, 5.1 mM) was first dissolved in methyl ethyl ketone (10.5 mL) in a RB. In that solution, the prepared diol 1 (1.1 g, 5.1 mM) in the above step was added followed by IPDI (2.14 mL, 10.2 mM) and dibutyltin dilaurate (4.7 μ L, 0.008 mM) were then added to the flask simultaneously. The reaction mixture was kept in an oil bath for homogenous heating at the temperature of 60 °C for 2 h. After the completion, the reaction mixture was used further without any purification.

Synthesis of polyurethane with Diels-Alder adduct (PU-A): In order to prepare polyurethane with DA network, the mixture PU-F in MEK (10 g) and BMI (0.54 g) was mixed in an RB at 260 rpm and heated at a temperature of 60 °C for 6 h. The BMI gets completely mixed with the mixture of PU-F in MEK during the time of reaction provided. The final mixture (PU-A) was faint yellow in color. This final reaction mixture was named as ‘Healable polymer’. The resulting solution was kept for further steps, without purification.

Surface modification of healable polymer with (3-Aminopropyl)triethoxysilane (APTES): In order to modify the surface of healable polymer with APTES, glass slides of dimension 2.5 * 2.5 cm² was first cleaned using decon soap solution, de-ionized water, acetone, and ethanol. Then, the prepared polyurethane with DA adduct (healable polymer) was spin-coated on the cleaned glass slide and kept in an oven for 50 °C for 8-10 h to yield the characteristics of healing of polyurethane with DA adduct. After

that, the dried healable polymer was dipped in 15 mM concentration of APTES solution (35.1 μL in 10 mL DI water) for 24 h. After 24 h, the substrate with healable polymer was dried and kept for the fabrication of a transparent electrode.

Fabrication of flexible and healable transparent electrode: The steps used for the fabrication of flexible and healable transparent electrode based on silver nanowires (AgNWs) are schematically shown in Figure 3.2. The surface-modified healable polymer was then spray-coated with AgNWs to form a transparent conducting electrode with sufficient amount of transparency and conductivity. The average diameter and length of silver nanowire used was 115 nm and 20-50 μm . Before spraying, AgNWs dispersed in Isopropyl Alcohol from Sigma Aldrich were further diluted in IPA (1:4 v/v) and sonicated in a bath sonicator for 15 minutes before spraying to prevent aggregation of AgNWs. Spray deposition of AgNWs on APTES treated healable films has been performed by an automated spray pyrolysis machine (HOLMARC Model HO-TH-04) with dry nitrogen gas as a carrier (dry nitrogen flow of 15psi, substrate distance of 11cm from the spraying nozzle and hot plate temperature containing substrate set to 60 $^{\circ}\text{C}$) until the desired sheet resistance and transparency was achieved. After spray coating of AgNWs, the AgNWs electrode over the healable polymer was then annealed at 100 $^{\circ}\text{C}$ for 5-10 min to remove other organic solvents and impurities. Finally, a healable transparent electrode with silver nanowires was allowed to cool down to room temperature and was used for further characterization. In order to heal the scratched healable transparent electrode, normal heating over hotplate at 120 $^{\circ}\text{C}$ was employed for 8-10 min.

Figure 3.2[19] **a)** The diagrammatic illustration for the fabrication of healable polymer (PU-DA) films with AgNWs to form a transparent conductive electrode. **b)** Device architecture of

healable transparent heater. **c)** Optical image of the healable and transparent heater. © Reproduced from “Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997” with permission from The Royal Society of Chemistry.

3.2.3 Polyurethane based ionic liquid composite for low-temperature self-healable electrodes [20]

Materials: All chemicals used in this study included poly (1,4-butylene adipate) commonly known as polyester diol or polyol (average molecular weight, $M_w \sim 12,000$ by GPC), Isophorone diisocyanate (IPDI), Furfurylamine, Dibutyltin dilaurate (DBDL), 1,1'-(methylenedi-4,1-phenylene)-bismaleimide (BMI), (3-Aminopropyl)triethoxysilane (APTES), silver nanowire (AgNW) of diameter 115 nm and length 20-50 μm dispersed in Isopropyl alcohol (0.5% by weight) and 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITFS) were purchased from Sigma-Aldrich, Singapore. Methyl ethyl ketone (MEK) and glycerol 1, 2-carbonate were purchased from Tokyo Chemical Industry, Japan. All the chemicals were used as received without any purifications.

Experimental procedure

Synthesis of Diol: Glycerol 1,2 carbonate (4.28 ml) was first added to furfurylamine (4.46 ml) into a 50 ml round-bottom flask. The mixture was heated at 60 °C for 3 hours in an oil bath and stirred on a magnetic stirrer at 260 rpm throughout. The resulting product (Diol 1) was used in subsequent steps without purification.

Synthesis of PU-F-EMITFS: Six different compositions of EMITFS (0.50 g, 0.75 g, 1.00 g, 1.25 g, 1.50 g, 1.75 g) was added into methyl ethyl ketone (MEK) (1.5 ml) into a 10 ml container. The mixtures were stirred at 260 rpm on magnetic stirrer for 10 min. Poly(1,4-butylene adipate) (polyol) (3.0 g) was added into MEK (6.5 ml) in seven separate 50 ml beakers and stirred on a magnetic stirrer until the polyol dissolves completely. The mixed EMITFS-MEK solutions from the previous step was then added to six of these mixed polyol-MEK solutions respectively and stirred on a magnetic stirrer until homogeneity was obtained. One polyol-MEK solution was kept as the control and hence did not contain any EMITFS-MEK solution. The composition of

EMITFS was determined with respect to polyol (0.00wt%, 16.7wt%, 25.0wt%, 33.3wt%, 46.7wt%, 50.0wt%, 58.3wt %).

The resultant mixtures were transferred into 50 ml round-bottom flasks and Diol 1 (0.65 g), isophorone diisocyanate (IPDI) (1.29 ml) and dibutyltin dilaurate (DBDL) (4.0 μ l) were added to each mixture respectively. The mixtures were then heated at 60 °C for 2 hours in an oil bath and stirred at 260 rpm on a magnetic stirrer throughout. The resultant products, polyurethane with a furyl moiety (PU-F) infused with EMITFS (PU-F-EMITFS) and PU-F for the control sample, were used subsequently without purification.

Synthesis of PU-DA-EMITFS: PU-F-EMITFS (PU-F for control sample) (10.0 g) and 1,1'-(methylenedi-4,1-phenylene)-bismaleimide (BMI) (0.5 g) were then each added into separate round-bottom flasks. The mixtures were heated at 50 °C for 6 hours in an oil bath and stirred at 260 rpm on a magnetic stirrer throughout. As the reaction proceeded, BMI was dissolved as demonstrated by the intensifying of the “yellowish-brown” color. The final products obtained were PU-DA infused with varying compositions of EMITFS (PU-DA-EMITFS) and PU-DA for the control sample. The as synthesized PU-DA-EMITFS is the self-healing composite as referred to in this work. Glass slides of requisite dimensions were cut and cleaned in acetone for 10 min and then in ethanol for 10 min, followed by purging with nitrogen gas. All the mixtures were spin-coated at 1000 rpm for 20 s onto these cleaned glass slides. After which, the samples were placed in the oven at 45 °C overnight. The thin films were then peeled off from the glass slides for subsequent characterization tests.

Fabrication of the alternating current electroluminescent device (ACEL): The ACEL devices were fabricated using the (PU-DA/ EMITFS) composite film as the substrate, with the following device structure as shown in Figure 3.3: Glass/ (PU-DA/ EMITFS) film/ AgNWs/ ZnS:Cu embedded in PU-DA/ Ag paint. The bottom electrode on the substrate film was prepared by spraying silver nanowire. Before spraying, the as-received AgNWs from Sigma Aldrich were further diluted in IPA (1:4 v/v). Spray deposition of AgNWs on the films was performed by an automated spray pyrolysis machine (HOLMARC Model HO-TH-04) with dry nitrogen gas as the carrier. After spray coating of AgNWs, the AgNW electrode over the healable polymer was then annealed at 70 °C for 2-3 mins to remove excess IPA. The ZnS:Cu/ PU-DA composite

was made by mixing ZnS:Cu powder with PU-DA solution in a ratio of 1:2 (w/w) in the planetary mixer (ARE 310, THINKY). Before mixing the PU-DA with ZnS:Cu powder, the PU-DA was synthesized as reported in the literature.¹⁶ The ZnS:Cu/ PU-DA composite was spin-coated onto the bottom electrode at 1000 rpm for 15 s followed by 2000 rpm for 10 s and then dried in an oven at 45 °C overnight. Finally, Ag paint or aluminum tape was applied over the ZnS:Cu/ PU-DA composite as a top electrode.

Figure 3.3[20] **a)** Device architecture of ACEL device. **b)** ZnS:Cu-PU-DA mixture after mixing in planetary mixer. **c)** Samples spin coated ZnS:Cu-PU-DA over the PU-DA/EMITFS film. © Reproduced from “Tiwari, Naveen, Fanny Ho, and Nripan Mathews."A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434” with permission from The Royal Society of Chemistry.

3.2.4 Ionic liquid as a global additive to induce self-healing

Materials: All chemicals used in this study included polyvinylpyrrolidone (PVP) (average molecular weight, $M_w \sim 360,000$), polyvinyl alcohol (PVA) (average molecular weight, $M_w \sim 13,000$ -23,000), poly(methyl methacrylate) (PMMA) (average molecular weight, $M_w \sim 100,000$), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) (average molecular weight $M_w \sim 400,000$), methanol, chloroform, acetone, 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI), 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITFS) and 1-Ethyl-3-

methylimidazolium trifluoroborate (EMITFB) were purchased from Sigma-Aldrich, Singapore. All the chemicals were used as received without any purifications.

Experimental Procedure

Preparation of PVP/EMITFS film: 4 sets of 3 grams of PVP was dissolved in 20 mL of methanol and 5 mL of chloroform. After polymer dissolved completely, some designated amount of EMITFS on weight percentage (5%, 10%, and 20%) was introduced. The solution was stirred for 15 minutes and the degassed inside a vacuum chamber to remove dissolved gases. The solution was cast into a plastic petri dish and air-dried at room temperature for 72 hours. Later these films are utilized for further characterizations. For the preparation of PVP/EMITFSI and PVP/EMITFB, polymeric composite film the same procedure was employed just by changing the ionic liquids.

Preparation of PVDF-HFP/EMITFS film: 4 sets of 3 grams of PVDF-HFP was dissolved in 15 mL of acetone at 80 °C. After polymer dissolved completely, some designated amount of EMITFS on weight percentage (20%, 30%, 40%, and 50%) was introduced. The solution was stirred for 15 minutes at 80 °C. Then the solution was degassed inside a vacuum chamber to remove dissolved gases. The solution was cast into a plastic petri dish and air-dried at room temperature for 72 hours. Later these films are utilized for further characterizations.

Preparation of PVA/EMITFS film: 4 grams of PVA polymer was taken in an RB in which 40 mL of DI water was added and heated at 90 °C with continuous stirring until the polymer was completely dissolved in water. The PVA polymer was mixed with DI water with a ratio of 1:10. After the polymer was completely dissolved, the PVA solution was divided into 4 sections of 10 mL each in which designated amount of EMITFS on weight percentage (5%, 10%, and 20%) was introduced. The solution was stirred for 15 minutes and then degassed inside a vacuum chamber to remove dissolved gases. The solution was cast into a plastic petri dish and dried in an oven at 45 °C overnight. Later these films are utilized for further characterizations.

Preparation of PMMA/EMITFS film: 4 sets of 2 grams of PMMA was dissolved in 15 mL of chloroform. After the polymer was dissolved completely, a designated amount of EMITFS on weight percentage (5%, 10%, and 20%) was introduced. The solution

was stirred for 15 minutes and the degassed inside a vacuum chamber to remove dissolved gases. The solution was cast into a glass petri dish and air-dried at room temperature for 48 hours. Later these films are utilized for further characterizations.

3.3 Characterizations

3.3.1 Materials characterizations

3.3.1.1 Fourier transform infrared spectroscopy (FTIR)

To determine the nature of the interaction between the ionic liquid and polymer matrix and within the polymer, Fourier transforms infrared (FTIR) spectroscopy was performed using FTIR spectrum GX, PerkinElmer.

Working Principle [21]: FTIR analysis is based on molecular bond vibration at frequencies particular to the type of components and bonds in the sample. Most molecules absorb light in the infrared (IR) region of the electromagnetic spectrum, typically measured as wavenumbers over the range from 4000 cm^{-1} to 400 cm^{-1} . A comparison of the emission spectrum of the IR source collected with an existing sample against a background spectrum results in a distinctive absorption spectrum of the chemical bonds and functional groups current in the sample. Due to the existence of a wide variety of functional groups and side chains, all of which portray distinctive vibrational frequencies in the infrared spectrum, this method is particularly helpful for identifying molecular groups and compounds.

3.3.1.2 Nuclear magnetic resonance (NMR)

In order to determine the chemical structures of the organic compounds or molecules quantitatively, a nuclear magnetic resonance instrument is widely used. For this study, NMR analysis was carried out on a Bruker Avance 400 (AV 400). This instrument has UltraShield 400MHz magnet with QNP probe (5mm) for proton (^1H) and carbon (^{13}C) NMR. Here, both solid-state NMR and liquid-state NMR were used. In Solid-state NMR, the solid-state ^1H and ^{13}C NMR spectra were collected on a 600MHz Bruker Avance III spectrometer using a 1.9 mm MAS probe and a MAS rate of 12 kHz.

Working principle of NMR [22]: Nuclear magnetic resonance (NMR) analysis relies on the spinning of the atomic nuclei. The magnetic measurement is based upon the spin of an unpaired electron, whereas the magnetic effect of nuclear magnetic resonance is

due to the spin of protons and neutrons present in the atomic nuclei. Both these nucleons have intrinsic angular momentum or spins, because of this nature, they act as an elementary magnet. The existence of nuclear magnetism was revealed in the hyper fine structure of spectral lines. We can observe the phenomenon of space quantization if the nucleus with a specific magnetic moment is placed in the magnetic field, and for each allowed direction there will be an energy transfer from the lower energy level to higher energy level. Now, this energy transfer depends upon the wavelength that resembles the radio frequencies. When these spins return to the lower energy level, they emit energy at the same frequency. Therefore, the signals that match this kind of transfer is quantized in various ways to produce the NMR spectrum of the encountered nucleus.

3.3.1.3 X-ray diffraction (XRD)

(XRD)-Bruker D8 Advance was used to probe the crystal structure of the semi-crystalline PVDF-HFP/EMITFS films.

Working Principle [23]: XRD is a fast analytical technique used mainly to identify a crystalline material in phases. The assessment is based on constructive interference with monochromatic X-rays and a crystalline sample when circumstances meet the law of Bragg's ($n\lambda = 2d \sin \theta$). The lattice parameters are calculated on the basis of the relationship between the electromagnetic radiation wavelength (λ) and the diffraction angle (θ). A characteristic x-ray diffraction pattern is produced when scanned over a range of locations, giving a distinctive "fingerprint" of the sample's crystallinity.

3.3.1.4 Differential scanning calorimetry (DSC)

The glass transition and the thermal phase in polymers and composites were investigated using differential scanning calorimetry (DSC TA Instruments Q10) at a ramping rate of 10 °C /min. The samples were placed in aluminum pans, and the measurements were carried out from the temperature range from -90 °C to 400 °C.

Working Principle [24]: Differential Scanning Calorimetry is a method in which the difference in heat needed to raise the temperature of a sample is controlled with regard to temperature. The sample holder temperature is usually improved linearly with temperature, and the sample and reference are retained at almost the same temperature. Physical transformations such as sample phase transitions change the heat flow needed to restore the same temperature, depending on whether the method is exothermic or endothermic. Endothermic procedures such as melting, increases the demand for heat

flow, while exothermic phase transitions such as crystallization reduce the demand for heat flow. The variations in heat flux corresponding to the quantity of heat absorbed or released during such transitions, allowing for an easy but accurate inquiry of all phase transitions involving changes in energy or heat capacity.

3.3.1.5 Thermogravimetric analysis (TGA)

The degradation (working) temperature of the polymers and composites were measured by thermogravimetric analysis (TGA TA Instruments Q500). The samples were placed in the platinum pan, and the measurements were carried out from room temperature (25 °C) to 600 °C. These equipment's, DSC and TGA, are the backbone in terms of characterization for polymers and composites.

Working Principle [24]: Thermogravimetric analysis is a technique in which a substance's mass is monitored with a controlled heating rate and temperature / time function in a controlled atmosphere. The equipment comprises a sample pan with a precise equilibrium that resides in a furnace. During the experiment, the sample is heated or cooled, and the mass is continuously monitored. The environment is controlled by a purge gas. Mass modifications in the differential thermogravimetric (DTG) curve produce strides in the TGA curve or peaks. Some of the impacts generally studied include evaporation of volatile constituents such as water, solvents, plasticizers, and fillers; organic substance oxidative and thermal decomposition, decarboxylation, and condensation reactions.

