Multifunctional magnet-polymer transducers

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Multifunctional Magnet-Polymer Transducers

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School of Materials Science and Engineering

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Abstract

A key goal of current research is to develop the next generation of materials, structures and systems which can mimic “life” functions, thus imparting extended service lifetime and reliability, while also decreasing maintenance and operating costs. Living organisms can sense and react to environmental stimuli, e.g., they can sense damage to their structure and respond appropriately via a healing mechanism. This phenomenon can occur over multiple cycles during its lifetime. The objective of this thesis is to develop a bioinspired artificial material which can mimic the functions of multicycle damage sensing, self healing and actuation. This material will be of great significance in applications such as biomedical coatings or novel aircraft wing “skin” where damage sensing, healing, flexibility, actuation capability and extended lifetimes are required.

Magnet filler-polymer matrix composites (Magpol) are an attractive material to combine multiple functions. This is because the inherent properties of both magnetic fillers and the polymer matrix can be readily tuned. Magpol can exhibit quick response, remote contactless actuation, high actuation strain and strain rate, remote heating in alternating magnetic fields (AMF), and self-sensing. These capabilities enable Magpol to respond to a range of stimuli to trigger self healing, sensing and actuation. In this work, a Magnet-polymer composite capable of actuation, damage sensing and self healing was developed by tuning the properties of a magnetic ferrite nanoparticle filler, commercial biocompatible thermoplastic shape memory matrix and stilbene dye molecules. The Curie temperature (T_c) of the Mn-Zn ferrite nanoparticles was tuned to provide a “failsafe” temperature stimulus required for sensing and healing *via* the application of an AMF; a constant (DC) magnetic field was utilized to induce actuation. Bis(benzoxazolyl)stilbene (BBS) mechanochromic dye was utilized as a colour changing damage sensor, while the shape memory properties of poly (ethylene-co-vinyl acetate) (EVA) was used to extend these functions over multiple cycles, increasing Magpol’s service life. Each of the three functionalities was studied and Magpol’s performance was compared to competing technologies through Ashby charts.

The self healing ability of Magpol was evaluated over multiple cycles of damage and repair by subjecting it to multiple types of damage, such as tear

tests, wear etc. The first study of the Tc dependence on healing efficiency was conducted and the healing efficiency obtained was comparable to self healing ionomers and supramolecular polymers. The heating behaviour of the magnetic nanoparticles and the healing efficiency was modelled and good agreement was found with experimental results. In a manner similar to biological sensing, colour change was used as a damage sensing mechanism. By studying the BBS interactions in the strained matrix, a linear relationship between the visible colour change and strain/damage was demonstrated in Magpol. The shape recovery property of Magpol was also utilized to develop the first multicycle thermoplastic strain sensor. These self healing and sensing properties are a prerequisite of candidate biomimetic materials for flexible coatings or morphing structures. The actuation behaviour in bending and buckling modes was also studied to demonstrate the work capability of Magpol. The stress, strain and work output was determined for each mode. The buckling mode of actuation showed the highest work output of 16 J/kg, which is comparable with other electroactive polymers. The Mn-Zn ferrite nanoparticle filler loading was optimized for each case and the actuation behaviour of Magpol was also compared to an analytical model. In both cases the experiments matched well with modelling results.

To demonstrate the significance of multifunctional Magpol in a technological application, a novel proof-of-concept biomedical guidewire coating was developed. The coating was capable of sensing wear, undergoing self healing and targeted positioning in a magnetic field. Thus, Magpol possesses attractive characteristics for the development of multifunctional, bioinspired materials with practical applications.

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“The true delight is in the finding out rather than in the knowing.”

-Isaac Asimov

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Abbreviations

μ	Magnetic Permeability
AC	Alternating Current
BBS	Bis(benzoxazolyl)stilbene
DA	Diels Alder
EAP	Electro Active Polymer
EVA	Poly (ethylene-co-vinyl acetate)
FRET	Fluorescence Resonance Energy Transfer
I_E/I_M	Intensity _{excimer} / Intensity _{monomer}
LLDPE	Linear Low Density Polyethylene
Magpol	Magnet Polymer composite
Ms	Magnetic Saturation
PDMS	Polydimethylsiloxane
PEAA	Poly (ethylene-co-acrylic acid)
PEO	Polyethylene Oxide
PMA	Polymethacrylate
PP	Polypropylene
PU	Polyurethane
RF	Radio Frequency
SEM	Scanning Electron Microscope
SMA	Shape Memory Alloy
SMP	Shape Memory Polymer
T _c	Curie temperature
TEM	Transmission Electron Microscope
T _g	Glass transition temperature

Tm melting temperature

UV Ultraviolet

Chapter 1

1. Introduction

The objective of this thesis is to develop a bioinspired multifunctional, artificial material with practical applications which can mimic the functions of multicycle damage sensing, self healing and actuation. This chapter describes the motivation behind the work undertaken in this thesis for the development of a multifunctional Magnet-polymer composite. The current unmet needs in existing materials are listed and the applicability of Magpol as a suitable solution is described. The objectives and scope of the work are provided. The novelty and significance of the work is also described.

1.1. Motivation

1.1.1. Multifunctional Materials

When considering the concept of multifunctionality, especially in a science or engineering framework, we often aim to add new, useful, functions to a structural material.¹ For example, one can focus on the addition of electric, optical, magnetic or other properties that can work in a synergistic fashion to enhance the performance of the material. A multifunctional material is defined to be any material or material-based system which integrally combines two (or possibly more) properties, one of which is normally structural and the other functional, e.g. optical, electrical, magnetic, thermal etc. Such materials show great promise for the next generation of “intelligent” structures which exhibit a significant degree of autonomy in their behaviour and response to the environment.²⁻³ Smart materials are defined as any materials with properties that react to changes in their environment, such that one of their properties can be changed by an external condition, such as temperature, light, pressure magnetic fields or electricity. This change is reversible and can be repeated multiple times. These multifunctional smart materials are relevant in a variety of application spaces due to their potential to reduce size, weight, cost, power consumption, and complexity of components while simultaneously improving versatility, efficiency, and safety. Smart multifunctional composites have found applications in defense, aerospace, structural health monitoring, haptics, adaptive optics, healthcare etc.³⁻⁴

Multifunctionality can be incorporated in a material by one of three design strategies, as proposed by Matic⁵(Figure 1.1). The simplest, is Type 1, where the secondary components are mounted on the primary structural materials; e.g., a coating or lamination on a structural material. The intermediate (Type 2) material consists of components which are embedded in the primary structure, resulting in reduced dimensionality and complexity; e.g., non load bearing antennae in a polymer matrix. The most advanced multifunctional material belongs to the type 3 category. In these materials, the different phases or components intermesh in such a way that it is difficult to distinguish between individual components; e.g., polymer batteries with airfoil shaped packaging is used as a load bearing structure. The third type shows the greatest promise in the development of tailored materials and is the ultimate goal in the development of multifunctional materials. Type 3 materials are designed from the start to cater to all the required functions.