3.3.2 Surface morphology characterization

3.3.2.1 Scanning Electron Microscopy (SEM):

Scanning Electron Microscopy (SEM) [25] is a microscope that uses an electron beam to form an image. The electrons interact with atoms of the sample, producing signals that are processed to get information about the surface topography of the sample, composition, and electrical conductivity. In SEM, the scanning of the sample is carried out in a special kind of scan pattern known as a rectangular pattern of the image, which captures and reconstruct the image in the LCD screen. The scanning electron microscopy has several benefits over traditional optical microscopes, such as a considerable depth of field. The SEM provides the wide range of higher resolution, in which the closely spaced sample is magnified at much higher levels. The degree of

magnification in SEM is well controlled since SEM utilizes the electromagnets instead of lenses as in the case of optical microscopy.

The requirement for imaging the sample under SEM is that the sample should be electrically conducting at least at the surface level, and electrically grounded to prohibit the accumulation of electrostatic charges at the surfaces of the sample. The moisture from the samples must be removed while imaging under SEM since SEM utilizes the vacuum condition in the presence of electrons to form an image. The presence of moisture in the sample would vaporize in the vacuum condition and might affect the imaging process. All metals are conductive and can be imaged without any preparation or coating. However, all non-metals and biological samples need to be made conductive by sputter coating of conductive materials such as platinum. In this study, SEM imaging was carried out on a JEOL, JSM-7600F instrument.

3.3.2.2 Atomic Force Microscopy:

Atomic force microscopy (AFM) was established to overwhelm the drawbacks of the scanning tunneling microscope (STM) [26]. While STM can only be applicable to generate the images of the conducting or semiconducting area of the samples, whereas AFM can be utilized for all sorts of surfaces which includes polymers, ceramics, composites as well as biological samples. AFM can measure force, image the surface, and manipulate a surface. AFM was used for topographical imaging of the substrates and analyzing the surface roughness at high resolution. For topographical imaging, a tip is firmly fixed on the cantilever, and then the cantilever is allowed to move around the sample, during this process, the tip attached to the cantilever scans the surfaces of the sample either in contact mode or in non-contact mode. While scanning the sample, the movement of the tip occurred, which is due to the forces generated between the tip and the surfaces of the sample. Therefore, this force causes the bending of the cantilever during the scanning of the sample. A laser beam is focused on the cantilever tip. The focused laser beam reflects from the cantilever and is detected with a four-sectional position-sensitive detector. Here, AFM Asylum Research Cypher S, atomic force microscopy was used to study the morphology and roughness of the samples.

3.3.3 Electrical characterization

In order to examine the electrical properties of the samples, dielectric spectroscopy was performed on fresh samples, and the dielectric constants were obtained. The

spectroscopy was performed on a dielectric spectrometer (Novocontrol Technologies, Alpha-A High-Performance Frequency Analyser). The amplitude of the alternating electric signal was set to 1 V. The EL intensity of the ACEL device was measured using an Ocean Optics QE Pro spectrometer which was connected to a DC-to-AC inverter (DC3V-to-AC, 110V, 1 kHz) purchased from Shanghai KPT Company. The conductivities of the samples were measured by two probes and four-probe resistivity measurement system.

3.3.4 Mechanical characterization

In order to determine the mechanical properties of the samples, uniaxial mechanical tests were performed on a mechanical tensile testbed (MTS, C42/C43), at a cross-head speed of 5 mm/min and 10 mm/min. The uniaxial tests for mechanical characterization of samples were performed on samples of 15 mm width and 26 mm nominal gauge length, in line with the aspect ratio of specimens mentioned under ASTM standards D638 and D3039/D3039M. The thickness of the samples was chosen to be 20 μm , representative of their dimensions to be used in practical scenarios and real-life devices [23]. In order to understand the effect of damage and healing on the mechanical properties of PU-DA with 50%wt EMITFS, samples of 15 mm width and 26 mm gauge length were made. The thickness of the samples was 200 μm [23]. The samples of PVP/EMITFS, PVA/EMITFS, PMMA/EMITFS, PVP/EMITFSI, PVP/EMITFB, and PVDF-HFP/EMITFS, with a desired thickness, were also tested before and after healing.

3.3.5 Optical characterization

In order to determine the transparency of the samples, UV-Vis spectrophotometer (Shimadzu; UV-3600) was used. The samples were placed in the integrating sphere, and measurements were carried out from 400 nm to 700 nm wavelength (visible range). Polarizing Microscope Olympus was utilized to determine the healing behavior of the samples. In this, the samples were cut and healed at respective temperature. Therefore they are monitored under a polarizing microscope to differentiate before and after healing samples.

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Chapter 4*

Polyurethane based DA mechanism for healable electrodes

Challenges associated with mechanical failure of electrical conductors hindered the realization of truly flexible high performance electronics. Here, transparent healable electrodes have been developed and examined to alleviate these problems. The composite electrode features a layer of interconnecting AgNWs network on a polyurethane film modified with Diels–Alder adducts (PU-DA). Surface modification using hydrophilic molecules improved adhesion of the AgNWs network and resulted in mechanically robust flexible electrodes with a figure of merit sheet resistance of $13.3 \Omega/\square$ and 77% transmittance at 550 nm. After deliberate damage, the electrodes healed and recovered its original conductivity via a simple heat treatment at 120 °C for 10 min. Uniquely, the healing process can also be triggered by utilizing electrical power. Transparent and flexible healable heaters (TFHH) with good mechanical and thermal stability were fabricated using these electrodes for potential applications in thermochromics, electrically driven displays and defrosters.

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4.1 Introduction

Transparent and flexible electrodes are critical in a wide range of optoelectronic, electronic and energy devices, e.g., smart glass, organic light-emitting diodes, photovoltaics, displays or touch screens [1-11]. These applications not only require good electrical conductivity but demand better mechanical properties like stretchability, flexibility and robustness where the conventional indium tin oxide (ITO) fails to perform [12, 13]. Additionally, the processing of ITO requires costly vacuum-deposition techniques and high raw material cost. Therefore, alternative materials and approaches for indium-free transparent flexible electrodes are needed [1, 14-17].

Metal nanowires based electrodes, are of particular interest owing to their excellent conductivity and optical transmittance in conjunction with superior mechanical properties. Among metal nanowires, Silver nanowires based electrodes have been the focus of recent research due to their high transmittance and high electrical conductivity [18, 19] for next generation flexible electronic, optoelectronic devices and wearable electronics such as E-skin for healthcare applications [1-4, 7-9, 20-23]. These AgNWs based flexible transparent electrodes (TEs) have several advantages over other conducting films [24] such as large scale facile fabrication through solution processing. Although AgNWs have been deposited on technologically relevant substrates to form hybrid flexible electrodes, poor adhesion between AgNWs and the substrate remains a challenge [18, 25, 26]. Additional challenges for flexible electrodes include innate problems like mechanical rupture, scratching and bending torsion induced failures due to their “soft” nature compared to their rigid counterparts. Hence, self-healing capability of the electrodes is highly desirable for flexible electronic devices.

The past few years have offered a few classes of reactions that offer self-healing materials via different chemistry of healing process [27-32]. Several research groups have reported various self-healable conductors and devices [33-38], but the conductivity and transparency were not comparable with the PU based on DA and retro-DA reactions. Under the class of covalent bonding, Diels-Alder reaction have attracted much attention as cross-linker in polymers because of its reversibility [39, 40]. Incorporating such DA adducts [41, 42] into a highly transparent and flexible polymer such as polyurethane (PU) [43] and integrating with a conductive layer would create a highly transparent healable electrode. Such a composite electrode would also have to

be carefully engineered for mechanical robustness in order to be relevant for flexible integrable electronics.

Herein, we report a method to synthesize a self-healable PU based on DA healing mechanism and fabricate a transparent electrode by the combination of highly conducting AgNWs with mechanically strong, self-healing and transparent PU-DA polymer. The healable and transparent polymer was treated with (3-Aminopropyl)triethoxysilane APTES solution, which forms an amine rich surface, improving the adhesion between AgNWs and the healable polymer. The transparent and healable electrode has a highly conductive surface with a sheet resistance of $13.3 \Omega/\square$ and 77% transmittance at 550 nm, and showed excellent bending tolerance with negligible change in conductivity of the electrode. The transparent and healable electrode is capable of both structural and electrical healing via heating. A cut was healed quickly and efficiently as the DA polymer matrix re-bonds to bring together the nanowire network, which reforges to restore the percolation network. Furthermore, this transparent and healable electrode was repeatedly cut and healed at the same location multiple times without significant loss of surface conductivity. The healing procedures can also be triggered by passing an electrical current through the electrode. The utility of the electrode was demonstrated in the form of a heater that was integrated onto transparent surfaces. To the best of our knowledge, this is the first time a transparent, flexible and healable heater has been successfully demonstrated.

4.2 Results and discussions

Figure 4.1a shows synthesis of diol 1 (scheme 1), PU-F (scheme 2) and PU-DA (scheme 3). In order to synthesize a healable polymer (PU-DA), there are three steps involved. First, glycerol carbonate was reacted with furfurylamine at 60 °C to form Diol 1 which is shown in the Figure 4.1a (scheme 1). Then, the diol 1 as synthesized in scheme 1 was further reacted with polyol and isophorone diisocyanate to produce polyurethane (PU-F) in which the polyester polyol molecule present in PU-F behave as a soft part in the polymer matrix (scheme 2). Due to the softness and lack of crosslinking, PU-F gets dissolved easily in organic solvents like ethyl acetone and acetone. In order to improve the physical properties of PU-F, it was further reacted with BMI to produce polyurethane with Diels Alder adduct (PU-DA) as shown in Figure 4.1a in scheme 3. The steps involved in the synthesis of PU-DA requires low temperature (50-60 °C),

which is one of the advantage of this synthesis. The grafting efficiency of the DA onto the PU backbone should be close to 100%, since the reaction process was one-pot synthesis and no by-product was obtained. Once, the polymer was synthesized, the viscous solution was spin coated over glass slide to form a film of PU-DA with desired thickness. Figure 4.1b depicts the fabrication of transparent flexible healable electrodes, the samples coated with PU-DA over glass slide were carried forward for the spray coating of silver nanowires, with varied sheet resistance and transparency.

Figure 4.1 a) The detailed chemical scheme for the synthesis of healable polymer (PU-DA). b) Schematic of the fabrication of transparent flexible and healable electrode. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Materials characterizations:

Fourier transform infrared (FTIR) spectra of the PU-F and PU-DA films are reported in Figure 4.2. FTIR spectra of PU-F film revealed the signature peak of urethane stretching at 1735cm^{-1} , which indicated complete conversion of amine to urethane (Figure 4.2a). The disappearance of isocyanate signature absorption band at 2260 cm^{-1} indicates the polymerization reaction was completed after 2 h of reaction (Figure 4.2a). After the addition of BMI, FTIR analysis revealed the same signature peak of urethane stretching at 1735 cm^{-1} , which indicates that urethane stretching was still present (Figure 4.2b), which states that BMI doesn't affect the chemical interaction of the polyurethane (PU-F).

Figure 4.2 a) FTIR spectra of polyurethane modified with furyl moiety (PU-F). b) FTIR spectra of PU-DA (Healable polymer). © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) of the polymer (Figure 4.3). From the DSC analysis, the T_g of the polymer (PU-DA) was $-25.3\text{ }^{\circ}\text{C}$. At $50\text{ }^{\circ}\text{C}$, the BMI was completely dissolved, when PU-F mixed with BMI suggesting that the DA reaction proceeded at $50\text{ }^{\circ}\text{C}$. The peak at around $50\text{ }^{\circ}\text{C}$ shows the phase change of the PU-DA.

Figure 4.3. DSC spectra of the healable polymer (PU-DA). © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Thermogravimetric analysis (TGA) was performed to determine the thermal stability of the polymer (Figure 4.4). During this analysis, the sample was heated from room temperature (25 °C) to 500 °C to determine the degradation temperature of the polymer (PU-DA). The TGA curve of the polymer was stable up to 220 °C, at which the weight loss of the polymer was 1%. So, the working temperature for this polymer was below 220 °C.

Figure 4.4. TGA spectra of the healable polymer (PU-DA). © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry

Contact angle measurement: The spin coated polymer (PU-DA) was dipped in APTES solution to improve its hydrophilicity and adhesion to AgNWs. Previously, similar treatments with APTES was used to increase the hydrophilicity of PDMS [44]. The hydrophilicity of the polymer was investigated by contact angle measurement. The variation in contact angle with different APTES concentration was shown in Figure 4.5 and 4.6. After trying different concentration of APTES (5mM, 15mM and 25mM) and time, the 15mM concentration of APTES solution proved to be better for the adhesion of silver nanowires on the PU-DA. The contact angle of the sample before APTES treatment was 84.75° and after treatment with 15mM APTES for 24 h was 50.95° as shown in Figure 4.7 a and b. The value of contact angle <90° indicates that the surface is hydrophilic. Increased hydrophilic nature of the polymer substrate surface resulted in better adhesion of AgNWs, thereby resulting in higher conductivity as shown in Figure 4.7 b. Due to the APTES treatment, the amount of silver nanowire consumption

during spray coating was less as compared with the sample without APTES treatment, which resulted in a higher transparency as lesser amount of AgNWs was now used to achieve a given conductivity.

Figure 4.5 Change in contact angle of the samples with 5mM and 15mM concentration of APTES solution at different time. The change in contact angle with 5mM APTES solution is not much effective and the contact angle for 15mM APTES solution after 24 h. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Figure 4.6 Change in contact angle of the samples with 25mM concentration of APTES solution at different time. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Figure 4.7 a) and b) represents the contact angle measurement of the sample before and after 15mM APTES treatment for 24 h. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

The most important observation was that the surface roughness remained constant (~4-5nm) before and after the APTES treatment as shown in Figure 4.8. The surface roughness was investigated by **atomic force microscopy (AFM)**. Figure 4.8 indicates that the APTES treatment does not affect the surface by modulating the roughness value, but increases the hydrophilicity of the polymer by possibly forming an amine

rich surface which has a better adhesion with AgNWs. After surface modification by APTES solution, the polymer was spray coated with AgNWs from IPA solution to form a transparent, flexible and conducting electrode. Increased hydrophilic nature of the polymer substrate surface resulted in better adhesion of AgNWs, thereby resulting in higher conductivity as shown in Figure 4.7b. Due to the APTES treatment, the amount of silver nanowire consumption during spray coating was less as compared with the sample without APTES treatment, which resulted in a higher transparency as lesser amount of AgNWs was now used to achieve a given conductivity.

Figure 4.8 AFM images in 2D and 3D with and without APTES treatment. The RMS value of unmodified and modified sample was 4.8 nm and 4.3 nm respectively. **(a) & (c)** were the images of the sample without APTES treatment and **(b) & (d)** were the images of the sample with 15mM APTES treatment. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Physical characterization of the electrode

Figure 4.9 (a, b and c) shows the optical image of the coated polymer with and without AgNWs on the glass substrate. This shows the uniform distribution and random orientation of the AgNWs over the entire area (6.25 cm^2) of spray coating. The images clearly depict the transparency and flexibility of the device

under use. The optical transparency of the polymer with and without AgNWs was measured by **UV-Vis spectroscopy**. Figure 4.9d depicts the optical transmittance (total) for AgNWs coated polymer with different sheet resistance. The total transmittance value for different electrodes are: 73% for 7 $\Omega/\square$; 77% for 13 $\Omega/\square$; 82% for 29 $\Omega/\square$ and 86% for 72 $\Omega/\square$ respectively. These total transmittance values are determined by taking the average from 400-700 nm (visible region). The optical transmittance of the sample depends upon the both polymer matrix as well as on the layers of silver nanowire. The haze factor of the PU-DA was less than 0.1% which reveals that the PU-DA is highly transparent and optically clear, but due to the spray coating of AgNWs on top of it, the transmittance of the electrode is decreased and its haziness is slightly increased. The haze factor was determined as the ratio of diffuse transmission to the total transmission. The haze value for 13 $\Omega/\square$ is $\sim 0.3\%$ (Figure 4.9e). The high flexibility of the transparent healable electrode was attributed to the flexibility of the polymer matrix and the conformity, adhesion of the silver nanowire network. The adhesion and bonding of AgNWs to the polymer matrix was evaluated by repeated cycles of peeling using Scotch 3M transparent tape. Figure 4.9f shows that the sheet resistance remains quite unchanged even after repeated adhesion and peeling of the sample. For the first few initial peel off cycles, the sheet resistance was not stable as compared to the subsequent cycles because of a few loosely bound AgNWs on different layers. But, after 20 cycles, the variation in sheet resistance was within 10%. The strong bonding between the polymer matrix and AgNWs is an essential requirement for self healing process to take place. In our case, strong bonding between the polymer matrix and AgNWs was because of the amine rich surface formed by APTES treatment which helps to adhere AgNWs more firmly with the polymer matrix, by increasing the hydrophilic nature of the polymer.