Figure 1.1: Schematic of the types of multifunctional materials (a) Type 1 – subsystems mounted on primary structure, (b) Type 2 - components are embedded within systems or subsystems and (c) Type 3 – Base material is responsible for the integrated functions of components and subsystems ⁵

In recent years, the development of multifunctional composites has focused mainly on soft/polymer systems due to their relative ease of synthesis and versatility in incorporating different components or phases necessary for multifunctionality.⁶

1.1.2. Soft Multifunctional Composites

Soft polymer composites have been in use since natural rubber was embedded with cotton fabric to create the Mackintosh. Compared to some other composites, polymer composites may offer higher corrosion resistance, high strength to weight ratio and more design flexibility.⁷⁻⁸ The properties of the composite can be tailored by changing the polymer matrix or the dispersed filler to obtain the desired functionality. Thus, polymers are an appropriate choice while designing multifunctional composites.⁹

Nature gives us the inspiration for archetypical type 3 multifunctional materials, which are generally made up completely of soft, polymeric protein molecules.⁵ For example, the human skin is capable of sensing, self healing, actuation, thermal regulation and various other processes, all in a single organ. This occurs due to the seamless interconnection between the cells, glands and blood vessels that make up the skin (Figure 1.2).¹⁰ Taking inspiration from biological elements, we can now mimic these designs to create multifunctional materials.

Figure 1.2: Schematic detailing the functions of the skin and structures responsible for each function¹⁰

A key goal of current research is to develop the next generation of bio-inspired multifunctional materials, with “life” functions, thus imparting extended service lifetimes and reliability while also decreasing maintenance and operating costs.^{1, 6, 11} A Living system is equipped for sensing and reacting to environmental prompts, for example, sensing damage to its structure and responding appropriately via a healing mechanism.¹²⁻¹³ Another area of interest is adaptive, flexible morphing structures.¹⁴ Morphing enables the structure to reconfigure its surface and shape to generate force, adapt its aerodynamics or meet styling requirements.¹⁵⁻¹⁶ There is large scope for a material capable of combining these properties in application areas like morphing aircraft wings, wind turbine blades, leading and trailing edges of helicopter rotors,

artificial muscles, structural materials, microfluidic devices, deployable space structures, medical implants and coatings, smart textiles etc.¹⁷⁻²²

1.2. The Problem

In addition to structural functions like strength, stiffness, fracture toughness, and damping, some of the sought after properties in soft materials now include non-structural functions like electrical and/or thermal conductivity, sensing and actuation, energy harvesting/storage, self-healing capability, electromagnetic interference (EMI) shielding, recyclability and biodegradability.⁹ Most research in multifunctional materials has managed to add one or two non structural functions to the basic structural material. However it has not been possible to increase the functionality beyond this number even though there is a requirement for such trifunctional materials.⁹ An example of this is the current unmet need for biomedical guidewires coating materials. Guidewires are a wire or spring inserted into a confined or tortuous space in the human vascular system, to act as a guide for subsequent insertion of a stiffer or bulkier instrument during minimally invasive surgical procedures. Guidewire coatings frequently undergo flaking and wear of the outer polymer coating which has caused serious problems and FDA recalls of these devices from several companies. In addition, enhanced steerability (using a magnetic field) and MRI (Magnetic Resonance Imaging) compatibility are just some of the current research interests in developing the next generation of guidewires.²³⁻²⁶ Here, the ultimate goal is to use a multifunctional material in a guidewire system that is capable of bio-inspired damage sensing, self healing and actuation over multiple cycles that can mimic biological functions. Sensing can include temperature, pressure or damage detection. Self-healing materials are a class of smart materials that have the structurally incorporated ability to repair damage caused by mechanical usage over time. Actuation involves converting mechanical, fluid, thermal, magnetic or electrical energy into mechanical motion

Current research has focused on integrating at the most two out of the three functionalities,^{16, 27-28} with only one group having demonstrated a multifunctional material incorporating all three attributes into a single composite.²⁹⁻³⁰ Thus, the main goal of this thesis is to develop a multifunctional material capable of sensing, self healing and actuation. Also, materials with these functionalities must also be able to undergo multiple cycles in order to prolong the lifetime of the material, in a manner similar to biological systems.

To achieve this goal requires the integration of three different functionalities into a single material. The traditional “best properties” material selection method used for applications having only a single function cannot be used. For multifunctionality, identification of material properties is done simultaneously for all functions. Thus the material selection criteria will have trade-offs.³¹ This poses a significant challenge in material selection and a new design methodology is required to develop a type 3 multifunctional material.^{5, 32}

The material chosen for multifunctional applications should have synergistic properties. In this work, to develop a tri-functional composite requires several steps; material selection, application of energy and its conversion, optimization of each functionality and finally development of a proof-of-concept product.

1.3. Magnet-Polymer composites: A solution

Magpol composites consisting of magnetic nanoparticle filler and a soft polymer matrix are an attractive system for combining multiple functions into a single material.^{16, 33} This is because of the adaptability of both the magnetic fillers and the polymer matrices. Such combinations of magnetic fillers with polymer matrices have also been named ferrogels, magnetic gels, magnetic field sensitive gels,³⁴⁻³⁶ magnetorheological elastomers³⁷⁻³⁸ and magnetoactive polymers³⁹⁻⁴⁰.by different groups depending upon the nature of the filler and the polymer matrix. For example, Hydrogels, silicones, polyurethanes and rubber are potential matrix materials for Magpol composites; The filler can differ in its magnetic properties and can include soft as well as hard magnet fillers.^{21, 41-43} Previous research has focused on imparting Magpol with the properties of remote, contactless magnetic actuation, actuation in various modes, high actuation strain, self-sensing and quick response.⁴⁴⁻⁴⁵ Magpol has been studied as an actuator in the presence of a static magnetic field and can also generate heat when placed in an AC (Alternating Current) magnetic field, also called an AMF (alternating magnetic field).⁴⁶⁻⁵¹ This energy conversion is useful for type 3 multifunctionality. Thus Magpol is a promising multifunctional material.

1.4. Objectives and Scope

The objective of the project was to perform an experimental and theoretical study of magnet-polymer composites to obtain a multifunctional, multicycle material that could ultimately be used in a next-generation guidewire coating. In particular, the strain/

damage sensing, self healing and actuation properties of Magpol were studied. The Mn-Zn ferrites ($\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$) were chosen as the magnetic filler due to their properties of tuning M_s and Curie temperature to enable self regulated heating for self healing and actuation. Thermoplastic EVA (Poly (ethylene-co-vinyl acetate)) was chosen as the polymer matrix. Thermoplastics are polymers that become pliable or moldable above a specific temperature and solidifies upon cooling. EVA is a copolymer of ethylene and vinyl acetate. Its chemical structure results in a low melting temperature which enables efficient self healing, shape memory properties promotes multicycle damage sensing and its low elastic modulus is required for actuation. The experimental work focused on the synthesis and characterization of magnetic $\text{M}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$ ferrite nanoparticle fillers, Poly (ethylene-co-vinyl acetate) (EVA) matrix and the Magpol composite. The magnetic properties of the Mn-Zn ferrite nanoparticle fillers were first optimized and tuned for each of the functionalities; e.g. Curie temperature of the filler was tuned to regulate the heating of the nanoparticles in an external alternating magnetic field (AMF) which in turn controlled sensing and self healing,^{48,189} while saturation magnetization (M_s) was optimized for actuation. EVA was chosen as the matrix and the mechanical and thermal properties were characterized. Visible color change indicating strain sensing was achieved by the addition of the mechanochromic dye Bis(benzoxazolyl)stilbene. The strain response was studied and dye concentration in Magpol was optimized. The self healing ability of Magpol was studied in response to various types of damage. The combined ability of sensing and self healing was also studied over multiple cycles. The actuation behaviour of Magpol was studied in two modes (bending and buckling). The work loop method was used to determine the efficiency of actuation and compared to other actuators using Ashby charts. After optimization of each functionality, a proof-of concept guidewire coating was developed. Mathematical modeling and computer simulation was also performed to understand the self healing and actuation behavior as a function of magnetic particle filler concentration.