Figure 4.9 Optical photograph of the prepared polymer (a) & (c) and polymer with AgNWs (b) with $2.5 \times 2.5 \text{ cm}^2$ area. **d)** Transmittance spectra of polymer with and without AgNWs (1-PU-DA; 2-PU-DA+AgNWs ($R_s=72.15 \text{ ohm/sq}$); 3-PU-DA+AgNWs ($R_s=29.71 \text{ ohm/sq}$); 4-PU-DA+AgNWs ($R_s=13.3 \text{ ohm/sq}$); 5-PU-DA+AgNWs ($R_s=7.26 \text{ ohm/sq}$). **e)** Haze factor of the PU-DA polymer with and without silver nanowires. **f)** Sheet resistance change of the sample with the cycle/times of peeling and adhesion with scotch transparent tape. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

The flexibility of the transparent healable electrode with AgNWs was examined by repeated cycles of bending (Figure 4.10). A sample with an area of $5 \times 2.5 \text{ cm}^2$ and thickness of $\sim 20 \text{ }\mu\text{m}$ was bent over a cylinder with an outer diameter of 20 mm diameter as shown in Figure 4.10a. After 500 cycles of bending and unbending, sheet resistance of the sample reduced from $11.96 \text{ }\Omega/\square$ to $10.82 \text{ }\Omega/\square$.

A similar test was done with lower sheet resistance and lower diameter of cylinder to determine the similar trend in the sheet resistance change. A sample with an area of $3 \times 2.5 \text{ cm}^2$ and thickness of $\sim 20 \mu\text{m}$ was bent over a cylinder with an outer diameter of 6 mm as shown in Figure 4.10b. After 500 cycles of bending and unbending, sheet resistance of the sample reduced from $7 \Omega/\square$ to $6.3 \Omega/\square$. In both cases, the conductivity was increased by about 10%, due to improved interconnection between the layers of the nanowires.

Figure 4.10 Sheet resistance change of the sample with the number of bending and unbending cycle/times. The image inset in the bending-unbending graph shows the sample was wrapped around a 20 mm (a) and 6 mm (b) diameter cylinder. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Healing behavior of the electrode

The transparent electrodes created by spraying AgNWs on the PU-DA films were cut with a sharp knife to study the healing properties. A green LED was connected in series with the electrode and driven by a battery source. Cutting the electrode breaks contact completely resulting in the LED being extinguished. Heating the electrode at 120°C restored partial connectivity in 2 minutes and the intensity of the LED was restored completely in 10 minutes. The local properties of the transparent healable polymer was examined by **field-emission scanning electron microscopy (FESEM)** as shown in the Figure 4.11. FESEM images in Figure 4.11 depicts the crack in the sample before and after heating. Figure 4.11a shows the as prepared polymer with AgNWs without any cut. Then, the sample was cut deeply forming a gap of $10 \mu\text{m}$ as shown in Figure 4.11b.

Figure 4.11c and d shows healing property of the sample after heating at 120 °C for 5 min and 10 min respectively. From Figure 4.11d, it was clearly seen that the sample gets completely healed after 10 min. This was due to the reversible reaction of the Diels-Alder adduct and the flowability of the polyurethane backbone chain, which was initiated during the heating of sample at 120 °C for 10 min.

Figure 4.11 Field-emission (FESEM) scanning electron microscopy images of transparent flexible and healable electrode with silver nanowires (AgNWs). **a)** The healable electrode as received from synthesis. **b)** After cut with knife. **c)** Healing of electrode at 120 °C for 5 min. **d)** Healing of electrode at 120 °C for 10 min. The dotted box indicates the location of the previous cut. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

The surface roughness of transparent electrode (TE) was examined by **atomic force microscopy (AFM)**. The samples were examined before and after healing at 120 °C for 10 min. The surface roughness of the transparent electrode before and after healing was 100.49 nm and 53.98 nm respectively as shown in Figure 4.12. It shows that the roughness tends to decrease, when the samples were healed at 120 °C for 10 min. The silver nanowires tend to immersed inside the PU-DA because of the flowability of the polymer.

Figure 4.12 Surface roughness of the transparent electrode (TE) before and after healing. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

A novel healing procedure is enabled by the electrical conductivity of the electrode. Applying an electrical voltage across PU-DA/ AgNWs films which had been damaged, was sufficient for recovery in a short time period (~2 minutes, 12V) showing the self-healing nature of the electrode (Figure 4.13). The healing mechanism of this system involved was that the passing of voltage of around 12 V, which was around the healing temperature, heated up the polymer and the AgNWs and the flowability of the PU-DA helped the healable electrode to heal within 2 min.

Figure 4.13 Electrical power induced healing illustrated by optical images of the electrode (2 minutes apart). © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Above mentioned the characteristics of the healable and flexible transparent electrode (PU-DA/AgNWs) was utilized to fabricate a transparent flexible heater.

Utilization of PU-DA/AgNWs electrodes as transparent flexible healable heater

Samples with specific sheet resistance were heated by applying voltage across a sample area of 4.68 cm^2 (Figure 4.14). Parameters such as the thickness of the film, network density, area occupied by the material, percentage of conducting phase, charge percolation behavior are linked to the transmittance and resistance of a given transparent electrode (TE) on which the heater were based. The determinant parameter for a transparent heater is the sheet resistance of the transparent conducting electrode. Lower the value of sheet resistance of TE, better is the power efficiency of TFHH. For a given applied voltage, the heating rate and temperature attained depend on thermal properties of the heating element, the polymeric substrate and the interface. Figure 4.15 (a) shows the temperature with respect to time for applied voltages between 2 V to 6 V. The sheet resistance of the transparent healable film was $13.3 \text{ } \Omega/\square$. Figure 4.14 (b) shows the corresponding results for a healable heater with a sheet resistance of $60.12 \text{ } \Omega/\square$. Figure 4.14 (c) shows the corresponding behavior of the healable heater with a sheet resistance of $29.7 \text{ } \Omega/\square$. In the case of the $13.3 \text{ } \Omega/\square$ heater, the temperature increases from room temperature to $102.4 \text{ } ^\circ\text{C}$ for the maximum voltage of 6 V was tested (measured by a non-contact IR thermal camera). After 150 s the temperature remains constant with time for all the heaters with different sheet resistance, which indicates that thermal equilibrium has been established. The steady state temperature is achieved by controlled joule heating of the transparent conducting electrode which depends on sheet resistance of the TE. The heat generated is linked to the applied voltage and resistance through the Joule's law of heating: $H=V^2t/R$, where V stands for voltage applied, R stands for the resistance and t stands for the time. Comparing the performance of both the heaters (Figures 4.14 (a), (b) and (c)), it is clear that the saturation temperatures obtained for the low resistance heater is higher for the same applied voltage ($102.4 \text{ } ^\circ\text{C}$ at 6 V for $13.3 \text{ } \Omega/\square$ heater, $88.5 \text{ } ^\circ\text{C}$ at 6 V for $29.7 \text{ } \Omega/\square$ and $58.8 \text{ } ^\circ\text{C}$ at 6 V for $60.12 \text{ } \Omega/\square$ heater). This is in line with Joule's heating law. Figure 4.14 (d) also displays the cooling behavior of the heaters having a sheet resistance of $29.7 \text{ } \Omega/\square$. The heating and cooling rate of the heater over the desired time is same for the $29.7 \text{ } \Omega/\square$ heater, which defines the good behavior of heater.

Figure 4.14 Temperature–time curves under different input voltages for 300 s. **a)** Evolution of generated temperature of healable polymer-AgNWs film with specified sheet resistance of $13.3 \, \Omega/\square$ at different bias voltage. **b)** Time – dependent temperature profiles at different input voltage with specified sheet resistance of $60.1 \, \Omega/\square$ **c) and d)** Time – dependent temperature profiles at different input voltage with specified sheet resistance of $29.7 \, \Omega/\square$. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Heat dissipation involves conduction, convection and radiation. In the transparent heater, convection is the relevant path for heat dissipation and thus stabilization of the temperature. Other modes of dissipation like conduction may not be significant since the heater is not placed on a good thermal conductor (polymer on glass). The temperatures attained in our experiment are also not significantly high to make it relevant for radiative heat dissipation. Thus the steady state temperature in transparent healable heater is achieved by controlled Joule heating of the transparent conductor and the convection mode of heat dissipation. Steady state is also achieved due to the small temperature coefficient of resistance ($R = R_0 (1 + \alpha \Delta T)$: $\alpha = 0.001384 \, \text{K}^{-1}$) also indicating the AgNWs network remains stable at elevated temperatures (Figure 4.15

(a)). The sheet resistance of the electrodes were also measured when cooling down as shown Figure 4.15 (b). In both the measurement, the film heater was heated and cooled from RT to 120 °C and vice-versa and for every increase or decrease in temperature the film was kept for 2 min at that temperature for stabilization of the temperature. This in conjunction with Figure 4.15 (a) and (b) clearly depicts that the heating process is reversible. Figure 4.15 (c) shows the thermal camera images for various applied voltages depicting uniform heating over the rectangular area.

Figure 4.15 Sheet resistance change of a healable heater film with change in temperature. a) The film heater was heated from RT to 120 °C. b) The film heater was cooled from 120 °C to RT. c) Thermal camera images for various applied voltages depicting uniform heating over the rectangular area. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

Thermal resistance is a heat property and a measurement of a temperature difference by which an object or material resists a heat flow, which gives the best explanation of heater. The thermal resistance of the transparent heater with sheet resistance $13.3 \Omega/\square$ is shown in Figure 4.16 a. The thermal resistance can be extracted from the linear regression of the peak temperature vs power density data [45]. The extracted thermal resistance value of the transparent electrode with sheet resistance of $13.3 \Omega/\square$ is $100 \pm 5 \text{ } ^\circ\text{C cm}^2/\text{W}$ at 6 V. This thermal resistance value was obtained from 2 V to 6 V in steps of 1 V. This thermal resistance ($100 \pm 5 \text{ } ^\circ\text{C cm}^2/\text{W}$) is higher than the values reported for other heater based on silver nanowires [46] ($\sim 85 \text{ } ^\circ\text{C cm}^2/\text{W}$). The variation of sheet

resistance with voltage was depicted in Figure 4.16 b. From this study it was observed that the insensitivity of the sheet resistance to applied voltage (temperature) is better for low resistance electrodes.

Figure 4.16 **a)** Peak temperature versus power density for transparent electrode (Sheet resistance 13.3 $\Omega/\square$). **b)** Variation in sheet resistance at different voltage for different transparent healable heater based on AgNWs. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

A simple defogging test was performed to demonstrate the advantages of the transparent heater. The test was performed on a goggle which was kept in the freezer at -20 °C for 5 h (Figure 4.17). Recovery of transparency was observed within few minutes by applying a bias voltage of 6 V. PU-DA /AgNWs based transparent and healable heater with uniform thermal response could therefore be employed in the area of defogging windows and goggles, especially in the cold countries.

Figure 4.17 Optical image of the goggle after the transparent healable heater had been applied to one of the sides. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with permission from The Royal Society of Chemistry.

4.3 Conclusion

A transparent, flexible and healable thin film heater was successfully demonstrated with AgNWs and polyurethane (PU) polymer. Healing ability of PU was enabled by reversible reaction of Diels-alder adducts, which heals the damaged surface of the film. Molecular modification of the PU-DA surface enables strong bonding of AgNWs with polymer matrix. The electrodes thus formed were highly transparent and conductive ($13.3 \Omega/\square$ and 77% transmittance) and mechanically robust (as evidenced by bending and peeling tests). Cuts on the electrode layer can be healed under the application of mild heat or by passing electrical current through the electrode. The transparent healable electrodes were employed as heaters, and showed excellent thermal performance with temperature independent sheet resistances. The healable heater based on AgNWs achieved high temperatures up to 102 °C at a voltage of 6 V and was demonstrated in defogging applications. Such robust healable transparent conductors would enable future applications in a wide variety of integrable devices for flexible and wearable electronics. This healable electrode (AgNWs/PU-DA) proves to be the best as compared to other electrode systems (Table 4.1).

Table 4.1. Comparison with other healable transparent electrode. © Reproduced from Tiwari, Naveen, et al. "Healable and flexible transparent heaters." *Nanoscale* 9.39 (2017): 14990-14997 with the permission from The Royal Society of Chemistry.

Material	substrate	T _{total} (%)	R _{sheet} (ohm/ sq)	Area (cm ²)	Healing temp (°C)	References
AgNWs/PU-DA	glass	77	13	3.9*1 .4	120	Present work
Cu NWs/DA-PU	glass	66.5	22.3	1*2	120	X. Zhang et. al, Materials Research Bulletin, 2017, 90, 175-181
Au@PCLx/rGO/Ag	Al foil	--	11.5	1*2	532 nm laser~122 °C	L. Chen et. al, Journal of Materials Chemistry C, 2016, 4, 10018-10025
RFGO/PU	On different pattern	--	--	3*0.2	800 W microwave oven for 5 min then 2 h at 70 °C	J. Li, G. Zhang, R. Sun and C.-P. Wong, Journal of Materials Chemistry C, 2017, 5, 220-228.
PEDOT/AgNW/FM-DA	PET	78	15	0.7*1	100	J. Li et. al, ACS Applied Materials & Interfaces, 2015, 7, 14140-14149
AgNW/PDMS-CPU	glass	91.1	61.5	--	120	D. H. Lee et.al, ACS Applied Materials &

						Interfaces, 2016, 8, 8129-8136
AgNWs/MDP B-FGEEDR	glass	50	9.5	8*12	110	C. Gong et.al, Adv. Mat., 2013, 25, 4186-4191

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Chapter 5*

Polyurethane based ionic liquid composite for low temperature self-healable electrodes

The ability to undergo healing upon mechanical damage is a highly sought after property for the new generation of flexible, integrable devices. Thermally-reversible Diels-Alder (DA) mechanism for self-healing are promising but have only been demonstrated healing at high temperatures (~120 °C). However, theoretically DA mechanism can be triggered at temperatures as low as 50 °C, indicating that the self-healing mechanism is limited by the thermal mobility of the polymeric chains. Herein, the incorporation of ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITFS) alleviates this challenge, rapidly accelerating healing, while concomitantly improving the dielectric constant and the mechanical properties of a polyurethane derivative based on the DA chemistry for PU. For optimized compositions, the healing temperature reduced from 120 °C to 60 °C and the maximum strain to failure significantly increased from 17.1% to 102.1%. Owing to the ionic polarizability of EMITFS, the composite exhibited highly attractive dielectric properties with the dielectric constant enhanced from 2.7 to 12.9. Finally, we demonstrate a highly flexible, healable and fully solution-processed electroluminescent device.

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5.1 Introduction

Restoration of properties after environmental degradation has always been a huge challenge. An elegant solution would be to introduce self-healing functionality into such materials. By possessing the ability to restore themselves upon mechanical damage [1], these materials have opened up a plethora of opportunities in various applications [2, 3]. Traditional polymeric healing procedures utilize encapsulated healing agents/ monomers which are activated under fracture or stimuli [4]. However, this has the disadvantage of limited healing cycles.

A more elegant approach would be to ensure that the polymer itself has the ability to self-heal [5-9]. Such chemistries have led to the development of polymeric films which act as self-healable substrates for electronic applications [10-15]. Self-healability achieved via the formation of reversible chemically-identical bonds have gathered much popularity due to its simple, straightforward nature. In particular, the Diels-Alder mechanism is one such highly viable mechanism to achieve self-healing behavior. Its attractiveness lies in its thermal reversibility, which allows for repetitive healing [15-19].

While existing DA-based polymer networks are chemically robust in terms of healing, certain physical limitations remain unaddressed. These include the need for high healing temperatures (~ 120 °C) as well as limited mechanical properties in terms of flexibility [16, 20]. However, the trend of high healing temperatures and low flexibility remains an unaddressed hurdle amongst existing DA-based polymer networks for any potential applications in flexible and wearable/implantable technologies. Importantly, the DA mechanism can be triggered at temperatures as low as 50 °C, indicating that the self-healing mechanisms in these polymers is limited by the thermal mobility of the polymeric chains. To tackle these challenges, ionic liquids may play an important role. Ionic Liquids are highly polar compounds consisting of loosely bound bulky cations and anions. Ionic liquids have been termed “green solvents” due to their negligible vapor pressure and stability which has lent its applications in batteries [21], dye-sensitized solar cells [22], fuel cells [23] and drug delivery [24]. Interestingly, they have also been applied in tribological applications and have been utilized as plasticizers for PVC and PMMA polymers [25, 26]. Thus, it could be hypothesized that ionic liquid addition into a healable polymer would allow for more efficient healing to occur due to the suppression of the glass transition temperatures. Moreover the addition of the ionic liquid should not interfere with the reversible DA mechanism of the healable polymers.

Herein, we have incorporated 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITFS) ionic liquid into a polyurethane with DA adducts (PU-DA). The resultant composite is a PU-DA polymer network with EMITFS ionic liquid molecules dispersed between the polymer chains. The attractiveness of this self-healing composite lies in its chemistry and configuration. By incorporating EMITFS, a synergistic co-working effect contributed by both the ion-dipole interactions between EMITFS and PU-DA and the Diels-Alder mechanism could occur. Due to the consequent increase in flowability, a tremendously reduced healing temperature of 60°C was achieved. The enhanced mechanical properties allowed the composite to stretch to twice its original length and enables fabrication of flexible devices. The highly transparent composite also possesses a high dielectric constant. Finally, we demonstrate a fully functional, self-healable alternating current electroluminescent device by incorporating emissive (ZnS:Cu) phosphors into the Diels-Alder polymer fabricated onto a healable transparent electrode.

5.2 Results and discussion

As mentioned in chapter 4, the polyurethane Diels-Alder adduct (PU-DA) was utilized as the polymer network to fabricate a self-healable electrode based on silver nanowires. To employ this reaction for self-healing, the Diels-Alder adducts are incorporated within polymer networks, enabling repetitive, robust healing [15, 27]. However, limitations that remain inadequately addressed include high healing temperatures (~120 °C), as well as limited mechanical properties in terms of stretchability [20]. To address these physical limitations, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITFS) ionic liquid was incorporated into polyurethane with DA adducts (PU-DA) as shown in further materials characterization. Here, the ionic liquid was incorporated during the synthesis of furyl modified polyurethane before the addition of crosslinking agent. The ionic liquid did not create any by-product in the reaction mixture, and displayed good interaction with the polymer. The EMITFS ionic liquid has good thermal stability, high ionic strength and intrinsic self-healing ability. More importantly, the EMITFS molecules are able to form electrochemically and thermally stable ion-dipole interactions with the polar polymers [1]. Such interactions would allow for a better dispersion of these molecules within the polymer chains, inducing a plasticizing effect [28]. The EMITFS molecules increase the free volume between the PU-DA chains, allowing for greater chain mobility which would

be reflected as lower glass transition temperatures (T_g) [26]. The increased flowability would allow the polymer to have increased mechanical flexibility, as well as vastly reduced healing temperatures. An added benefit would be the resultant high transparency of the composite given that both its constituents are highly transparent and well miscible. Hence, the incorporation of ionic liquids does not affect the healing process; rather speeds up the healing mechanism which was proven by the characterization done as below.

Materials characterizations

Nuclear magnetic resonance (NMR) was used to determine the interaction between EMITFS (IL) and PU-DA. Both solid state and liquid state nuclear magnetic resonance (NMR) spectroscopy analysis were performed for the PU-DA/ 50 wt% EMITFS. In the ^{13}C solid state NMR spectra (Figure 5.1 (a)), the peaks at 137.2, 156.9, 174.2 ppm confirm the PU-Diel's Alder adduct (PU-DA). The presence of 15.9 ppm peak (*) in the ^{13}C NMR spectra and a peak at 8.8 ppm peak (d) in the ^1H solid state NMR spectrum (Figure 5.1 (b)) of PUDA-IL film confirm the presence of IL in PU-DA/IL film.

Figure 5.1 a) ^{13}C solid-state NMR spectra of PU-DA/ 50 wt% EMITFS. b) ^1H solid-state NMR spectra of PU-DA/ 50 wt% EMITFS © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

The liquid state NMR analysis was used to determine the molar ratio of ionic liquid to the DA adduct in PU as shown in Figure 5.2. The solvent used in this analysis was DMF (d_7). The molar ratio of ionic liquid to the DA adduct in PU is 1.88 as estimated from their ^1H liquid state NMR as shown in Figure 5.2a & b.

Figure 5.2 a) ¹H liquid-state NMR spectra of EMITFS (IL). **b)** ¹H liquid-state NMR spectra of PU-DA/ 50 wt% EMITFS © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." Journal of Materials Chemistry A 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Fourier transform infrared spectroscopy (FTIR) was performed for all the composition of PU-DA and EMITFS, as stated in experimental methodology (chapter 3, section 3.2.3). FTIR spectra of the PU-DA and different compositions of EMITFS films, was reported in Figure 5.3. Signatures of urethane stretching (1735 cm^{-1}) and N-H stretching in the EMITFS ionic liquid could be noted in the PUDA/IL mixture.

Figure 5.3 FTIR spectrum of PU-DA, 16.7 wt % EMITFS in PU-DA, 25 wt % EMITFS in PU-DA, 33.3 wt % EMITFS in PU-DA, 41.7 wt % EMITFS in PU-DA, 50 wt % EMITFS in PU-DA, 58.3 wt % EMITFS in PU-DA and EMITFS (IL). © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." Journal of Materials Chemistry A 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

To investigate in details of the chemical bonds present in the FTIR spectra after the addition of ionic liquid in polymer, PU-DA with 50 wt% EMITFS film was examined.

FTIR measurements of the system (Figure 5.4a and b) indicated no new signatures associated with spurious reactions between the components of the composite. 3500-2000 and 2000-1000 cm^{-1} were chosen for detailed analysis of the interaction between PU-DA and EMITFS (IL) film. The urethane stretching is observed to have generally shifted to lower wavenumbers (1745 cm^{-1} - 1694 cm^{-1} to 1749 cm^{-1} - 1629 cm^{-1}) suggesting interactions between the urethane region of PU-DA and EMITFS and the formation of an intimate composite [1].

Figure 5.4 FTIR spectrum of PU-DA/ 50 wt% EMITFS. FTIR spectrum of the film at range from a) 3500-2000 cm^{-1} and b) 2000-1000 cm^{-1} . © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Optical microscopy images of PU-DA and PU-DA with EMITFS (50 wt%), as shown in Figure 5.5, reconfirm that EMITFS (IL) is homogeneously mixed within the healable polymer (PU-DA).

Figure 5.5 The optical microscopy images of PU-DA and PU-DA/ 50 wt% EMITFS. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Thermogravimetric analysis (TGA) (Figure 5.6 a), showed that the polymer with EMITFS (50 wt%) and without EMITFS was stable up to 200°C, at which the weight loss of the polymer was 1%. The TGA curves for other different concentrations of EMITFS/PU-DA are shown in Figure 5.6 b. It is important to note that the thermal degradation of the PU-DA was not affected by the incorporation of ionic liquid (EMITFS). Generally, this is not usually the case where incorporating the plasticizers will not effect the degradation temperature. Here, it shows a positive effects that no by products are formed during the synthesis of PU-DA with EMITFS.

Figure 5.6 a) TGA curve of PU-DA and PU-DA/50 wt% EMITFS film. **b)** TGA curves of PU-DA, 16.7 wt % EMITFS in PU-DA, 25 wt % EMITFS in PU-DA, 33.3 wt % EMITFS in PU-DA, 41.7 wt % EMITFS in PU-DA, 50 wt % EMITFS in PU-DA and 58.3 wt % EMITFS in PU-DA. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Differential scanning calorimetry (DSC) analysis was performed to determine the glass transition temperatures (T_g) of the samples from the heat flow vs temperature graphs as depicted in Figure 5.7 and Figure 5.8. Upon the addition of 16.7 wt% EMITFS in PU-DA, there is a huge drop in T_g from -25.3 °C (Figure 5.7 a) to -53.4 °C as shown in the Figure 5.8. As the composition of EMITFS increases, the T_g decreases further to a remarkably low T_g of -117.1 °C in PU-DA containing 50.0% of EMITFS as depicted in Figure 5.7 b in line with our original hypothesis. The EMITFS ionic liquid molecules disperse into the regions between the PU-DA polymer chains and thus reduce chain entanglement, hence, making the polymer composite soft by reducing the T_g of that composite.

Figure 5.7 Effect of Ionic liquid (EMITFS) on healable polymer (PU-DA). DSC curves of **a)** PU-DA film and **b)** PU-DA/50 wt% EMITFS film. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Figure 5.8 DSC curves of 16.7 wt % EMITFS in PU-DA, 25 wt % EMITFS in PU-DA, 33.3 wt % EMITFS in PU-DA, 41.7 wt % EMITFS in PU-DA and 58.3 wt % EMITFS in PU-DA. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

To evaluate the performances of these polymeric composite films in electronic applications that demand flexibility, we conducted the mechanical testing of these film for flexible electronic devices.

Mechanical characterization (stress vs strain) was performed for all the composition of PU-DA and EMITFS, as stated in experimental methodology (chapter 3, section 3.2.4). A lower T_g in addition to being an indicator of higher flowability [29] also indicated a lower Young's modulus. Figure 5.9 shows the stress-strain curves for PU-DA and ionic liquid incorporated PU-DA measured upon uniaxial extension of samples at constant strain rate (or predetermined constant crosshead speed). The slope of the curve in the linear regime provides information about the Young's modulus. PU-DA shows linear behavior only till 4% strain whereas 50% EMITFS-containing PU-DA composites show linear behavior till 11% strain. While the maximum strain at break and Young's modulus remain hugely non-coherent till 25% concentration of EMITFS, it starts showing gradual softening and associated lowering of Young's modulus with increasing concentration of EMITFS (Figure 5.9). Young's modulus of the PU-DA containing the 50% EMITFS (43 MPa) was more than 10 times smaller than that of the pristine PU-DA (595 MPa) indicating superior flexibility and increased compatibility with deformable/wearable electronics. The ultimate strain, which is the maximum strain at break, was also extracted. With increase in the composition of EMITFS, the maximum strain at break of the samples increased significantly. While PU-DA had an unimpressive maximum strain of 17.1%, the samples start showing improved stretchability with increasing concentration of EMITFS. The PU-DA samples containing 50.0% of EMITFS had a highly enhanced maximum strain of 102.1% respectively. Furthermore, as the percentage of EMITFS increased in PU-DA, the stress-strain curve showed a shift from brittle (PU-DA) to ductile (50% EMITFS in PU-DA) deformation, while at the maximal concentration (58.3%) a quasi-rubber-like behavior could be observed [30] (Figure 5.9). Even during mechanical testing, no leaching of ionic liquid was observed, indicating good stability of the composite, which is most important factor for any liquid fillers added in any matrix.

Figure 5.9 Stress-strain curves of PU-DA, 16.7 wt % EMITFS in PU-DA, 25 wt % EMITFS in PU-DA, 33.3 wt % EMITFS in PU-DA, 41.7 wt % EMITFS in PU-DA, 50 wt % EMITFS in PU-DA and 58.3 wt % EMITFS in PU-DA. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

To evaluate the performances of these polymeric composite films in electronic applications that demand transparency, the optical transparency of the polymer with and without ionic liquid (EMITFS) was measured by **UV-Vis spectroscopy** as stated in the chapter 3 (section 3.3.5). The transmittance was measured for all the compositions of PU-DA with EMITFS. Figure 5.10 depicts the optical transmittance (total) of PU-DA and PU-DA/50 wt% EMITFS film. The total transmittance value for PU-DA and PU-DA/50 wt% EMITFS film are: 98% and 94% respectively (across 400-700 nm) indicating good dispersion. The transmittance spectrum for other concentrations of EMITFS in PU-DA was also been shown in Figure 5.10. The change in transmittance of 58.3 wt % EMITFS in PU-DA was due to the non-uniformity of the film. At the maximal concentration (58.3%), a quasi-rubber-like behavior could be observed, as seen from the mechanical characterization result, due to which the film was not uniform and UV-Vis spectra for 58.3 wt % EMITFS in PU-DA was not linear as for the other concertation's of ionic liquid in PU-DA.

Figure 5.10 Transmittance spectrum of PU-DA, 16.7 wt % EMITFS in PU-DA, 25 wt % EMITFS in PU-DA, 33.3 wt % EMITFS in PU-DA, 41.7 wt % EMITFS in PU-DA, 50 wt % EMITFS in PU-DA and 58.3 wt % EMITFS in PU-DA. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Healing behavior of the polymer composite electrode

To evaluate the performance of these polymeric films in electronic applications, healable electrodes were prepared by spray coating with silver nanowires over the polymeric composite film (details in Experimental section). We utilize self-healing temperature to refer to the temperature at which a physical cut heals to be visually indistinguishable from before it was cut (in 10 minutes). Figure 5.11 depicts the optical microscope images of the healing process of the PU-DA electrodes containing 50.0% EMITFS as prepared (Figure 5.11 (a)), before heating (Figure 5.11 (b)) and after heating at 60 °C for 10 min (Figure 5.12 (c)). Regarding the healing of these electrodes, the cuts were made multiple times to check the rapidity of healing of the polymeric composite film. Upon healing, the electrodes appear to be almost indistinguishable from pre-cut sample, suggesting fast healing even after multiple cuts. The Figure 5.11 shows that the healing temperature has been reduced to 60 °C, just by incorporation of ionic liquid in the polymer (PU-DA), which was in line with the original hypothesis as stated in Chapter 1.

Figure 5.11 Healing behaviour of PU-DA/50 wt% EMITFS film. **a)** As prepared film. **b)** Before heating. **c)** After healing at 60 °C for 10 min. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Impressively, the healing temperature of PU-DA was drastically reduced from 120 °C (as shown in chapter 4) to 60 °C upon the addition of 50.0% of EMITFS as shown in Table 5.1. This indicates that previously unviable skin integrable applications could now be explored with these substrates that are more thermally fragile. All the film were of the same thickness (20 µm) and kept at the required healing temperature according to the composition of EMITFS for 10 min.

Table 5.1 The healing temperatures of the different composition of EMITFS in PU-DA film. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Composition of EMITFS (%)	Healing Temperature (°C)
0.00 (PU-DA)	120
16.7	90
25.0	80
33.3	70
41.7	70
50.0	60
58.3	60

From the above optical microscopy images (Figure 5.11) and Table 5.1, it can be stated that the ionic liquid helps to reduce the healing temperature. The robustness of healing was also proved by performing the mechanical testing of the pristine and cut-and-healed samples. Figure 5.12a depicts the uniaxial tensile tests for pristine, damaged and healed

samples (60 °C for 30 min) were done. As shown in Figure 5.12a, the damaged sample showed a considerably lower ultimate strain (40.1%) when compared to the pristine sample (184.9%) with the fracture originating at the position of the cut. Remarkably, the stress-strain curve for the healed sample shows almost complete recovery of the fracture strain (ultimate strain) as shown in Figure 5.13b. After healing, the sample could sustain strain upto 171.3% with a high healing efficiency of 92.6 % comparing favorably against recent reports [1, 12].

Figure 5.12 a) Stress-strain curves of PU-DA/50% EMITFS; pristine, cut and healed samples. **b)** Image of the fracture of the damaged sample and the healed sample. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Next, the utility of this polymeric system for optoelectronic applications was evaluated. **Broadband dielectric spectroscopy** measurements were carried out in order to determine the electrical properties of PU-DA and PU-DA compositions with various amounts of EMITFS. The relative permittivity- provides direct information about polarizability of material under an applied electric field and indirect information about energy storage and dissipation behavior of the material [31]. A higher dielectric constant is generally regarded as more favorable for dielectric applications.

Broadband dielectric spectroscopy analysis were carried out for all the samples with and without EMITFS in PU-DA. The measurements were carried out from 1 Hz to 100 kHz frequency as shown in Figure 5.13 a. Based on Figure 5.13b, as the composition of EMITFS increases, the dielectric constant at a given frequency increases. This is

likely due to additional ionic polarization contributions from the EMITFS molecules. In fact, to investigate the electrical properties present in the dielectric spectroscopy spectra after the addition of ionic liquid in polymer, PU-DA with 50 wt% EMITFS film was examined from 100 Hz to 10 kHz. In most of the cases, electrical application requires at max of 10 kHz, hence a range from 100 Hz to 10 kHz was investigated. The dielectric constant at 1 kHz increased significantly from 2.7 in PU-DA to 12.9 in PU-DA containing 50 wt% of EMITFS respectively. Hence, given the enhanced dielectric constants, the novel self-healing composite is a highly attractive dielectric material. This finds applications in optoelectronic devices like thin film transistor, photovoltaics, electroluminescent devices etc.

Figure 5.13 Dielectric constant of PU-DA/EMITFS film with various concentrations of EMITFS added. **a)** From 1 Hz-100 kHz. **b)** From 100 Hz-10 kHz. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from The Royal Society of Chemistry.

Based on the mechanical, healing and electrical properties as discussed in the previous sections, as the composition of EMITFS increases, the properties become more favorable. Hence, it would seem that the PU-DA sample containing the highest composition of EMITFS (58.3%) would be the most optimal. However, there is an unfortunate trade-off. As the composition of EMITFS increases, there is a marked increase in flowability of the as-synthesized mixtures. The reduced viscosity compromises the ability of the PU-DA/EMITFS mixture to form a uniform film. The surface uniformity of the PU-DA sample containing 58.3% EMITFS is extremely poor as compared to that containing 50.0% EMITFS, for same spin coating conditions

(Figure 5.14). Due to improved properties, and better workability, we have utilized 50.0% EMITFS for the fabrication of electroluminescent devices.