1.5. Novelty and significance

The novelty of this project lies in the simultaneous incorporation of three functionalities into a thermoplastic polymer-magnet composite. The functionalities are; actuation by an external magnetic field, strain sensing molecules and self healing ability. There is a synergistic interplay between magnetic ferrite nanoparticle fillers, a thermoplastic

shape memory matrix, and organic dye molecules. This interplay has resulted in the synthesis of a new Magpol composite capable of multifunctionality.

Magnet-polymer composites represent a versatile class of magnetic field controlled elastic materials.⁵² The polymer matrix together with the magnetic properties of the filler particles allows the manipulation of the behavior of the composites by remote, external magnetic fields. These characteristics show great potential for various applications where low weight, high strain, soft actuators are required; e.g. in artificial muscles, morphing (shape changing) aerospace structures like airplane wings, optical and biomedical devices, etc.^{4, 53-54}

The ability of the magnetic particles to generate heat through hysteresis losses in a radio frequency AC field is used to drive thermally activated reactions. The ability of the polymer matrix to self heal using the heat generated by the nanoparticles has been studied. In order to prevent matrix degradation or scar formation during the self healing process, healing in Magpol is controlled by Curie temperature tuned magnetic nanoparticles. The heat generated by the magnetic filler for healing to occur, must not exceed the decomposition temperature of the individual components of the Magpol composite. Thus, the use of T_c tuned magnetic nanoparticles to drive the self healing process over multiple cycles is a novel factor in this composite.⁵⁵ This is an advantage over current methods where limited healing and scarring at the healed region can result in problems.²⁹

Magpol was found to be capable of sensing plastic deformation, displaying a change in its fluorescence emission spectra. Deformation sensing using dye molecules has only been studied in homopolymers like linear low density polyethylene (LLDPE) and polypropylene (PP) over a single cycle.⁵⁶⁻⁵⁷ This work extends the strain sensing ability to the shape memory ethylene vinyl acetate (EVA) copolymer. Shape memory based recovery of the original dimensions of Magpol is used to aid in the subsequent recovery of strain sensing ability to develop a multicycle strain sensor. This dual mechanism of magnetic nanoparticle heating for multicycle self healing and strain sensing is important in the development of bio-inspired materials.

The third functionality; actuation, was also studied in different modes in order to impart a flexible, artificial muscle behaviour to Magpol. Novel buckling based actuation behaviour was observed. Buckling was achieved through the use of high modulus EVA

and suitable sample constraints. The work capacity that could be obtained via buckling of thermoplastic Magpol exceed that obtained by bending in this study as well as in previous reports. In fact, work capacity increased to a level sufficient to compete with buckling based electro active polymer actuators.

The significance of this project was enhanced by the choice of a commercial biocompatible polymer, widely used in manufacturing, as the matrix of the composite. The strain sensing is also achieved through incorporation of commercial additives. By combining the functionalities into a single composite, Magpol becomes a candidate material for the development of next generation applications.

Magpol was used, for the first time, to construct a proof of concept medical guidewire coating that can be used for MRI interventional therapies. This opens new avenues for the development of damage sensing, self healing and magnetically steerable guidewire for MRI compatible biomedical applications.

1.6. Description of the report

Chapter 2 introduces the theoretical background related to the project. It includes a description of the self healing and strain sensing properties of magnet-polymer composites, along with a brief discussion of their actuation properties.

Chapter 3 consists of the experimental procedures used for synthesis and characterization of Magpol. It includes material selection, preparation and characterization of the magnetic nanoparticle filler, polymer matrix and composite. Experimental methods to evaluate the sensing and self healing efficiency of Magpol are described. The procedure used to calculate work output during actuation is described. Details of the computer software packages used during the different modeling work are provided.

Chapter 4 details the characterization of the magnetic filler and the polymer matrix as well as the properties of the composite. The physical, thermal, and magnetic properties as well as the heating ability of the composite are studied.

Chapters 5 to 7 describe the three functionalities of Magpol in detail. The response, efficiency and mechanism of self healing, sensing and actuation of Magpol are discussed.

Chapter 8 describes the development of a proof of concept Magpol guidewire that can be used for MRI based surgical interventions.

Finally, in chapter 9 the important conclusions of this work are listed and future avenues for research in Magpol based multifunctional materials are discussed.

Chapter 2

2. Literature Review

This chapter reviews the background and current technologies involved in creating the functionalities which will be incorporated in to Magpol. Beginning with self healing, the currently available technologies are described and the rationale for choosing thermally triggered healing is discussed. Next, mechanochromic strain sensing is reviewed and the strategy used for strain sensing in Magpol is elucidated. Finally different types of actuation mechanisms are reviewed and their efficiency compared to Magpol. State-of-the art technologies for each of the functions are also described. The theoretical models of magnetic nanoparticle heating, self healing and actuation used in this work are also discussed.

2.1. Multifunctional soft composites

Composite materials lend themselves naturally to the concept of multifunctionality, i.e., where a material performs more than one function. Traditionally, polymer composites have been used to improve mechanical or load bearing structural properties of polymers, but there is a demand for, additional functions being added to polymers.⁸ The design of such composite materials is usually influenced by biological structures, where the material continues to retain its functionality even at small size. This correlates to Matic's classification of type 3 multifunctional materials.⁵ Such composites will usually have one phase dispersed at the nano scale, such that the different material phases are in complete contact and are difficult to distinguish.

According to a recent review by Gibson, polymer composites are largely classified as either having a) multiple load bearing or structural functions, b) a function unrelated to structure or mechanical properties and c) both a structural and non-structural component.⁹ Structural composites encompass conventional composite materials as well as hybrid, multiscale materials. Non-structural applications cover a broad range from electrical or thermal conductance, self healing, energy harvesting and storage, sensing, actuation, electromagnetic shielding etc.^{18, 21, 58-59}

When designing a polymer composite for load bearing applications, mechanical properties such as strength, fracture toughness, modulus, fatigue etc. are given priority. It has been shown that the introduction of nanoscale fillers can dramatically improve these mechanical properties. For example, Manjunatha et al. showed that increased strength was obtained by introducing silica micro particles as a filler, while rubber particles were shown to increase the tensile fatigue life of glass fiber-epoxy composites threefold⁶⁰. The use of nanoparticles instead of the more commonly used micron sized fillers has also been shown to have a positive effect on the composite structural properties.⁶¹ Improvements in strength, strain and modulus have been found by the addition of different nanofillers such as alumina nanoparticles, carbon nanofibers and silica nanoparticles.^{60, 62}

The addition of nanoscale fillers to composites has broadened the scope of composites beyond their traditional role as load-bearing elements. The most common additional function is that of electrical or thermal conductivity. Generally, polymers are poor conductors, but there have been significant improvements in these areas through the

addition of carbon and nanometallic based fillers. If the concentration of these fillers exceeds the percolation threshold limit, the polymers become conducting.⁶³⁻⁶⁴ The conducting nature of the composite can also be exploited for sensing and/or actuation. Sensing using carbon based fillers are the most popular and have been reviewed by Li et al.⁶³ Shape-memory polymers (SMPs) are polymeric smart materials that have the ability to return from a deformed state (temporary shape) to their original (permanent) shape induced by an external stimulus (trigger), such as temperature change. Such shape memory polymers have also shown promising results for the development of actuators, but piezoelectric based composites remain the most popular materials for electromechanical transduction.⁶⁵ The Stanford multi actuator receiver transduction (SMART) layer is a good example of a commercially produced piezoelectric technology.⁶⁶ The electromechanical transduction ability of the composite can also be utilized for energy harvesting and storage, where the material itself can act as a battery; e.g. Pereira et al. used carbon/epoxy laminates embedded with lithium cells to store energy while maintaining the mechanical properties.⁶⁷

Due to the urgent need for sustainability, another set of functions that have become the focus of current research, are self healing and recyclability.⁶⁸ There are several self healing technologies currently being researched. These will be discussed in the next section. Thus, by the addition of suitable fillers, we can obtain multiple functions in a polymer matrix composite.