Figure 5.14 Comparison of Surface Uniformity between PU-DA + 50.0% EMITFS with different concentration of EMITFS in PU-DA. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission The Royal Society of Chemistry.

As a final demonstration of the above concepts, the polymeric composite films were utilised to fabricate self-healable electroluminescent devices.

Utilization of PU-DA/50 wt% EMITFS film as flexible healable electroluminescent devices

AC electroluminescent display consist of a thin film of phosphorescent material sandwiched between two electrodes in a capacitive configuration. Due to the thicknesses associated with these layers, the devices typically require high operating voltage. This issue has been partially addressed by incorporation of high dielectric constant materials such as barium titanate (BaTiO_3) particles into the active emissive layer to enhance the internal electric field [32]. A fully functional self-healable and flexible ACEL device with optoelectrical properties was thus fabricated by blending

the self-healable polymer into the phosphor layer (zinc sulfide doped with copper (ZnS:Cu)). Silver nanowires spray coated over PU-DA/ 50 wt% EMITFS film was utilized as the bottom electrode. Unlike previous reports where surface treatments were necessary for nanowire adhesion [15], the ionic liquid modified polymer surfaces were sufficiently hydrophilic. ZnS:Cu phosphor microparticles blended with the healable polymer was spun coated over the film of healable electrode and finally silver paint was utilized as top electrode. Figure 5.15a represents the device architecture of the ACEL device fabricated via solution process without using any vacuum. The ACEL device was driven by a DC-AC inverter (rectangular pulse function) and emitted blue light, as shown in Figure 5.15b-d. Due to the flexibility of the healable polymeric layers and the low thickness of the complete device (260 μm), the functionality is maintained without degradation when the devices were bent over a 6 mm diameter cylinder (Figure 5.15b). The devices were tested over different curved surfaces to prove the flexibility of the EL devices as shown in Figure 5.15 b and d. Optical emission from ACEL devices is attributed to the combined effect of a series of electron relaxation, triggered due to excitation by the applied electric field [33]. Figure 5.15c, clearly indicates that the ACEL device has an emission maxima at 452 nm (18 cd m^{-2}) confirming the visually observable blue emission (Figure 5.15(b) and (d)). Figure 5d shows the different patterning of ACEL devices, which were made over 25 cm^2 area film. Figure 5.15e-f shows the optical microscope image of the PU-DA/phosphor emissive films before and after healing respectively. This is an interesting fact that, even upon addition of phosphor microparticles inside the PU-DA, which is a healing polymer as shown in chapter 4, heals at the same temperature. The incorporation of microparticles does not affect the healing mechanism of the polymer.

Figure 5.15 Flexible healable electroluminescent device. **a)** Schematic diagram of the device structure. **b)** Photographs of the device ‘flat’, ‘flexed’ and wrapped around a 6 mm diameter cylinder. **c)** Electroluminescent spectrum of the device, which is centered at 452 nm. **d)** Patterned luminance from the device. **e, f)** Optical microscope image of the film (PU-DA+ZnS:Cu) before and after healing. The healing temperature for this layer was 120 °C. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from and The Royal Society of Chemistry.

5.3 Conclusion

In this work, we have incorporated ionic liquids into Diels-Alder based healable systems for enhanced performance. This approach addresses the limitations of high healing temperatures, limited stretchability, less-than-ideal dielectric properties of existing self-healable materials. The EMITFS ionic liquid was found to be homogeneously dispersed within the PU-DA polymer chains resulting in a tremendous

reduction in the glass transition temperature of the composite. This also resulted in greater flexibility and maximum strain values, as well as significantly lowered healing temperatures. Figure 5.16 shows the overview of the results which was discussed above. The self-healing composite was also shown to be an attractive dielectric material. Upon consideration of the mechanical, healing and electrical properties, including surface uniformity, the most optimal composition of EMITFS was determined to be 50 wt%. The healing temperature is 60 °C for our optimum sample (PU-DA+50 wt% EMITFS) whereby the polymer with the electrode appears to be indistinguishable from before it was cut. Finally, the PU-DA/ 50 wt% EMITFS film was utilized to fabricate flexible healable electroluminescent devices. Such robust healable transparent film would enable future applications in a wide variety of integrable devices for flexible and wearable electronics.

Figure 5.16 Schematics of the overview of the design concept for a self-healable polymeric composite film based on ILs. © Reproduced from Tiwari, Naveen, et al. "A rapid low temperature self-healable polymeric composite for flexible electronic devices." *Journal of Materials Chemistry A* 6.43 (2018): 21428-21434 with permission from and The Royal Society of Chemistry.

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Chapter 6*

Ionic liquids as a global additive to induce self-healing

Implementation of flexible electronic devices with enhanced capabilities and integrity requires the development of functional materials that combine excellent optoelectronic properties with high mechanical tolerance and self-healing ability. However, to combine and tailor such multiple characteristics, usually requires sophisticated multi-step synthesis processes, which adversely affects their practical usage. Plasticizers such as ionic liquid could be a good option to increase the flowability of the polymer matrix by reducing the glass transition of the polymer. As it was been observed in the previous chapter that with the increase in the concentration of ionic liquid, the polymeric films have improved in mechanical, electrical as well as healing properties. Taking that concept as a motivation, in this chapter we devise a composite system with healing behaviour in polymeric systems without DA recovery mechanism. This chapter studies the influence of ionic liquids on different classes of polymer structure and its effects on the healing properties. This simple additive principle enables healing tendency to be introduced in a wider variety of functional polymers.

*This chapter is currently being prepared as a manuscript.

6.1 Introduction

Novel materials with various desirable properties are highly sought for a wide range of applications. For futuristic flexible electronic device application, an ideal material requires important characteristics such as flexibility, transparency, and self-healing property. While transparency and flexibility are intrinsic characteristics of most polymers, the crucial challenge lies in inducing a self-healing property to the system. A wide range of polymeric systems have shown self-healing property driven by different mechanisms [1-13]. However, the commercialization of such novel materials is usually hindered by complicated multi-step synthesis affecting the product yield. The need for intricate and expensive equipment and controlled atmospheric conditions [14] also adds to the difficulty in fabrication of such materials. Furthermore, the raw materials are not readily available due to the specificity of the requirement of healing functionalities, such as the DA recovery mechanism in PU-DA. In the previous chapter, the influence of ionic liquids on PU-DA based healable polymers was explored. As indicated previously, we incorporated IL (EMITFS) in the PU-DA system to reduce the healing temperature and improve the mechanical properties like Young's modulus and ultimate strain, which are required features for flexible electronics. PU-DA films with EMITFS displays rapid healing behaviour owing to the impact of reduced T_g , which makes it easier for the polymer chains to flow and heal the cracks completely, similar to functional healing in pristine PU-DA system [7]. There are a number of common polymer systems like PVP, PMMA, PVDF-HFP, and PVA that are used in various domestic as well as industrial applications (Figure 6.1). However, these conventional polymers do not have any healing recovery mechanism. Herein, we hypothesize that incorporation of ionic liquids in these polymers may increase the plasticizing effect, which may allow the polymeric composite to heal. Based on the study of the addition of IL in these systems, the healing ability could be imbibed to a wider variety of functional polymer with specific optical, chemical properties.

Figure 6.1 List of polymers which are investigated in this chapter.

Firstly, Polyvinylpyrrolidone (PVP), a linear polymer consisting of 1-vinyl-2-pyrrolidone monomer, is chosen owing to its amorphous nature similar to polyurethane based DA polymer. PVP is biocompatible [15-24] and has been widely used for biomedical applications as an antiseptic [20, 25], pharmaceutical binder [15, 21], and emulsion stabilizer [16, 22]. The amide group on the side chain of PVP is nucleophilic and interacts well with positively charged moiety, while the bulky hydrophobic carbon chain repels each other due to steric hindrance. This particular feature has been utilized in metal oxide nanoparticle synthesis as an individual cation stabilizer [17, 23]. Additionally, PVP is inherently transparent and has also been employed in a wide range of transparent electronic devices such as supercapacitors [24] and anti-fog coatings [25]. Another amorphous polymer chosen within the scope of this study is poly(methyl methacrylate) (PMMA), also known as acrylic or acrylic glass. It is a thermoplastic material that is transparent and rigid and widely used as a shatterproof glass replacement [26]. In electronics, PMMA is commonly used in LCD /LED TV screens, laptops, smartphones and equipment displays due to its outstanding transparency and scratch resistance behavior [27, 28]. Due to its outstanding UV resistance and excellent light transmission, PMMA also finds application as encapsulation layer in high-efficiency solar panels [29-31].

Apart from the aforementioned amorphous polymers such as PVP and PMMA, ionic liquid induced healing behavior was further investigated in semi-crystalline polymers (like PVA and PVDF-HFP). PVA (Polyvinyl alcohol) is a semi-crystalline polymer, which is water-soluble, and exhibits unique physical characteristics owing to the coexistence of its crystalline and amorphous phase and its interfacial properties [32]. These interesting properties make PVA an attractive option [33-35]. PVDF-HFP (poly(vinylidene fluoride)) is also a semi-crystalline polymer extensively used in the manufacture of piezoelectric devices due to its excellent piezoelectric characteristics. The piezoelectricity of PVDF-HFP is mainly contributed by polar crystalline phases such as β -phase and γ -phase, rather than the α -phase. Among the various crystalline phases, the electroactive β -phase imparts the highest dipole moment resulting in high piezoelectricity [36-38]. In last few years, PVDF and its copolymers have also been used in self-powered devices. They are also flexible and can be readily adapted and molded to different structures for various applications. [39, 40].

Eventhough the above mentioned polymer systems such as PVP, PMMA, PVA, and PVDF-HFP can be suitable matrices for the next generation transparent electronic device applications, they lack the self-healing ability desired for durability and reliability of the devices. These systems also have limited stretchability and break at lower strains, rendering them practically unusable for a variety of applications such as stretchable devices. As has been mentioned in previous chapter, Ionic liquids are salts containing a pair of bulky anion and cation and existing as liquids at room temperature [41, 42]. ILs have excellent thermal stability, good electrical conductivity, and high ionic mobility which enables their utilization in various applications like conductive polymers [43], battery electrolytes [44], and organometallic catalysis [45]. Upon mixing with a polymer, the ionic liquid can act as a plasticizer and an ion supplying material [46-48].

Previously, EMITFS has been shown to improve significantly on the healing behavior (reduced healing temperature and rapid, repeated healing) and mechanical property (lower Young's modulus and enhanced stretchability) of a Diels-Alder based polymer network [7] by acting as a plasticizer. ILs were found to reduce the glass transition temperature of the polymer matrix without interfering with the reversible DA healing mechanism. To begin with, an ionic liquid, EMITFS, is introduced into the PVP matrix.

The resulting composite of PVP and EMITFS is a homogenous solid with ionic liquid molecules dispersed in the polymer matrix without any sign of phase separation. Significantly, the composite material shows healing property proven by healing of an induced cut after heating at 60 °C for 15 minutes. Additionally, the inclusion of ionic liquid alters the mechanical properties of PVP matrix, showing an increase in the flexibility of the polymer film. To the best of our knowledge, this is the first time that healing behavior was imbibed into PVP system. To further analyze the effect of addition of ILs, healing behaviour and mechanical characteristics of composites of, PMMA (amorphous polymer), PVA (semi-crystalline polymer) and PVDF-HFP (semi-crystalline polymer) were compared with PVP-IL composites. The impact of other ionic liquids like (EMITFB and EMITFSI) on the healing behaviour and mechanical characteristics was also explored for PVP, owing to its standout mechanical properties and healing behavior among other polymer systems for EMITFS composites.

6.2 Results and discussion

6.2.1 Polyvinylpyrrolidone (PVP) with EMITFS

Figure 6.2 depicts the schematic of polymeric composite fabricated by using PVP as the polymer matrix and 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate as an additive inside the PVP matrix. PVP is a linear polymer and its side-chain tautomeric form shows the existence of dipole moment. The interaction of EMITFS with the polymer matrix was based on imidazolium cation ring (viz.) forming a complex with the oxygen of C=O of the pyrrole group present in the PVP polymer side chain [1, 46, 48]. The schematics of the overview of the design concept and chemical interaction of PVP with EMITFS is shown in Figure 6.2. The EMITFS gets well dispersed without any separation/leaching, as EMITFS has a hydrophilic anion [49], and PVP is also hydrophilic in nature [50]. Hence, EMITFS has good compatibility with the PVP polymer matrix enabling higher loading of EMITFS in the composite.

Figure 6.2 Schematic of the chemical structure and the molecular views of PVP and EMITFS before and after the addition of EMITFS in the PVP matrix.

Characterizations of the PVP/EMITFS composite film:

DSC studies: Differential scanning calorimetry (DSC) is an instrument capable of detecting physical/chemical transformations occurring at a specified temperature. The DSC thermograms for samples with different concentrations of EMITFS in the PVP matrix are shown in Figure 6.3. PVP usually exists in amorphous form and has a glass transition temperature (T_g) of around 70 °C, as shown in Figure 6.3 (b). Addition of EMITFS additive results in interesting effects on the bonding of the polymer chain and reflected in the shapes of the DSC curves. EMITFS has a flashpoint of ~130 °C which contributes to the endothermic peak occurring above 135 °C for all concentrations of EMITFS in the composites (PVP5 (containing 5 wt% of EMITFS), PVP10 (containing 10 wt% of EMITFS) and PVP20 (containing 20 wt% of EMITFS)). More importantly, the ionic liquid acts as a plasticizer and reduces the interaction between polymer chains resulting in the observable reduction of glass transition temperature [51]. The effect can be observed clearly in the 0-90 °C region (Figure 6.3 (b)) where the local gradient changes, representing a transition from glassy state to rubbery state, and the trend of leftward shift is noticed as the ionic liquid concentration increases. PVP0 (pristine PVP) has a glass transition temperature of 70 °C. The T_g of the composite decreased to 47 °C, 35 °C and 23 °C for PVP5, PVP10, and PVP20, respectively, as shown in Figure 6.3 (b). Hence, the incorporation of ionic liquid reduces the T_g of polymer matrix significantly (reduction of 47 °C for PVP20).

Figure 6.3 a) DSC curves of PVP with EMITFS. b) DSC curve of the PVP/EMITFS composite with the arbitrary unit along the y-axis to depict the T_g of the samples clearly.

TGA Studies: Thermogravimetric analysis (TGA) is a useful technique for studying thermal degradation and stability behavior of a material. TGA curves of PVP0, PVP5, PVP10, and PVP20 are shown in Figure 6.4. The degradation temperature of samples is measured at 380 °C for PVP0 and it reduces to 340 °C for all PVP-EMITFS composites. There is a decrease of 40 °C in the degradation temperature upon the incorporation of EMITFS in the polymer matrix. However, it is important to note here that the degradation temperature does not vary with increasing concentration of EMITFS.

Figure 6.4 TGA curve of PVP and EMITFS composites. The degradation temperature of PVP-EMITFS composite is 340 °C.

FTIR analysis: Fourier transform infrared spectroscopy (FTIR) was employed to investigate the interaction between EMITFS and PVP in the composite film and changes to the chemical bonding. The FT-IR spectrum for pristine PVP, EMITFS and the composites are shown in Figure 6.5. As mentioned previously, the EMI⁺ cation (Imidazolium) may interact with the oxygen of the pyrrole carbonyl group (C=O) of the PVP side chain (Figure 6.2). The Imidazolium cation complexing with the oxygen of the C=O group will result in changes in the frequencies of bands associated with the cation ring and C=O of pyrrolidone [46-48]. The stretching of C=O due to complexation will also affect the C-N and C-H bonds of the pyrrolidone side chain. Upon incorporation of EMITFS, the carbonyl related peak at $\sim 1660\text{ cm}^{-1}$ shifted to 1670 cm^{-1} , and C-N related peak at $\sim 2140\text{ cm}^{-1}$ shifted to $\sim 2135\text{ cm}^{-1}$. For peak related to imidazolium cation ring, NC(H)N-CH stretching peak shifted from $\sim 3120\text{ cm}^{-1}$ to $\sim 3115\text{ cm}^{-1}$, and HC-CH symmetric stretching peak shifted from 2990 cm^{-1} to 2985 cm^{-1} . Hence, it can be concluded that imidazolium ring forms a complex with the carbonyl group of PVP side chain, which in turn, contributes to the compatibility of EMITFS with the PVP matrix.

Figure 6.5 FTIR spectrum of PVP with EMITFS. a) Overall view of the FTIR spectrum of PVP with EMITFS. FTIR spectrum of the samples film at range from b) $2900\text{--}2200\text{ cm}^{-1}$ and c) $2100\text{--}1700\text{ cm}^{-1}$.