Based on the current challenges and opportunities, the focus of this thesis is the development of a damage sensing, self healing and actuating composite material. Such materials are of great importance in the development of structural health monitoring and remediation systems, advanced aerospace structures, biomedical and optical devices etc.^{3, 7, 31, 69} An actuating material which is also capable of strain sensing and self healing is extremely useful in these applications since there is continuous feedback on the integrity of the component and the capability of repair in case of damage. The literature review will be focused on these three attributes. Prior research has been carried out on the development of composites having a combination of, at the most, two of the functionalities. Simultaneous damage sensing and self healing have been investigated by several groups; e.g. visible color change on damage and self healing on exposure to visible light has been recently reported by Urban et al.²⁸ Bleeding of fluorescent markers on damage and self healing via infiltration of the damaged area by

a healing agent supplied through hollow fibers was demonstrated by Bond et al.² Combined strain sensing and actuation has also been studied. Nguyen et al. studied actuation and were able to measure the strain using a magnet-polymer composite material containing a graphite filler.⁷⁰ Ionomeric polymer-metal composites which were capable of self healing and actuation were synthesized by Aabloo et al.⁷¹ Duenas et al. also developed a self healing morphing composite based on magnet-polymer composites.²⁹⁻³⁰ Figure 2-1 shows a schematic of the development of tri-functional Magpol which will also underlie the structure of the thesis.

Figure 2-1: Schematic representation of the development of Magpol with multicycle self healing, optical damage sensing and magnetic actuation functionalities

Synthesis of a damage sensing, self healing and actuatable polymer composites is provided below.

2.2. Self Healing Polymer systems

When we compare different classes of materials to which self healing can be imparted, polymers stand out due to their chemical structure. Polymers are chain like structures constructed from monomers; bio-polymers form the basis of biological systems. These polymer chains are capable of greater mobility compared to other rigid materials. This mobility is advantageous for self healing as it allows for the molecules responsible for self healing to repair damage in reduced time and at greater volumes.

To mimic biological systems a self healing material must possess the following properties: a) ability to function in a variety of environments, b) Capable of undergoing

repeated damage and recovery. The components required for self healing (e.g. monomers or catalysts) should not get depleted. And c) After undergoing a cycle of self repair, the properties of the material should be restored, including mechanical, chemical and thermal properties.

Self healing can occur in either thermoset or thermoplastic polymers. We concentrate on polymers that can undergo multiple cycles of self healing. Self healing can be achieved by via intrinsic mechanisms or stimulated repair e.g. light induced healing is already commercially available as a coating material from Bayer.⁷²

2.2.1. Self healing thermosets

Thermosets are chemically crosslinked polymers. To achieve self healing chemical reactions should occur. These chemical reactions can be of two types, depending on the healing strategy; (a) when bonds between different polymer chains are damaged, new precursors can be introduced into the region, which will undergo polymerization and repair the damage with new material.⁷³⁻⁷⁴ This method is suitable when there is wear type of damage and material is continuously lost during operation. (b) Scission of existing bonds, followed by re-polymerization. This strategy is more applicable when fracture occurs.⁷³

In cases where new material must be introduced into the damaged region, the precursors can be stored in vascular networks or microcapsules that are dispersed throughout the material. The idea of microcapsules was initially proposed by White et al., who utilized an encapsulated dicyclopentadiene (DCPD) precursor in a urea-formaldehyde (UF) shell (Figure 2-2).⁷⁴⁻⁷⁶ The polymerization reaction was carried out with the help of a ruthenium-based Grubbs' catalyst also embedded in the epoxy resin matrix. When the specimen fractured, the microcapsules embedded within the matrix also cracked, resulting in release of the precursor and catalyst and subsequent mixing within the crack volume. This resulted in "filling up" of the crack due to in-situ polymerization, ultimately rebonding the damaged surfaces together.

The disadvantage with the microcapsule based method is the limited precursor content that can be added to the epoxy matrix. Healing cannot take place when the supply of precursors is exhausted. A method that can circumvent this problem is to introduce a vascular network within the matrix which has a larger volume of the healing agent spread through the system (Figure 2-3). Hollow glass fibers have been used by Bond et

al. to simulate the vascular network within the composite material.² The glass fibers are filled with resin and a hardener, damage and healing then occur in a manner similar to that of the microcapsules, but with the added advantage of higher precursor availability.

Figure 2-2: Microcapsule based self healing. Damage to the matrix causes cracking of capsules holding DCPD precursors and Grubbs catalysts. The contents spill out into the crack, mix and polymerize, resulting in crack closure.⁷⁷

Toohey et al.⁷⁸ developed a self-healing material with a 3D vascular network containing two separate phases of healants. Their design was inspired by the epidermis of the skin, which is continuously supplied with nutrients and healing agents *via* blood vessels. In a manner similar to blood being pumped through veins, the healing agent in their material was placed under constant pressure, resulting in larger healing volumes and a greater supply of the healing agent. This allows the material to undergo a large number of healing cycles. However, the cost and scale up of this material will be extremely

challenging.

A different approach to self healing in thermosets involves the scission and subsequent formation of chemical bonds within the material (intrinsic self healing) (Figure 2-4).

Figure 2-3: Vascular network of hollow glass fibers containing healing resin and hardener. The fibers are refillable and hence the composite is capable of multiple cycles of damage and recovery.⁷⁷

This approach does not require the addition of external precursor healing agents, hence such materials are easier to manufacture and do not suffer a loss in mechanical properties. This technique also allows for multiple healing cycles to occur without any complicated material architecture. A typical example of bond scission and re-formation is the Diels-Adler (DA) reaction using furan-maleimide functionalized polymers that cross-link through the DA bond.⁷⁹⁻⁸¹ DA bonds have been introduced into epoxy matrices as well as elastomers and rubbers, demonstrating its versatility. The DA reaction is temperature dependent, an external heat source is required to drive the self healing reactions.

Figure 2-4: Intrinsic self healing without the addition of healing agents involves bond scission at the damaged site followed by formation of new bonds within the cracked region. In the DA reaction, bond formation occurs between the furan and maleimide moieties through a cycloaddition reaction with an appropriate thermal stimulus⁸¹

Another thermally activated system which utilizes the addition of a second thermoplastic phase within the thermoset was devised by Hayes et al.⁸²⁻⁸³ A thermoplastic solution of poly(bisphenol-A-co-epichlorohydrin) (PBE) was blended with epoxy resin. After damage, the material can be heated above the melting temperature of the thermoplastic. This will cause the thermoplastic to flow into the crack and seal it. Meure et al. also adapted this method to poly(ethylene metacrylic acid) (EMAA).^{77, 84} and mixed EMAA particles into the epoxy matrix and used an edge notched bar to damage the specimen. After heating the matrix above 150°C, they observed healing efficiencies of up to 100%.

2.2.2. Self healing thermoplastics

Due to the non cross-linked nature of thermoplastics, the polymer chains have far greater mobility and are thus able to undergo self healing reaction at a much faster rate and in a similar manner. Thermoplastic polymer chains do not require large input of energy for self healing. Simply heating a polymer above its glass transition temperature (T_g) is sufficient to promote chain mobility. The glass transition temperature (T_g) is defined as is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle "glassy" state into a molten or rubber-like state, as the temperature is increased. Jud and Kausch studied the ability of a poly(methyl methacrylate) (PMMA) -poly(methoxy methacrylate) (PMEA)

copolymer to heal after fracture. They clamped the damaged copolymer surfaces together and heated the sample to 5°C above its T_g . They observed recovery in mechanical properties of upto 80-120%.⁸⁵

The self healing process can be described by the reptation model. Reptation is the thermal motion of very long linear, entangled macromolecules in polymer melts, while the reptation theory describes the effect of polymer chain entanglements on the relationship between molecular mass and chain relaxation time (or similarly, the polymer's zero-shear viscosity). This theory states that, when the temperature of the polymer is raised above its glass transition temperature (T_g) the polymer chains show higher mobility causing them to diffuse across a damaged region and entangle, restoring the material properties and increasing the chance of bond formation.⁸⁶ This process occurs in sequential steps; (a) surface rearrangement, (b) surface approach, (c) wetting, (d) diffusion and randomization (Figure 2-5). Temperature influences the efficiency of the reptation process.

In their work, Jud and Kausch observed that as the temperature exceeded the T_g , the interface between damaged surfaces gradually disappeared.⁸⁵ Above T_g , polymer chains at the damaged interface could interdiffuse into the opposite side. This diffusion process resulted in chain entanglement and interfacial closure. Over time the orientation of the chains will randomize and the crack will completely disappear. A schematic presentation of this process is presented in Figure 2-5

A special case of thermoplastic repair was observed by Fall et al.⁸⁷ who found that ionomers were able to self heal after ballistic puncture. It was noted that self healing was achieved due to the heat generated at the impact site by the ballistic projectile. The maximum temperature exceeded the melting temperature of the polymer, enabling the polymer to flow into the puncture site and seal the wound. Subsequent studies by Kalista suggested that ionic groups present in Surlyn[®] were not necessary to obtain healing as non-neutralized Nurcel[®] polymers also showed healing under similar conditions.⁸⁸ Varley et al. further elucidated the self healing process.⁸⁹ According to their experiments, self-healing was a two-stage process. Immediately after impact, an elastic response dominates healing. The material showed a partial elastic recovery of extension. This is followed by the more traditional interdiffusion process described by Jud and Kausch. This work provided a new insight into the mechanism of self healing which can be extended to other materials that exhibit such elastic recovery. A

significant drawback of this method is that low velocity damage cannot heal due to inadequate heat generation during damage.

Figure 2-5: Mechanism of self healing in thermoplastics according to the reptation theory: surface rearrangement, approach, surface wetting, diffusion across interfaces and finally chain randomization⁷⁷

This combination of elastic recovery followed by interdiffusion is also observed in biological wound healing. As a wound begins to heal there is a change in the mechanical stress around the wound as material is redistributed around the damaged region. An analogous material system that can mimic this effect is Shape Memory Assisted Self Healing (SMASH) developed by Mather et al.⁹⁰ When the transition temperature of the polymer is exceeded, it contracts, bringing the cracked surfaces in contact with each other. Application of heat for longer time results in welding at the interface. This method was later applied to corrosion resistant coatings where repeated healing could be achieved.

2.2.3. Other State of the art Self Healing systems

Current research continues to focus on microcapsule based healing agents as seen by work done by Braun et al.⁹¹ and Binder et al.⁹² as well as Diels-Alder based reactions. Exchange reactions are also being studied to obtain self healing properties. Thiol based disulfide exchange reactions for reversible room temperature based crosslinking were studied by Matyjaszewski et al.⁹³⁻⁹⁴ This group also studied thiuram based disulfide crosslinking. Supramolecular chemistry based self healing is generating the most interest recently and several groups are actively studying these polymer systems including Weder et al. , Bao et al. , Guan et al. and Waite et al.^{13, 95-97} Bao et al. synthesized a supramolecular organic polymer using nickel microparticles as a filler. The composite could self heal mechanical and conductivity damage in ambient conditions.⁹⁸ Their material was also pressure- and flexion-sensitive, and therefore suitable for electronic skin applications. Li et al. developed a shape memory polymer (SMP) based syntactic foam containing dispersed thermoplastic particles to repair impact damage.⁹⁹ The shape memory capability requires the material to be “programmed” within a temperature range before it is subjected to damage, after which heating causes cracks to close and intermolecular diffusion to occur, allowing the material to heal.

A recent review by Mauldin et al. and Roy et al. gives an current overview of the different self healing polymers under study.¹⁰⁰⁻¹⁰¹ From the review, it is evident that self healing thermoplastics are more efficient and scale-up is less challenging as compared to thermosets. A commonality amongst self healing thermoplastics is the need for thermal energy to drive self healing reactions. A major disadvantage in this approach is the inability to achieve heating and healing *in situ*. The components must be removed and placed in a furnace or other device to raise the temperature. Smaller hand held devices can produce inhomogeneous heating, which can cause material degradation or pyrolysis in the region closest to the heating element, while insufficient heat is transferred to components away from the source.

Magpol provides an ideal alternative to the development of a self healing thermoplastic due to the capability of magnetic nanoparticles to generate heat in the presence of an AC field through relaxation losses. Uniform heating and efficient healing is possible due to the homogenous distribution of nanoparticle filler in the matrix.

2.2.4. Self Healing in Magpol

Duenas et al. used iron oxide nanoparticles as fillers in ionomer composites to achieve localized heating and healing *in situ*.³⁰ Corten et al.,¹⁰² and Bowman et al.⁴⁷ also followed a similar strategy to develop self healing composites. To overcome the problem of overheating and pyrolysis observed with the use of iron oxide fillers, Bowman et al. used low Curie temperature CrO₂ nanoparticles as a heating agent. CrO₂ has a T_c of 113°C which was suitable to reverse the DA linkages in the polymer matrix. The T_c of CrO₂ cannot be tuned and has limited use in materials where the processing temperature differs from its T_c. Frequently used filler like iron powder and Ni particles have a high T_c and exhibit thermal degradation, pyrolysis and prolonged heating can cause distortion of the matrix.⁴⁷ Thus there is a need for a T_c tuned filler that can be used to trigger self healing.

To prevent uncontrolled heating of the composite, “failsafe” or self-regulated heating in Curie temperature controlled nanoparticles can be utilized for heating by an external AC magnetic field;¹⁹⁵ this can be combined with a shape memory polymer to enable shape recovery. The Curie temperature switch prevents overheating/ pyrolysis, extending the lifetime of the composite. Therefore, to develop the self healing functionality in Magpol, a shape memory thermoplastic polymer matrix with Curie temperature tuned magnetic nanoparticle fillers is required.

The next section describes the second functionality; strain/ damage sensing and the technologies available to achieve it.