Mechanical properties analysis: Mechanical properties for pristine PVP and different PVP-EMITFS composites are measured by performing uniaxial tensile testing, and the measured stress-strain curves are plotted in Figure 6.6. PVP0 remains elastic for very small strains and has a relatively stiff matrix, with a measured Young's modulus of 770 MPa. Additionally, it has limited stretchability and the ultimate strain is measured at $\sim 90\%$, as shown in Figure 6.6 (a). The introduction of EMITFS alters the bonding and packing of the polymer matrix, and results in softer and more stretchable composite matrices. The Young's modulus for PVP0, PVP5, PVP10 and PVP20 are 580 MPa, 1

MPa, 0.3 MPa and 0.2 MPa respectively. The Young's modulus reduces drastically to 0.2 MPa for PVP20. Furthermore, the addition of 5% EMITFS drastically increases the ultimate strain to ~2400%, an increase of more than 26 times. The composite's enhanced softness and stretchability can be attributed to ionic liquid molecules sliding in-between the polymer chains. Ions might interact with the PVP back-bone forming reversible bonds which can reconnect with the similar functional group in adjacent chains. This reduces the probability of disconnections in a chain, which is macroscopically observed as breaking. This is supported by the DSC studies in the previous section, in which the glass transition temperature of composites are reduced to around room temperature, allowing the composite to be in the rubbery state during testing. Increasing concentration of EMITFS results in a reduction of the ultimate strain for the composites, with values of ~2000% and ~1700% recorded for PVP10 and PVP20 respectively, as shown in Figure 6.6 (b). It is important to note that the maximum strain of PVP10 and PVP20 was limited by the maximum gauge of the tensile tester and they did not break during testing.

Figure 6.6 Stress-strain curve of (a) pristine PVP (PVP0) and (b) PVP-EMITFS composites (PVP5, PVP10, and PVP20)

Based on the analysis of the material characterization data for PVP-EMITFS composites, a similar trend as seen in chapter 5 is observed.

Healing behaviour of the composite film: In order to evaluate if the incorporation of EMITFS in PVP matrix could induced a healing behavior, composites are cut and heated at a particular temperature. A razor-induced 10-mm-deep cut was made on the surface of the composite. Microscopic images of the composite are taken for the cut

sample and after healing of sample (heat at a 60 °C for 15 minutes). Figure 6.7 (b) shows the image of PVP20 with signs of partial recovery and material filling up the cut region. Lack of complete recovery and removal of cut mark may be attributed of the absence of any healing functionalities like DA- which might be essential for a full recovery as seen in PU-DA system with EMITFS. Healing ability of the PVP-EMITFS composites is also studied through uniaxial tensile tests. Stress-strain curve for the damaged PVP20 sample (PVP with 20% IL_Before healing) and healed PVP20 sample (PVP with 20% IL_After healing) are depicted in Figure 6.7 (c), showing significant recovery of mechanical properties. When compared to the pristine sample, healed PVP20 sample shows similar Young's modulus. It is however, accompanied with reduction in the ultimate strain, with plastic fracture happening at 700% strain for the healed sample. When compared between PVP-EMITFS composites, healed PVP10 samples undergo mechanical failure at 350% strain, which is much less compared to the pristine PVP 10 sample and even the healed PVP20 composite Figure 6.7 (d). Among all the composite samples, PVP20 shows the best self-healing capability. This observation was in agreement with our hypothesis: as the amount of ionic liquid increases, more ionic liquid molecules can conform to different molecular environment, inducing self-healing property. Hence, an increasing amount of ionic liquid in the composite matrix would increase the self-healing capability of the system.

Figure 6.7 Healing behaviour of PVP with EMITFS. (a) Microscopic image of the cut before healing and after healing (b) Stress-strain curve of PVP20 before and after healing (c) Stress-strain curve of PVP10 and PVP20 after healing.

6.2.2 Poly(methyl methacrylate) (PMMA) with EMITFS

Moving ahead, EMITFS is added to another amorphous polymer system (PMMA) to understand the compatibility within the polymer matrix and EMITFS's role in introducing the healing behaviour in PMMA polymer. However, with the results presented below, it is quite evident that the polymer system does not seem to be compatible with the ionic liquid.

Characterizations of the PMMA/EMITFS composite film:

DSC studies: The DSC thermograms for all samples of PMMA-EMITFS composites are shown in Figure 6.8 (a). PMMA is a tough, and lightweight material, having the glass transition temperature of 110 °C as depicted in Figure 6.7 (a). Addition of EMITFS tends to increase T_g of the polymeric composite [52], which shows that the composite may be moving towards a brittle behavior, similar to materials like glass. The T_g of composite remains similar for 5% EMITFS addition (110 °C for PMMA5 (containing 5 wt% of EMITFS)) and increase with further increase in EMITFS concentration (115 °C and 160 °C for PMMA10 (containing 10 wt% of EMITFS) and PMMA20 (containing 20 wt% of EMITFS) respectively) as shown in Figure 6.8 (a). Hence, the increasing trend observed in T_g points at the fact that incorporation of EMITFS makes the PMMA-EMITFS composites harder and stronger, in contrast to the PVP-EMITFS composites which shows reduction in T_g for similar concentrations of EMIFTS. This may be due to the greater chain mobility of PVP-EMITFS composites at that specific concentration.

TGA studies: TGA curve for different PMMA-EMITFS composites are shown in Figure 6.8 (b). The degradation temperature for PMMA0, PMMA5 and PMMA10 samples is observed ~300 °C and reduces slightly to 280 °C for PMMA20. Figure 6.8 (b) shows that the working temperature for the PMMA-EMITFS composites is ~300 °C, which is lower as compared to PVP-EMITFS composites by a factor of 40 °C.

Figure 6.8 a) DSC curve b) TGA curve of PMMA with EMITFS composite.

FTIR analysis: Figure 6.9 shows the FTIR spectra of pure PMMA film and PMMA-EMITFS composite films containing different concentrations of EMITFS. The absorption peak at $2927\text{--}2986\text{ cm}^{-1}$ represents C-H stretching, $1700\text{--}1744\text{ cm}^{-1}$ represents C=O stretching, 1439 cm^{-1} represents CH_3 stretching, and 1195 cm^{-1} represents $-\text{OCH}_3$ stretching, which confirms the structural integrity of PMMA matrix [53]. There no observable peak shifts on addition of EMIFTS, which hints at the compatibility of EMITFS with the PMMA matrix. However, it is physically observed that the EMITFS is not compatible with the PMMA matrix and EMITFS can be observed leaching out of the PMMA matrix.

Figure 6.9 FTIR spectrum of PMMA with EMITFS polymeric composite.

Mechanical properties of the composite film: The stress-strain curves for PMMA-EMITFS composites with different concentration of EMITFS are shown in Figure 6.10. The PMMA0 shows poor stretchability with mechanical fracture observed around 3% strain (Figure 6.10). Upon addition of 5% EMITFS, ultimate strain increases to 22%. This is still not sufficient to meet the demands for the current generation of flexible electronic devices. Upon further increase in the EMITFS concentration, PMMA-EMITFS composite (PMMA10) shows a very similar stress-strain curve to PMMA0, with a recorded maximum strain of 3%. Leaching out of EMITFS from the composite matrix is observed while performing the uniaxial tensile test, pointing towards the non-compatibility of EMITFS with the PMMA matrix. For PMMA20, there is profuse leaching of EMITFS, which results in the slipping of PMMA20 film from the grip of the mechanical tester. Due to this, the stress-strain behaviour of PMMA20 could not be recorded.

The increase in the ultimate strain for PMMA5 can be attributed to the amorphousness of the polymer. The ultimate strain decreases as the amount of EMITFS starts increasing, which can be attributed to increase in T_g noticed on the increase in IL content inside the polymer matrix. Therefore, the maximum strain for the PMMA-EMITFS composites is measured at 22%, which is significantly smaller as compared with the PVP-EMITFS polymeric composites.

Figure 6.10 Stress-strain behaviour of PMMA with EMITFS polymeric composite.

Healing behaviour of the composite film: Based on the results from the mechanical testing of PMMA-EMITFS composites in previous section film, PMMA5 shows better performance and hence is tested for healing ability by performing a cut-and-heat test. A razor-induced 10-mm-deep cut is done on the surface of the composite. Microscopic images of the composite surface are taken before and after heating at a temperature of 60 °C for 15 minutes. Figure 6.11 (b) shows the surface images of PMMA5, which possesses no observable signs of recovery.

Figure 6.11 Healing test of PMMA with EMITFS. Optical image of the cut before healing (a) and after healing (b).

After analysing the effect of EMITFS in amorphous polymers like PVP and PMMA, the role of EMITFS in different semi-crystalline polymers is explored. Similar to the amorphous polymer systems in the previous sections, the effect of EMITFS as an additive in semi-crystalline polymers like Polyvinyl alcohol (PVA) and Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is investigated by performing DSC, TGA, uniaxial tensile tests and cut-and-heat healing tests.

6.2.3 Polyvinyl alcohol (PVA) with EMITFS

Polyvinyl alcohol (PVA) is chosen as the first semi-crystalline polymer matrix and the composite is formed by adding EMITFS inside the PVA matrix.

Characterisations of the PVA/EMITFS composite film:

DSC studies: The DSC thermograms for pristine PVA and all PVA-EMITFS composites are shown in Figure 6.12 (a). PVA is basically an atactic material, which means that the PVA possess crystallinity [54] and has a glass transition temperature (T_g) around 72 °C (Figure 6.12 (a)). The addition of ionic liquid has no impact on the

polymer bonding, as observed from the similar forms of DSC curves for the pristine PVA and PVA-EMITFS composites. The T_g for different composites (PVA5 (containing 5 wt% of EMITFS), PVA10 (containing 10 wt% of EMITFS) and PVA20 (containing 20 wt% of EMITFS)) are in same range as pristine PVA (PVA0), as shown in Figure 6.12 (a). Hence, the incorporation of ionic liquid hardly changes the glass transition temperature (T_g) of the polymer matrix. However, there is a slight observable shift in the melting temperature (T_m) of the PVA from 220 °C to 200 °C upon addition of EMITFS filler. This shift may be attributed to the change in the content of amorphous and crystalline phases.

TGA Studies: The TGA curves for PVA-EMITFS composites are shown in Figure 6.12 (b). Similar degradation temperature is observed for pristine PVA (240 °C) and PVA-EMITFS composites (240 °C). Hence, it can be inferred that the working temperature for the PVA-EMITFS composites is 240 °C, which is significantly lower as compared to PVP-EMITFS composites (a difference of 140 °C) and implies that PVA-EMITFS composite films cannot be utilized above 200 °C.

Figure 6.12 a) DSC curve and b) TGA curve of PVA with EMITFS polymeric composite.

FTIR analysis: Figure 6.13 shows the FTIR spectra of pure PVA film and PVA-EMITFS composite films containing different concentrations of EMITFS. The observed absorption bands at 2938 cm^{-1} represents C-H stretching, 1429 cm^{-1} represents C-H bending and 1094 cm^{-1} represent C-O stretching, pertaining to the PVA polymer matrix. Similar to the case of PVP-EMITFS composites, EMIM⁺ (imidazolium) cation ring forms a complex with the carbonyl group of PVA side chain, contributing to the compatibility of EMITFS with the PVA matrix. Additionally, the

PVA-EMITFS composites show no leaching of the ionic liquid, owing to the compatibility of EMITFS with the PVA matrix.

Figure 6.13 FTIR spectrum of PVA with EMITFS. a) Overall view of the FTIR spectrum of PVA with EMITFS. b) FTIR spectrum of the samples film at range from 2700-1500 cm⁻¹.

Mechanical properties of the composite film: The stress-strain curves for PVA-EMITFS composites with different concentration of EMITFS are shown in Figure 6.14. Here, the observed stress-strain behaviour is quite different from the previously observed stress-strain behaviour for amorphous systems like PVP-EMITFS composites, where the increase in the concentration of IL tends to increase the ultimate strain and the polymers become soft. As shown in Figure 6.14, PVA0 shows mechanical failure at at 58% strain. The addition of 5% EMITFS increases the strain-at-breaking to 125%, an increase of more than 2 times compared to the pristine sample. Interestingly, further increase in the EMITFS concentration leads to a reduction of ultimate strain, with a strain-at-breaking of 70% and 40% observed for PVA10 and PVA20 respectively. Hence, no conclusive trend is observed and no concrete relationship between concentration of EMITFS filler and mechanical properties can be established. Even for the best sample (PVA5), the maximum strain (at break) is observed to be only 125%, which is very less as compared with PVP-EMITFS composites.

Figure 6.14 Stress-strain curve of PVA with EMITFS composite.

Healing behaviour of the composite film: Based on the mechanical testing of PVA - EMITFS composites, PVA5 shows better performance and hence is tested for healing behaviour by performing a cut-and-heat test. A razor-induced 10-mm-deep cut is made on the surface of the composite. Microscopic images of the cut mark on the composite sample's surface are taken before and after heating at a temperature of 60 °C for 15 minutes (Figure 6.15 (b)). As observed from the images of the damaged surface, there are no observable signs of healing.

Figure 6.15 Healing test of PVA with EMITFS. Optical image of the cut before healing (a) and after healing (b).

6.2.4 Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) with EMITFS

The polymeric composite is fabricated by mixing PVDF-HFP as polymer matrix with 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate, EMITFS, where EMITFS acts as an additive inside the PVDF-HFP matrix.

Characterisations of the PVDF-HFP/EMITFS composite film:

DSC studies: The DSC thermograms for pristine PVDF-HFP and its composites with EMITFS are shown in Figure 6.16 (a). PVDF-HFP is basically a ferroelectric polymeric material which possesses semi-crystalline structure [55] and has a glass transition temperature (T_g) around $-8\text{ }^{\circ}\text{C}$ (Figure 6.16 (a)). The addition of ionic liquid has no impact on polymer bonding and has no impact on the form of the DSC curves for the composites, similar to the case of PVA-EMITFS composites. The T_g of composites (PVDF-HFP20 (containing 20 wt% of EMITFS) $-9\text{ }^{\circ}\text{C}$, PVDF-HFP30 (containing 30 wt% of EMITFS) $-10\text{ }^{\circ}\text{C}$, PVDF-HFP40 (containing 40 wt% of EMITFS) $-11\text{ }^{\circ}\text{C}$ and PVDF-HFP50 (containing 50 wt% of EMITFS) $-11\text{ }^{\circ}\text{C}$) are in the same range as pristine PVDF-HFP (PVDF-HFP0) for as shown in Figure 6.16 (a). Hence, the incorporation of ionic liquid hardly produces any observable change in the glass transition temperature (T_g) of the polymeric composites (PVDF-HFP/EMITFS); similar to previously detailed semicrystalline-IL (PVA-EMITFS) composite. Similar to the observation for PVA-EMITFS composites, the melting temperature (T_m) of the PVDF-HFP also shifts from $144\text{ }^{\circ}\text{C}$ to $128\text{ }^{\circ}\text{C}$ as the percentage of ionic liquid increases.

TGA Studies: The TGA curve of the PVDF-HFP with EMITFS was shown in Figure 6.16 (b). The degradation temperature of PVDF-HFP0 is observed at $420\text{ }^{\circ}\text{C}$, and reduced to $340\text{ }^{\circ}\text{C}$ for PVDF-HFP/EMITFS composites (Figure 6.16 (b)). The working temperature for the PVDF-HFP/EMITFS composites is $340\text{ }^{\circ}\text{C}$, which is significantly higher (a difference of $100\text{ }^{\circ}\text{C}$) as compared to previously mentioned semicrystalline-IL (PVA/EMITFS) composite.

Figure 6.16 Thermal properties of PVDF-HFP with EMITFS a) DSC curve and b) TGA curve of the composite film.

FTIR analysis: Figure 6.17 shows the FTIR spectra of pristine PVDF-HFP film and PVDF-HFP/EMITFS composite films containing different concentrations of EMITFS. The absence of the absorption bands at 976 cm^{-1} , 796 cm^{-1} , 760 cm^{-1} and 530 cm^{-1} , which are all associated to the α -phase crystals of the VDF units [56, 57] in the PVDF-HFP, from the PVDF-HFP/EMITFS composites indicate that the addition of EMITFS to PVDF-HFP results in the reduction of crystallinity of PVDF-HFP. The absorption band of PVDF-HFP detected at 1383 cm^{-1} and 490 cm^{-1} is assigned to the wagging vibrations of CH_2 and CF_2 groups [57, 58] respectively. These peaks were observed to shift to 1398 and 482 cm^{-1} , respectively, in the composite film. EMITFS additives are found compatible with PVDF-HFP matrix with no observable leaching, and this compatibility may be attributed to the favourable interaction of EMITFS with the the amorphous phase in the PVDF-HFP matrix.

Figure 6.17 FTIR spectra of PVDF-EMITFS polymeric composite film.