2.3. Damage sensing in polymer composites

The first step in the development of a self repairing system is the detection of damage or stressed areas before critical failure occurs. Very few structural materials are inherently capable of sensing damage or strain and rely on external sensing elements. The prevalent trend is to introduce sensor networks that cover the structure and generate a signal when damage is detected. Damage can be classified as macroscale cracks, pores, inclusions, microscale precipitates, voids etc.¹⁰³ Different technologies are currently being used to detect this damage depending on the size of the damaged region. Figure 2-6 gives an overview of the different sensor sizes and the damage detectable by each sensor

Figure 2-6: Sensor selection space comparing size of detectable damage with sensor size for various sensing methods¹⁰⁴

From Figure 2-6, it is obvious that there is a need for developing a material capable of sensing damage at small size scales where conventional methods encounter problems such as resolution and cost. Unlike integrated sensor networks or optical fibers that cannot cover the entire volume of the material, and require continuous energy input, there is a need for homogenous distribution of strain sensing moieties within the material such that an integrated composite is formed. Self sensing can be achieved by incorporation of carbon nanotubes or graphite at percolation concentration into the polymer matrix.^{63-64, 70} Changes in resistance with deformation and initiation of microcracking during loading have been monitored. S. Karagiovanaki et al. developed a polymer composite consisting of polyester matrix and iron oxide nanoparticle fillers capable of strain sensing via the alternation of Reluctance induced by strain. The sensing probe consisted of an electromagnet and a Hall sensor.²⁵⁴ A. Trinchi et al. used magnetic nanoparticles embedded into anti-corrosion primer coatings to detect corrosion. By monitoring changes in the magnetic state of the nanoparticles due to oxidation between magnetite and haematite, corrosion could be detected.²⁵⁵ The methods discussed above require continuous monitoring and identification of the damaged region can be difficult. An alternative to this energy intensive process would be to enable damage detection through an optical method. A few strategies exist that

utilize either visible, ultraviolet (UV) or near infra red (NIR) light to detect strain in a material, with varying success as described below.

Bruns et al. utilized a biological protein template to detect nanoscale strain within a polymer matrix.¹⁰⁵ They utilized an engineered thermosome chaperonin protein containing a donor and receptor Fluorescence Resonance Energy Transfer (FRET) molecule to a polymer chain. Nanoscale cracks in the polymer caused the donor and acceptor molecules to separate, resulting in decreased fluorescence signal. They also studied the reverse mechanism, where strain caused the thermosome to relax into a state where the FRET pair can form, resulting in increased signal. Another optical method for strain sensing was devised by Prakash et al.¹⁰⁶ They synthesized grapheme-poly(methyl methacrylate) coatings and used Raman band shifts to detect strains of ~0.3% in the films. Withey et al. developed a similar technique, using SWCNTs (Single wall carbon nanotubes) embedded in a polymer.¹⁰⁷ Any strain in the underlying structure is transferred to the CNT causing a shift in the NIR spectra allowing strains measurements of ~0.55%. Although these methods are suitable for large area coverage, it is difficult to incorporate these materials into structural composites.

The incorporation of mechanoresponsive molecules into the polymer composite has been suggested as an alternative to external sensing elements. Though these methods are relatively recent, they show great promise for low cost facile detection without the need for complex instrumentation.¹⁰⁸ Colour change is observed due to break-up of nanoscale aggregates, which suggests that displacements of ~100 nanometers can be detected by these dyes.

2.3.1. Mechanochromic sensing

Mechanochromic sensing relies on molecules called mechanophores. Mechanophores are molecules that are susceptible to mechanical force, such that bond scission can be achieved by the application of a suitable mechanical stimulus.¹⁰⁹ The type and magnitude of bond scission depends on applied force and can be predicted accurately. A mechanophore is capable of several different responses including scission of selected regions in the polymer chain, extrusion of a small molecule from the chain and cycloreversion or isomerization reactions of selected groups. (Figure 2-7). Mechanophores have been adapted as strain sensors through different strategies. The first method is to covalently attach the mechanophore to the polymer chain, such that

the molecule forms part of the polymer backbone. The second method uses physical interactions between the mechanophore molecules and the polymer chains to sense mechanical deformation.¹¹⁰⁻¹¹³ In both methods, force is transferred through the polymer backbone to the mechanophore molecules and interaction strength between the matrix and the molecules determines the usefulness of the mechanophore as a sensor.

Figure 2-7: Schematic of mechanophore responses to applied force. Reactions include both bond scission and isomerization due to presence of mechanically labile bonds.¹⁰⁹⁻¹¹⁰

2.3.2. Chemical Mechanophore Polymer interactions

In covalently linked mechanophore-polymers, the applied force causes a chemical change in the molecule. This chemical transformation is usually detected via a visible colour change or a change in the fluorescent emission spectrum. The chemical transformation can be an isomerisation reaction or a scission reaction that includes the release of a component group or a cycloreversion reaction.

Sottos et al. developed the first covalently linked mechanophores by integrating a spiropyran dye into the backbone of poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA).^{109-110, 114-115} Both tension as well as compression of the material led to a visible colour change from colourless to deep red/purple. The colour change could be attributed to a selective scission reaction in the spiropyran molecule. Specifically, the C-O bond of the spiropyran was broken in a ring opening reaction. The planar merocyanine thus formed had a longer absorption wavelength than the spiropyran molecule, causing a change in colour from yellow to purple/red. This reaction was reversible on exposure to light, which triggered a loss of colour and re-formation of spiropyran. Figure 2-8 shows a schematic representation of the colour

change on elongation on the macro scale as well as the reversible ring opening that occurs on the molecular level within the polymer chains.

Figure 2-8: Mechanism of Spiropyran based mechanophore strain sensing. Both elongation and compression cause the spiropyran molecule to undergo a ring opening reaction to produce red merocyanine.¹⁰⁹⁻¹¹⁰

2.3.3. Physical Mechanophore Polymer interactions

In the previous chemical based system, it has been reported that the introduction of spiropyran molecules into the polymer backbone causes a reduction in the mechanical properties of the polymer. To overcome this problem, it would be preferable to introduce mechanophores that can physically interact with the polymer matrix without chemical side reactions. An alternative strain sensing mechanism was developed by Pucci et al. and Weder et al. using this concept.^{56-57, 108, 116-121} They called the physically interacting molecules “mechanochromic” dyes. These mechanochromic dyes could self assemble within the polymer matrix into supramolecular aggregates, called excimers, whose emission spectrum differs from that of a single dye molecule. The size of the supramolecular aggregate excimers depends on the miscibility and concentration of the dye within the matrix as well as the crystallinity of the surrounding polymer.⁵⁷ On plastic deformation, these supramolecular aggregates dis-assemble under the influence of the interacting polymer matrix. When the matrix is plastically deformed, the polymer chains slip and align along the force direction. This movement of chains caused the mechanochromic molecules associated with the chains to separate, breaking up the

supramolecular aggregates. The break-up of the aggregates resulted in either bathochromic shift J-bands or hypsochromic shift H-bands due to the presence of individual dye molecules that had broken away from the aggregate.¹⁰⁸

The unique optical properties of the mechanochromic aggregates could be attributed to π - π stacking interactions between the mechanophore planar aromatic backbones. The change in the emission bands of the mechanophores in different arrangements can be explained by the theory of molecular exciton coupling where interactions between an excited aromatic molecule and its ground state result in excimer (excited dimer) formation. Figure 2-9 is a schematic representation of the mechanism of strain sensing of mechanochromic dyes.

Figure 2-9: Mechanism of strain sensing using mechanochromic dye molecules. In the original state, the molecules stack together as supramolecular assemblies with a certain emission spectrum. Strain causes polymer chains to slip and reorganize, overcoming supramolecular interactions between dye molecules. Individual dye molecules exhibit change in the emission spectrum, indicated by a color change.^{120, 122}

Weder *et al.* reported the first Oligo(p-phenylene vinylene) (OPV) based molecular strain sensor in linear low density polyethylene matrix.¹²³ With mechanical deformation applied to the polymer, the macromolecule chains unfolded, leading to microfibrils in the crystalline and amorphous region, breaking up a majority of the OPV aggregates. These molecular rearrangements resulted in change in colour of emission from orange-red (~650nm) aggregates to green monomeric species (500-550nm), and this change was related to the increment in monomer to excimer ratio due to mechanical stimuli. Similar studies were reported employing bis(benzoxazolyl) stilbene (BBS) and perylene individually as mechanophore in polymer matrices.^{57, 116, 119} They demonstrated the effect of dye concentration and material deformation on the emission

characteristics of BBS/polypropylene and BBS/ poly(1,4-butylene succinate) systems. At low BBS concentration (0.02wt%), the film exhibited blue monomer emission. However, at higher BBS concentration (>0.02wt%), green excimer emission was generated. During tensile deformation, molecular reorganization broke up BBS excimer-type arrangements, resulting in blue emission of single molecules. Another study demonstrated this effect with perylene/polyethylene) and perylene/poly(vinyl alcohol) systems. Upon tensile deformation, perylene aggregate broke up, changing the emission from red to yellow-green.¹¹⁹

2.3.4. State of the art mechanochromic sensors

The Spiropyran based mechanochromic sensors pioneered by Sottos, White and Moore are popular due to the visible detection of strain by the unaided eye.^{114-115, 124} A similar sensing technology has also been developed by Urban et al. They developed an azobenzene crosslinked brominated vinyl ester polymer network. The covalently “built-in” azobenzene crosslinker acts as a reversible, light emitting group that can sense stress/damage, and respond by changing its fluorescence emission.^{28, 125} Reversible metal ligand – polymer interactions were used to produce a mechanochromic response. Such behaviour has been observed in platinum(II) complexes where force-induced structural rearrangement results in an increased number of shorter intermolecular Pt–Pt interactions, yielding a change in the PL spectra. This phenomenon has been used in the construction of mechanochromic Pt-PMMA films by Burnworth et al.⁹⁵ Recently, a new concept using diffraction of light through soft polymer based photonic crystals has been investigated as a mechanochromic sensor. 2D and 3D self assembled polystyrene (PS) microspheres in a PDMS matrix could produce a mechano-responsive colour change. The PS microspheres assemble into a certain crystal structure which changes on deformation, thus changing the lattice constant and the diffraction wavelength.¹²⁶⁻¹²⁹ A FRET process was also studied as a mechanochromic material for nanoscale force sensing. Donor (D) and acceptor (A) molecules interact *via* dipole–dipole interactions which forms the basis of FRET. Jee and Lee quantified the colour change due to mechanical deformation of a rhodamine based polyethylene FRET system.¹³⁰ Reversible strain sensing using mechanochromic dyes was achieved by Wu et al. using a shape memory polyurethane matrix and a tetraphenylethylene dye.¹³¹ The composite was also responsive to temperature and solvent changes. Bao et al. used a different methodology to obtain reversible sensing, using BBS mechanophores covalently

attached to a polyurethane elastomer.¹³² Cellini et al. used a thermoplastic polyurethane elastomer to obtain reversible sensing.¹³³⁻¹³⁴ A recent review article by Haehnel et al. gives an overview of current dye based mechanochromic sensing technologies.¹³⁵

From the review above, it can be determined that mechanochromic dye incorporation is a promising method to develop a strain sensing Magpol composite; while among the available dyes, the Stilbene BBS derivative has proved to be the most viable as it is a commercially available dye commonly used as a plastic additive; it has high resistance to solvent extraction and high melting point. The use of BBS dyes as commercial plastic brighteners is advantageous from the cost perspective and chemical processes are not required for dye incorporation. A drawback with the mechanochromic dye based sensing method is the single cycle use of such materials.^{133, 136} Once the material is plastically deformed and changes color, it is not possible to regain the original material. This limitation provides an opportunity for the development of a shape memory material, where the material recovers its original shape, it can also recover the original color through re-formation of the excimer dye aggregates.¹³² Therefore for the development of the second functionality of multicycle strain sensing, Magpol requires both the BBS dye molecules as well as a shape memory polymer matrix as described below:

2.3.5. Strain sensing Magpol

The shape memory of Magpol can be utilized for a dual role; Firstly, Magpol can return to its original shape following an extended period of large inelastic deformation. Secondly, this shape control can be used for multicycle strain sensing. Magpol can act as a “memory chromic polymer”; the shape memory effect (SME) can be exploited to change color on inelastic deformation, indicating damage. Application of suitable external stimulus triggers shape memory properties, resulting in self healing. The original color is also recovered, which demonstrates successful repair. In both cases, the temperature stimulus is generated *via* an applied alternating magnetic field (AMF) which induces heating of the magnetic nanoparticle filler. The resulting temperature rise triggers recovery of the original dye aggregates, enabling repeated sensing.

This multicycle strain sensing fulfills the second requirement for the development of a bio-inspired multifunctional Magpol. The next section reviews the current research on the different types of actuator technologies and compares it to actuation studied in

magnet-polymer composites; thus presenting the third functionality of Magpol.

2.4. Actuation

According to Huber, an actuator is defined as “a controllable work-producing machine”.¹³⁷ Commercially available actuation systems rely on either high modulus – low strain materials or multi-component systems. The former includes piezoceramics and magnetostrictors, while the later more commonly used systems include hydraulic, pneumatic or electromagnetic devices. While one type of system may operate at high stresses but low strains, others may produce large strains or displacements with a tradeoff of low stress. New research is focusing on shape memory alloys (SMAs) which generates large strains as well as high stresses.¹³⁸ Unfortunately, the requirement for a thermal trigger limits the material’s response time as well as its service life. This has resulted in a gap in current actuator technologies available. This gap lies between the high stress-low strain and the low-stress – high strain groups and is the region where most current research in soft actuator systems is focused. Figure 2-10 shows the limits of actuation stress and strain obtained in current actuator systems.

Figure 2-10: Actuation stress vs actuation strain observed in current actuator systems. The bold lines indicate the upper limit of each system¹³⁷

Soft actuators function on the principle of achieving strain through the coherent movement at a molecular level which translates to large scale deformation resulting in

shape change or volume change of the material. This type of actuation differs from the more conventional mechanical transducers, like hydraulic pumps, electric motors or engines, where displacement occurs due to movement between entire components.¹³⁹ Table 2.1 gives an overview of some of the conventional and soft actuators that are currently being researched and their driving forces.