Mechanical properties of the composite film: The stress-strain curves of pristine PVDF-HFP film and PVDF-HFP/EMITFS composites are shown in Figure 6.18. Here, the behaviour of the stress-strain curves are very similar to that of the PVA-EMITFS composites and conclusive trend in the shift or changes in the stress-strain curves are observed. PVDF-HFP0 show significantly better stretching compared to PVA0, with a strain-at-breaking measured at 600% strain, as shown in Figure 6.18. With addition of 20% EMITFS, the strain-at-break increases to 735%, an increase of by 135% over the pristine sample. However, with further increase in the EMITFS concentration, reduction in the ultimate strain is observed with a strain-at-break of 690% and 560% measured for PVDF-HFP30 and PVDF-HFP40 respectively.

Figure 6.18 Stress-strain curve of the PVDF-HFP with EMITFS polymeric composite

Healing behaviour of the composite film: Based on the mechanical testing for PVDF-HFP/EMITFS composites, PVDF-HFP30 shows better results and hence was tested for healing ability by performing a cut-and-heat test. A razor-induced 10-mm-deep cut is made on the surface of the composite (Figure 6.19 (a)). Figure 6.19 (b) shows the surface image of damaged PVDF-HFP20 sample after being heated at 60 °C for 15 minutes, with no visible signs of healing of the damaged region.

Figure 6.19 Healing test of PVDF-HFP with 20% EMITFS. Optical image of the cut before healing (a) and after healing (b).

For the above mentioned sections, the effect of addition of EMITFS on different amorphous (PVP and PMMA) and semi-crystalline (PVA and PVDF-HFP) polymer systems was investigated. Overall, the observed materials properties for PVP-EMITFS composite are much better as compared with the other polymeric composite systems, which points at better compatibility of the EMITFS additive with the PVP matrix, compared to PVA, PVDF-HFP, and PMMA matrices (Table 6.1).

Table 6.1 Comparison of the properties of polymeric composite based on ionic liquids

Composite film	Nature of the polymers systems	Glass transition temperature (T_g)	Effect of addition of ILs in polymers	Degradation temperature (T_d)	Max strain (%) before healing	Max strain (%) after healing
PVP with 10% wt EMITFS	Amorphous	35 °C	T_g decreases	340 °C	2000*	350
PVP with 20% wt EMITFS	Amorphous	23 °C	T_g decreases	340 °C	1700*	700
PVA with 5% wt EMITFS	Semi-crystalline	75 °C	T_g remains same	240 °C	125	90
PMMA with 5% wt EMITFS	Amorphous	110 °C	T_g increase	300 °C	22	2.5
PVDF-HFP 20% wt with EMITFS	Semi-crystalline	-9 °C	T_g remains same	340 °C	735	17

*implies strain % without the detection of the break.

Based on the results obtained in the previous sections, it is decided to analyze the effect of addition of two different ionic liquids with the same imidazolium cation as EMITFS into the PVP matrix. This is done to understand the role of cation or anion (present

in EMITFS) in the favorable changes in the observed properties PVP-EMITFS composites. The structure of the chosen ionic liquids is shown in Figure 6.20.

Figure 6.20 The chemical structure of EMITFS, EMITFSI, and EMITFB

6.2.5 Polyvinylpyrrolidone (PVP) with EMITFSI (IL)

The polymeric composite is formed by using PVP as polymer matrix and adding 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, EMITFSI as a filler inside the PVP matrix.

Characterisations of the PVP/EMITFSI composite film:

DSC studies: The DSC thermograms are shown in Figure 6.21 (a) for all samples (PVP0 (pristine PVP), PVP5 (containing 5 wt% of EMITFSI), PVP10 (containing 10 wt% of EMITFSI) and PVP20 (containing 20 wt% of EMITFSI)). As mentioned in the previous section, PVP usually exists in an amorphous form and has a glass transition temperature (T_g) around 70 °C (Figure 6.3 (a) and Figure 6.3 (b)). PVP0 has a glass transition temperature of 70°C. The T_g of the composite decreases to 60 °C, 50 °C and 46 °C for PVP5, PVP10, and PVP20, respectively, as shown in Figure 6.21 (a). Hence, the incorporation of EMITFSI reduces the T_g of the polymer matrix by 24 °C (for PVP20). This change is half the magnitude of change achieved for PVP with 20 wt% EMITFS. This may be attributed to the effect of presence of a bulky anion in EMITFSI compared to EMITFS, which may restrict the flowability between the polymeric chains.

TGA studies: TGA curves of PVP0 and different composite (PVP5, PVP10, and PVP20) are shown in Figure 6.21 (b). The degradation temperature of samples is measured at 380 °C for PVP0, which reduces to 340 °C for PVP5 and PVP10, and further reducing to 320 °C for PVP20. This shows a change in the working temperature of the composite.

Figure 6.21 a) DSC curve b) TGA curve of PVP with EMITFSI composite.

FTIR analysis: Figure 6.22 shows the FTIR spectra of pure PVP film and PVP-EMITFSI composite films containing different concentrations of EMITFSI. The absorption peak at 1930 cm^{-1} and 1840 cm^{-1} shows the presence of EMITFSI in the composite matrix and no peaks (at these wavenumbers) are observed for pristine PVP [59].

Figure 6.22 FTIR spectrum of PVP with EMITFSI polymeric composite.

Mechanical properties of the composite film: As shown in Figure 6.23 (a), PVP0 has similar stress-strain behavior as in the previous section and shows mechanical failure at ~90% strain. The Young's modulus of PVP0 is measured to be 770 MPa (same as previous section), which reduces to 461 MPa for PVP20. This change in mechanical softness is much smaller compared to the PVP20 with EMITFS (0.2 MPa). The introduction of EMITFSI alters the bonding and packing of the polymer matrix. The addition of 5% EMITFSI increases strain-at-breaking to 110% (Figure 6.23 (b)). PVP10 and PVP20 were recorded to have a maximum strain of 130%, as shown in Figure 6.23 (b). This shows that although, the polymeric composite becomes soft, but the magnitude of induced softness and stretchability does not compare to the PVP-EMITFS composites. This may be attributed to different anion present in EMITFSI compared to EMITFS, since all the other measuring parameters remain similar.

Figure 6.23 Stress-strain behaviour of the PVP with EMITFSI composite film.

Healing behaviour of the composite film: Based on the mechanical testing of PVP - EMITFSI composite film, the film with 20% EMITFSI shows better properties and is tested for the healing behaviour by performing a cut-and-heat test. A razor-induced 10-mm-deep cut was made on the surface of the composite (Figure 6.24 (a)). Microscopic images of the composite surface were taken before and after heating at temperature of 60 °C for 15 minutes. Interestingly, as observed in Figure 6.24 (b), the surface images of the heated PVP20 sample shows no signs of healing.

Figure 6.24 Healing test of PVP with EMITFSI. Optical image of the cut before (a) and after heating (b).

6.2.6 Polyvinylpyrrolidone (PVP) with EMITFB (IL)

The polymeric composite is formed by dispersing 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMITFB) fillers inside the PVP polymer matrix.

Characterisations of the PVP/EMITFB composite film:

DSC studies: The DSC thermograms for all samples are shown in Figure 6.25 (a). PVP shows the glass transition temperature (T_g) around 70 °C, similar to previously mentioned thermograms for PVP in the chapter. Addition of EMITFB had interesting effects on the bonding of polymer and affected the shape of the composite's DSC curves. EMITFB has a flashpoint at ~130 °C which contributes to the endothermic peak occurring above 135 °C for PVP5 (containing 5 wt% of EMITFB), PVP10 (containing 10 wt% of EMITFB) and PVP20 (containing 20 wt% of EMITFB), as observed in Figure 6.3 (a). The effect is especially significant in the “0-90 °C” region. The T_g of the composite decreases to 50 °C, 27 °C and 15 °C for PVP5, PVP10, and PVP20, respectively, as shown in Figure 6.25 (a). Hence, the incorporation of EMITFB dramatically reduces the T_g of the PVP polymer matrix, with a change of 55 °C for 20% concentration, a trend very similar to PVP-EMITFS composites.

TGA studies: TGA curves of PVP0 and the composites (PVP5, PVP10, and PVP20) are shown in Figure 6.25 (b). The degradation temperature of pristine PVP is 380 °C, similar to previous TGA curves for pristine PVP mentioned in the chapter, and it reduced to 340 °C for PVP-EMITFB composites. There is a decrease of 40 °C in degradation temperature for the composites. And the degradation temperature does not

change further with increase in the concentration of EMITFB. The working temperature for these PVP-EMITFB composites is 340 °C (Figure 6.25 (b)). The TGA curves for PVP-EMITFS and PVP-EMITFB composites are very similar.

Figure 6.25 a) DSC curve b) TGA curve of the PVP with EMITFB polymeric composite

FTIR analysis: Fourier transform infrared spectroscopy (FTIR) was employed to investigate the interaction between EMITFB filler and the PVP polymer matrix in the composite film, especially with respect to changes in chemical bonding (Figure 6.26). As has been mentioned before, the EMI⁺ cation (Imidazolium) may interact with the oxygen of the pyrrole carbonyl group (C=O) of the PVP side chain (schematic shown in Figure 6.2) and the stretching of C=O bond due to complexation will also affect the C-N and C-H bonds of the pyrrolidone side chain. The carbonyl related peak at ~1660 cm⁻¹ shifted to 1670 cm⁻¹, and C-N related peak at ~2140 cm⁻¹ shifted to ~2135 cm⁻¹. For peak related to imidazolium cation ring, NC(H)N-CH stretching peak shifted from ~3120 cm⁻¹ to ~3115 cm⁻¹, and HC-CH symmetric stretching peak shifted from 2990 cm⁻¹ to 2985 cm⁻¹ [46]. Hence, it can be concluded that EMIM⁺ imidazolium ring is forming a complex with the carbonyl group of PVP side chain, leading to the compatibility of EMITFB with the PVP matrix.

Figure 6.26 FTIR spectrum of PVP with EMITFB polymeric composite

Mechanical properties analysis: Mechanical properties are measured through uniaxial tensile testing, and the stress-strain curve are presented in Figure 6.27. Introduction of EMITFB alters the bonding and packing of the polymer matrix, and a clear trend is observed in the changes occurring in the stress-strain behavior. Addition of 5% EMITFB increases the strain-at-breaking to 190%, an increase of more than 2 times. On further increase of concentration of EMITFB in the composite matrix, there is an increase in the ultimate strain, with a measured maximum strain of 580% and ~1580% for PVP10 and PVP20 respectively, as shown in Figure 6.27 (b). It is also important to note that the maximum strain of PVP20 was limited by the maximum gauges of the tensile tester and it did not break during testing. The Young's modulus of PVP0 measured at 770 MPa, reduces drastically to 0.3 MPa for PVP20, which is comparable to 0.2 MPa for PVP20 (PVP with 20% EMITFS). The reason for the observed changes in the mechanical properties of the PVP-EMITFB composites are similar to what has been discussed previously for PVP-EMITFS composites. The composite's enhanced softness and stretchability can be attributed to ionic liquid molecules sliding in-between the polymer chains. Ions might interact with the PVP back-bone forming reversible bonds which can reconnect with the similar functional group in adjacent chains. This reduces the probability of disconnections in a chain, which is macroscopically observed as breaking. This is supported by the DSC studies in the previous section, in which the glass transition temperature of composites are reduced to around room temperature,

allowing the composite to be in the rubbery state during testing. It is also essential to note that there is no leaching of IL from the composite matrix.

Figure 6.27 Stress-strain behaviour of the PVP with EMITFB composite film.

Healing behaviour of the composite film: Based on the mechanical testing of PVP - EMITFB composites, the film with 20% EMITFB shows better properties and is tested for healing behaviour by performing a cut-and-heat test. A razor-induced 10-mm-deep cut is placed on the surface of the composite (Figure 6.28 (a)). Microscopic images of the composite surface were taken before and after heating at an elevated temperature of 60 °C for 15 minutes. Figure 6.28 (b) shows the surface images of damaged PVP20 sample after 15 minutes of heating, which shows considerable flow of material into the damaged region. However, the sample did not heal completely and only a partial healing is observed.

Figure 6.28 Healing test of PVP with EMITFB. Optical image of the cut before healing (a) and after healing (b).

In summary, the effect of different ionic liquids is investigated with the PVP polymer system, where the IL cation remains the same, but the group of anions attached to ionic liquids are different. The properties of PVP-EMITFS and PVP-EMITFB are much better compared to PVP-EMITFSI composite. Owing to the presence of similar hydrophilic anions in EMITFS and EMITFB ILs with the cations fixed, it is observed that the compatibility of an additive to the polymer matrix is the critical aspect (Table 6.2).

Table 6.2 Comparison of the properties of PVP composites with different ionic liquids

Composite film	Nature of ionic liquids	Glass transition temperature (T_g)	Degradation temperature (T_d)	Max strain (%) before healing	Max strain (%) after healing	Healing behaviour of the composites
PVP with 20% wt EMITFS	Hydrophilic	23 °C	340 °C	1700*	700	Healed
PVP with 20% wt EMITFSI	Hydrophobic	24 °C	320 °C	130	5	Not healed
PVP with 20% wt EMITFB	Hydrophilic	15 °C	340 °C	1580*	130	Partially healed

*implies strain % without the detection of the break.

6.3 Conclusions

Healable, transparent and flexible composite is successfully synthesized by the incorporation of ionic liquids into PVP polymer matrix. The EMITFS ionic liquid is found compatible with PVP matrix and dispersed homogeneously within the polymer chain without signs of phase separation. The optimum concentration of EMITFS in PVP is found to be 20 %. Promising healing ability emerges after the incorporation of EMITFS in the PVP matrix, with the sample showing the most significant reduction of scratch width after heating. Additionally, the composite showed magnificent stretchability up to 2400%, a 26-fold increase compared to the base polymer matrix. In all, the resulting self-healable transparent flexible composite is a suitable scaffold matrix for the flexible electronic device.

A detailed analysis was carried out to understand the underlying mechanism for this good performance. Different class of polymers (like PVA, PVDF-HFP, and PMMA) with the same base structure are analysed with EMITFS, with PVP matrix emerging as a clear choice. PVP-EMITFS systems provides better T_g , working temperature as well as mechanical properties compared to other system. Fixing PVP as the polymer matrix, further studies incorporating different ILs (EMITFSI and EMITFB) has been performed with same cations in these ILs but different anion. This is done to investigate the role of cations and anions present in the IL for determining the properties of the final composite. Owing to similar hydrophilic nature of anion present in EMITFB compared to EMITFS, PVP-EMITFB composites show very similar behaviour to PVP-EMITFS composites. However, the properties obtained by incorporating EMITFSI are drastically different owing to the hydrophobic nature of the anion, which proves that the anion has a critical role to play in changing the properties of polymer matrix.

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Chapter 7

Discussion and future work

This chapter threads together a summary of all the chapters in this dissertation. The scope to which the hypotheses were introduced is concisely explained in the form of a summary of the every achieved results in this dissertation, as discussed in the results and discussion chapters. The conclusions of the achieved results are also described in this chapter. Next, the limitations of the present materials and devices with their implications are highlighted and new opportunities and strategies for future work are identified. In this chapter, the future work is designed as to investigate new ways of fabrication of self-healing materials and device fabrication, along with the highlighting their structural engineering challenges. Some of the suggested future work includes-self-healing mechanism via photo-thermal effect, fabrication of self-healable semiconducting polymer and utilising these materials for the other potential applications are described in brief in this chapter.

7.1 Summary

Initially, the low-temperature synthesis method was used to prepare transparent, healable and flexible polymer through Diels-Alder reaction [1]. This research demonstrates the benefits of the reversible system, including repeated healing at a specific place even after repeated damage and single-component material systems, rather than composite, which further decreases the complexity of the system. Once the self-healable polymer (PU-DA) was synthesized, it was further utilized to fabricate flexible healable electrode based on silver nanowires. To the best of our understanding, to demonstrate the application, it was the first transparent self-healing heater based on healable electrodes. Despite the advantages, the reversible system also poses challenges, as the system requires higher healing temperatures without hampering the properties of the materials, which was well sorted from the first in the next study.

A rapid low-temperature self-healing polymeric composite based on EMITFS ionic liquid for flexible electronic devices was well demonstrated [2]. The vital point for selecting ionic liquids in the self-healing polymer is because the ILs have enhanced the self-healing ability of PU based DA polymer, because of their liquid state which allows them to flow in between the polymer chains and was incorporated into a continuous phase of the polymer matrix immediately when they come into contact with each other. They form a secondary bond with the polymer chains and extend them apart which increases the mobility of the polymer chains and improve the elasticity and processability of polymers by lowering the glass transition temperature (T_g) of the polymer, which was proved in this study. The reported work on the ionic liquid in self-healing materials (PU-DA) suggest that the dynamic character of the ionic bonds of the liquid improves the flexibility of polymer chains and generate the materials with self-healing property by allowing cracks or breakage to be healed by retransforming of bonds. This method of making self-healing composites with ionic liquids have the advantage of being transformed into the desired geometry. The system of PU-DA/IL based on silver nanowire was explored as a healable electrode. Therefore, this electrode was designed in the form of an optoelectronic device (ACEL) as an application was well demonstrated in this study.

Firstly the PU-DA based healing was explored, but the limitation was high healing temperature for that system which forced us to investigate a new healing mechanism

without altering the chemical composition of the polymeric composite. In order to do so, we incorporated ILs in the PU-DA system to enrich the properties like lower healing temperature and mechanical which are the required features for flexible electronics. The PU-DA with IL shows healing mechanism more easily because of the effect of lowering T_g , due to which the polymer chains are able to flow more easily and can heal the cracks as compared to functional healing. This mode of healing mechanism was further investigated in the others polymer system. Hence, in this portion of the study, the effect of EMITFS ionic liquid was investigated with two different types of polymers such as an amorphous polymer (PVP and PMMA) and a semi-crystalline polymer (PVA and PVDF-HFP). And to have a better understanding the role of ILs in healing mechanism based on ILs, two different ILs (EMITFB and EMITFSI) which have the same cation but different anions were also used to determine is that any role of cation and anion in this healing mechanism. A detailed analysis was done to demonstrate the effect of ILs in terms of mechanical and healing properties.

7.2 Conclusions

Polyurethane accomplished by reversible reaction with Diels-Alder adducts was synthesized to fabricate self-healable polymers. The advantage of using this self-healable polymer is that the steps involved in the synthesis of PU-DA require low temperature (50-60 °C). Based on the materials characterization, the PU-DA film depicts the glass transition temperature (T_g) was -25.3 °C, and the degradation temperature was observed to be 220 °C. It was also demonstrated the strong bonding of AgNWs with polymer matrix by the APTES treatment for 24 h at a concentration of 15 mM, which was tested by scotch tape under the name of adhesion and peeling test. The transparent and healable electrode has a highly conductive surface with a sheet resistance of 13.3 $\Omega/\square$ and 77% transmittance at 550 nm, and showed excellent bending tolerance with negligible change in conductivity of the electrode. The transparent and healable electrode is capable of both structural and electrical healing via heating. The healing temperature was noted as 120 °C of this system. Excellent electrical, robustness, optical and thermal properties of the healable electrodes were utilized as a transparent, flexible, and healable thin-film heater was successfully demonstrated.

Herein, EMITFS was added to PU-DA to form a self-healing composite. This novel composite depicts the disadvantages of high healing temperatures, limited stretchability, less-than-ideal dielectric properties of current polyurethane-based self-healable materials. EMITFS (ILs) was found to be homogeneously mixed into the PU-DA matrix without chemically altering it, which are confirmed by FTIR and optical microscopy. The T_g of the composite was lowered tremendously from $-27.3\text{ }^{\circ}\text{C}$ (PU-DA) to $-117.1\text{ }^{\circ}\text{C}$ (PU-DA/50% IL), which indicated that the EMITFS molecules were homogeneously mixed within the polymer chains, which results in lowered healing temperatures, maximum strain values from 17% (PU-DA) to 102% (PU-DA/50% IL) and enhanced with greater flexibility. Upon the critical analysis of the healing, electrical and mechanical properties, also taking into an account of surface uniformity, the optimum composition of EMITFS was determined to be 50.0%. By incorporating innately flexible and self-healable PU-DA-based constituents, a remarkable self-healable and flexible ACEL device were achieved without compromises to optoelectronic performance. This novel device possessed comparable optoelectronic properties, with a luminance of 18 cd/m^2 at 110 V with a frequency of 1 kHz. Furthermore, high flexibility was achieved, and the device performed optimally even when wrapped around a 6 mm diameter cylinder. The ability to self-heal and operate optimally under bent conditions would make it suitable for biocompatible products like electronic skins (E-skin).

In order to understand the healing and mechanical properties of these composites, EMITFS was incorporated in PVP, PMMA, PVA and PVDF-HFP polymers. As the concentration of EMITFS increases in the PVP matrix, the polymeric composite becomes soft and tends to show a lower glass transition temperature from $70\text{ }^{\circ}\text{C}$ (PVP0) to $23\text{ }^{\circ}\text{C}$ (PVP20). The strain value has reached above 2000% with just 5 wt% incorporation of EMITFS in PVP. The optimum composition of EMITFS in PVP/EMITFS composite was determined to be 20 per cent after the experimental analysis of the healing and mechanical properties, also taking into account the surface uniformity. The PVP20 composite films show self-healing behaviour as PU-DA50 film. Based on PMMA with IL composite films, PMMA was also known as acrylic glass which people have used in the alternative of glass in terms of the lightweight. This glassy behaviour was investigated in the mechanical testing of these film composite. The most critical issues with PMMA was that it was not compatible with the EMITFS as compared to

other composite films. The leaching of ILs was observed even in the 5% concentration of IL was incorporated in the polymer matrix.

Because of the crystalline nature of the PVA and PVDF-HFP, they did not show similar trends as PVP with IL. The T_g of these composite increase with the increase in IL which shows the transition towards the glassy state which was well demonstrated by the mechanical properties. The concentration of EMITFS in PVDF-HFP was also high as compared to another polymer system. In PVDF-HFP the composition of ILs was from 20% to 50% which is 2-times higher than the other composition of composite films. Based on the different ILs was used to understand the role of cation and anion in the polymer matrix was investigated. The EMITFSI has a hydrophobic anion compared to EMITFB and EMITFS, which shows that since PVP was a hydrophilic polymer, EMITFSI is not the best option to incorporate into the PVP matrix. As we know, like dissolves in like. EMITFS based on experimental analysis was the best option to incorporate ILs into PVP. Thus, this study clearly shows that ionic liquid compositions are dependent on polymer chains alignment.

7.3 Limitations and their implications

Flexible electrodes are critical in a broad range of optoelectronic, electronic and power systems. These applications not only involve excellent electrical conductivity, but also involve better mechanical characteristics such as stretchability, flexibility, and robustness where standard electrodes are not performed. With the AgNWs based on PU-DA, these kinds of problems were chosen as a self-healing electrode that offers better conductivity with high transparency and mechanical characteristics. But it is quite difficult with regard to the robustness of these electrodes, as the electrodes are covered over the polymeric films.

This leads to further inquiry of conventional self-healing chemistry approaches to the construction of self-healing electrodes on the novel material scheme, which can solve the current electronic device restriction. Because of the above composite approach's constraints, it opens the door to the future job where an intrinsically healable system needs to be developed. During the course of this dissertation, the elastomeric self-healable polymers were not investigated. These elastomeric polymers have great

potential that could be explored in the future for the next generation of electronic devices.

7.4 Future work

In this dissertation the key limitation with respect to fabricating a self-healing material with low-temperature processing condition along with the lower healing temperature and higher mechanical properties were addressed significantly. However, these self-healable materials restrict the wide scope of the self-healable electronic devices. This dissertation primarily addresses the limitations regarding the basic material design with the clear prospect of this material system on self-healing electronic devices. This paves a way in further investigation of standard self-healing chemistry approach on a novel material system to construct self-healable electronic devices. It also open up new innovative possibilities of healing the materials, addressing the present technological limitations for the next-generation electronic devices. Hence, the future work can be divided into three groups: (1) Investigation of new ways of self-healing through choice of materials, (2) Self-healable device fabrication, and (3) Addressing the structural engineering challenges.

7.4.1 Self-healing mechanism via photo-thermal effect

During the course of this dissertation, thermal healing was only the method used to demonstrate the healing behaviour of the self-healable polymeric systems. It was clearly shown that the thermal mode of healing mechanism was well studied and the healing temperature has been reduced from 120 °C to 60 °C by incorporating ionic liquids in the polymer matrix. However, self-healable polymers are the representative examples of smart materials that can be repaired by one or more external stimuli [3, 4]. Light is likely the most interesting stimulus of all possible to cause changes in form as it is necessary to regulate the material's reaction both spatially and temporarily to facilitate the self-healing mechanism. Furthermore, the chance of using the stimulus remotely considerably improves the potential of these systems, particularly in those applications where direct contact with the material is hard or impossible [4].

Recently, research groups have already shown, light as a source, to investigate the various approaches and fabrication strategies to trigger the healing mechanism in the polymers. Based on the literature of the work, researchers have utilised UV-light and

visible light sources to induce healing mechanism for the self-healable polymers [5, 6]. Currently, the focus is on conventional material systems like polyurethanes based DA polymers and silver nanowires based electrodes systems (Figure 7.1). This demonstrates the healing of AgNW's self-healing electrodes based on PU-DA. However, the novel self-healable polymeric materials with different systems and electrodes developed within the scope of this dissertation can be investigated with these techniques.

Figure 7.1 Light-induced healing mechanism in PU-DA based AgNWs self-healable electrodes. a) Before healing and b) After healing.

7.4.2 Self-healable semiconducting polymers

Self-healable semiconducting polymers have received considerable attention because of their unique combination of reparability to restore electronic properties. However, experimental evidence for practical device applications lacks, especially for self-healing of sizable damages. These defects, even at micron sizes, can cause serious degradation of conductivity, permanent disconnection and device malfunction. However, these failures can be remedied or prevented if the existing defects are repairable or healable under the action of appropriate stimuli. Although such an approach may be reasonable for conducting elements [7, 8], a more critical challenge lies in enabling a self-healing semiconductor. Therefore, there is a need semiconducting thin film is indispensable for a wide range of optoelectronic and energy devices, e.g. photovoltaics, logic circuits, displays. Several recent reports have focused on the composite strategy of combining highly flexible elastomers (as a matrix) with various conductive elements (e.g. semiconducting nanofibrils, nanoparticles, nanowires etc.) [8-12]. However, the self-healability is facilitated by the repair within the nonconductive matrix, which cannot reliably remedy the defects sustained by the

conductive elements. Due to the limitations of this composite approach, an intrinsically healable semiconducting system needs to be developed.

In line with the above rationale, a recent report in explored the interesting concept of “dynamic noncovalent crosslinking” for intrinsically self-healable semiconducting polymer [13]. Incorporation of dynamic non-covalent bonding between flexible polymer chains is critical to achieving high stretchability and self-healing properties while also retaining high charge transport in the conjugated regions (as shown in Figure 7.2). Thus, the dynamic bonds can easily be broken to allow energy dissipation upon strain, thus making the system more tolerant of mechanical stimuli. The technical approach is still challenging research for the fabrication of fully self-healable organic-based transistor.

Figure 7.2[13] Intrinsically self-healable conducting polymer for OTFT application and healing mechanism. © Reproduced with the permission from “J. Y. Oh, S. Rondeau-Gagné, Y.-C. Chiu, A. Chortos, F. Lissel, G.-J. N. Wang, B. C. Schroeder, T. Kurosawa, J. Lopez, T. Katsumata, J. Xu, C. Zhu, X. Gu, W.-G. Bae, Y. Kim, L. Jin, J. W. Chung, J. B. H. Tok and Z. Bao”, *Nature*, 2016, 539, 411–415.

Here, we propose to advance the self-healing of semiconducting polymers to cater for improved robustness in reparability of micrometre-sized cracks or cuts. The synthesis strategy will demonstrate an innovative combination of a semiconducting segment with linkage molecules, where self-healing is facilitated by hydrogen bonding and re-bonding mechanism. Although several mechanisms have been proposed for ultra-flexible and tough polymers with self-healing capability, these material design strategies have not been investigated and efficiently applied to semiconductors.

Development of the intrinsically self-healable semiconducting polymer using dynamic hydrogen bonding as non-covalent crosslink: Utilizing the strategy of dynamic non-covalent crosslinking via hydrogen bonding, we plan to exploit the vast selection of semiconducting monomers that can be copolymerized with the linkage molecules. Despite the wide variety of organic semiconductors such as carbazoles, arylamines, thienothiophenes acenes, etc., the 3,4-Ethylenedioxythiophene (EDOT) and Diketopyrrolopyrrole (DPP) will be the material which will be examined. These two material classes have been extensively studied in a wide variety of electronic devices such as TFT, solar cells, sensors and LED. DPP polymers have excellent aggregating properties due to the strong donor-acceptor interactions induced by the electron-deficient chromophores, allowing charge mobility $>5 \text{ cm}^2/\text{Vs}$ to be achieved. The EDOT and DPP cores will be covalently grafted with the hydrogen-bonding moieties to provide the intrinsically self-healable semiconducting polymer-based with our early experiments. As a starting point, utilisation of ureidopyrimidinone (UPy) as the moiety that induces healing. UPy's long chain will allow the formation of strong hydrogen bonding, promoting the formation of a network without degrading charge transport mobility. The introduction of alkyl spacers to enhance the flexibility of the dynamic moieties. Semiconducting polymers incorporating different ratios of non-conjugated UPy will be synthesised to elucidate the change in mobility of the polymer semiconductor (Figure 7.3).

Figure 7.3 Proposed synthesis scheme for linkage molecule UPy (1) and linking with semiconducting monomer EDOT (2) and DPP (3)

7.4.3 Investigation of self-healing polymers/conductors for other potential applications

1. Demonstration of flexible thin-film transistor composing of self-healable contact electrodes and semiconducting channel: Thin-film transistor (TFT) is the building block of every electronic circuit. Demonstration of self-healing in TFT has been limited to a single component e.g. dielectric or semiconducting layer. Here, the aim is to demonstrate the self-healability for both materials of the semiconducting layer (utilizing the materials described above) and the source/drain (S/D) electrode (based on our ready-developed materials [1, 2]) in a single device platform. As mentioned earlier, the performance of semiconducting polymers strongly depends on the charge carrier across the S/D electrode interface. Moreover, self-healable conductive materials are often prepared via composite strategy, which combines highly conductive filler materials (e.g. nanowires, nanotubes) with a polymeric matrix. The embedding of fillers within the matrix usually leads to high contact resistance due to a limited amount of conductive fillers existing on the surface. This can deteriorate the transistor performance due to high contact resistance and uncontrollable charge injection barrier. As shown in this dissertation, a new synthesis method to form highly dense silver nanowire (AgNW) network supported by the self-healable base of polyurethane with Diels-Adder adducts serving as healing agents. The unrestricted contact of AgNW network (existing on the surface of the flexible conductor) to the semiconducting channel not only alleviates the contact resistance but also allow possible tuning of injection barrier via functionalization of AgNW using self-assembled monolayers. Figure 7.4 presented the proposed structure of such TFT.

Figure 7.4 Proposed structure of TFT composed of self-healable AgNWs source/drain electrode and semiconducting channel.

2. Self-healable soft robots: During the course of this dissertation, the elastomeric self-healable polymers were not investigated. These elastomeric polymers have great potential for next-generation electronic devices. Mechanical damage to the elastomers and their surfaces can render them susceptible to premature failure. Self-healing smart materials have the structural capability incorporated in it to repair itself either by itself or by some external stimuli [14]. Poly(dimethylsiloxane) polymer chains cross-linked by coordination complexes that combine high stretchability, high dielectric strength and autonomous self-healing have been reported [15]. Transparent Diels-Alders elastomeric polymer, with the acronym FM-DA, have been synthesized through a reversible DA cycloaddition reaction of three cross-coupling co-monomers [16]. Layer-by-layer assembled Polyelectrolyte multilayer (PEM) films have been shown to self-heal in the presence of DI water [17]. Poly(dimethylsiloxane) based polyurethane (PDMS-CPU) cross-linked by Diels-Alder (DA) adducts have been shown to have self-healing abilities, which is enhanced by DMF vapours [18]. The liquid metal-polymer composites have also shown to have self-healing abilities [19].

With our approach, we would like to incorporate self-healing to the elastomeric polymers which could be applicable for healable soft robotics. This is very important if we want soft robotics to venture to unknown environments. The damaged elastomers can self-repair and will render a longer useful life to the robots. We will synthesize self-

healing soft elastomers which can match the mechanical and electrical properties of the existing material systems in self-healing polymers. Device fabrication and characterization will be done for actuation strain and operating voltage. The study of the electrical and mechanical properties before and after healing of the elastomer will be done. Different triggers like localized heating, DI water, and pH change for healing the elastomer will be investigated. Time study for different types of failure of elastomers and duration of self-heal will be done for small-scale and large-scale devices. This will help in predicting the device performance and applicability with better precision. Approaches to trigger self-healing through electrical means either through resistive heating or electrochemical methods will also be pursued.

Figure 7.5 (a) Top view of a scratched electrode and PDMS-CPU polymer [18]. (b) Top view of the electrode and PDMS-CPU polymer after DMF treatment [18]. (c) Schematic representation of water-enabled healing capability of PEM films [17]. (d) Poly(dimethylsiloxane) polymer film (cross-linked by coordination complexes), (e) A pointed object severely puncturing the self-healing polymer, &, (f) Films self-heals completely at room temperature [15]. Liquid metal- Polymer Composite bar being cut by scissors (g), damaged composite bar (h) and self-healed composite bar (i) [19].

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