Table 2-1: Overview of selected actuator technologies and their driving forces^{137, 14}

Actuator Driving force	Actuator Type	Device and application examples
Electric Field	Piezo and Electrostrictive	Stack actuators, composites, single crystals used in precision positioning
	Electroactive polymers	Similar to piezo devices, with increased strain, lower force
	MEMS	Inkjet printers, micropumps and valves
	Moving coil transducer	High force and strain required for active aerodynamic surfaces
Magnetic Field	CNT-based composites	Potential dry actuators
	Magnetostrictors Magnetic SMA	Vibration isolation
Temperature	Solenoids	Valves or switches
	SMA	Pipe couplings, robotics
Fluid	SMP	Medical device prototypes, deployable and morphing structures
	Hydraulic and pneumatic	Pumps, cylinders and motors
	ER fluids, MR fluids	Shock absorption, vibration damping

Soft actuators can be designed from various materials with different driving forces depending on the end application. From an engineering perspective, soft actuators are advantageous because of their potential to be light weight, low cost, low noise, reduced pollution, and high efficiency.^{16, 141-142} Applications for such actuators range from micro- and macro-artificial muscles and soft robotic systems to morphing (shape changing) aerospace structures and biomedical devices.^{18, 21, 143-148} A brief overview of some technologies used for soft actuator development is given below

2.4.1. Soft actuators

The initial studies on soft actuators utilized gel based systems which relied on changes of pH or solvent to achieve displacement. For example swelling of gels in water and its use as an actuator was first reported by Katchalsky and Kuhn in 1960.¹⁴⁹ They observed that crosslinked poly (acrylic acid) (PAA) or esterified poly (vinyl alcohol) (PVA) was

capable of converting chemical energy provided by the introduction of water into mechanical work under isometric conditions. The PAA gel could undergo repeated and reversible contraction and expansion by $\sim 20\%$ when an acid or base is added to the material. In addition to the acid and base solutions, Katchalsky et al. added solutions of salts such as LiBr, and urea to crosslinked collagen fibers and designed chemomechanical actuators.¹⁵⁰ In addition to solvent, materials that react to temperature are also good candidates to design actuators. Poly(N-isopropylacrylamide) (PNIPAM), a typical thermo-responsive polymer has shown promising results for applications in actuators, sensors, and also for drug delivery systems. Okano et al. utilized PNIPAM gel to obtain rapid swelling and deswelling of gels, where the force generated during operation was much higher than passive swelling materials.¹⁵¹

The first instance of applying electric currents to gels for actuation was by Hamlen et al. in 1965.¹⁵² They synthesized PVA-PAA fibers with finely dispersed platinum powder. A negative voltage caused an evolution of hydrogen, which turned the solution alkaline and resulted in fiber expansion. The opposite could be achieved by applying a positive voltage making the solution acidic. Another technology, which has continued interest today, was the development of ionic polymer-metal composite (IPMC). IPMCs consist of a Nafion[®] membrane on which a gold or platinum electrode is deposited. (Figure 2-11) The IPMC works on the principle of electrophoretic transport of protons which carry water molecules from one electrode to another. When an electric field is applied across the membrane, it will bend towards the anode, as the protons move across the membrane, resulting in differential swelling.¹⁵³⁻¹⁵⁴ Light has also been used to trigger actuation as demonstrated by Suzuki and Tanaka, who used light induced heating of gels to trigger actuation via phase transformations.¹⁵⁵

Polypyrrole, polythiophene, polyaniline, and their derivatives are conductive polymers (CP), similar to IPMCs. They can change their dimensions depending upon the electrochemical doping. Baughman obtained large dimensional changes upon electrochemical doping which provided the mechanical response for proposed extensional and fibrous actuators.¹⁵⁶

In addition to CPs, Dielectric elastomers (DEs) are also voltage-responsive polymers that produce large strains and belong to the electroactive polymers (EAP) group.¹⁵ In DEs, a passive elastomer film is sandwiched between two compliant electrodes. An applied voltage causes an electrostatic pressure to develop due to Coulomb forces

acting between the electrodes (Figure 2-12). This results in reduced thickness and increase in surface area of the polymer film.

Figure 2-11: Mechanism of an IPMC actuator. Electrophoretic transport of protons carrying water molecules results in differential swelling of the membrane on application of an electric field ¹⁵³

Usually, strains of DEs are in the order of 10–35%, with maximum values reaching 300%. Hirai et al. investigated electrostrictive properties of polyurethane elastomers with hard and soft segments.¹⁵⁷ When an electric field was applied through both electrodes, the polyurethane elastomer contracted, strain was proportional to the square of the electric field in the range of 200 V/m. Although the DE actuators have advantages such as simple structure and a variety of elastomeric materials, they have drawbacks such as high driving voltages (>1,000 V), few flexible and stretchable electrodes are compliant with the large deformation of the DE actuators, and the prior pre strains needed to operate the DE actuators.

Baughman and coworkers developed the first CNT actuator based on sheets of single-walled carbon nanotubes (CNTs), using the double-layer charge injection method.¹⁵⁹⁻¹⁶⁰ A CNT electrode could function as a capacitor after charge injection. A change in the C atom's charge caused the C-C bond length to change. This expansion and contraction of the CNT was used as an actuator. The CNT actuator showed the strain and stress of >0.2 % and 0.75 MPa, respectively, for more than 140,000 cycles between 0.5 V at 1 Hz and still works at >1 kHz. To improve electrically powered artificial muscles, CNT aerogel actuators, having giant elongations (220 %) and elongation rate at 5 kV, have been developed which can operate at temperatures from 80 to 1,900 K ¹⁶¹

Figure 2-12: Mechanism of actuation of dielectric elastomers: A passive elastomer film is sandwiched between two compliant electrodes. Applied voltage causes an electrostatic pressure to develop resulting in compression in thickness and stretching in area¹⁵⁸

2.4.2. Magnet-polymer actuators

The use of Magpol as actuators was studied by Zrinyi et al. and several other groups.^{44, 162-164} It has been shown that deformation of Magpol can occur in either a uniform or non-uniform magnetic field. When the magnetic field is non-uniform, the magnetic field gradient is responsible for the force which acts on the particles. The force acting on the magnetic particles is transferred to the polymer chains, causing changes to occur at the molecular level. These changes accumulate; resulting in shape change on the macro scale.⁷⁰ An equilibrium is reached between the elastic stiffness of the polymer matrix and the magnetic force acting on the particles, leading to a final shape. Shape change can be bending, elongation, contraction, or a combination of these modes (Figure 2-13).¹⁶ Remote activation, high strain rate and quick response make it an attractive candidate for an actuating material. An in-depth review of the current status of Magpol is given by Nguyen et al. and Thevenot et al.^{16, 41}

Figure 2-13: Actuation modes of Magpol: a) Bending b) Elongation c) Contraction and d) Coiling⁷⁰

2.4.3. State of the art Magpol actuators

The versatility of Magpol and its actuation properties have been adapted for various actuator applications, including, artificial muscles, biomedical drug delivery devices, microfluidics, peristaltic pumps, etc. as described below. External magnetic fields have been used to change the mechanical properties of Magpol for use in dampers and seals.^{43, 165-176}

Langer et al. first developed the idea of using Magpol composites for drug delivery.¹⁷⁷ This work was further investigated by Zhao et al. who designed a drug loaded ferrogel for controlled drug release.¹⁷⁸ Zhou et al. and Pirmoradi et al. used a membrane of PDMS with embedded magnetic fillers as a controllable drug delivery device.^{170, 173}

The use of Magpol has also shown promise in microfluidics. Hong et al. used a shape memory polymer, to construct a micropump which could be activated through induction heating of embedded Ni nanoparticles.¹⁶⁹ By replacing Ni with carbonyl iron Li et al. developed composite membranes for microfluidic mixing.¹⁷⁹ Artificial magnetic cilia and flagella based systems have also been developed for particle sorting and microfluidic mixing.¹⁶⁷

Wang et al. developed 3D micromachines using nickel–phosphorus particles embedded in a-polymer. The composite could be manipulated on exposure to a magnetic field.¹⁸⁰ Similarly, semitransparent MnFe_2O_4 /thermoplastic polyurethane elastomer (TPU) nanocomposites have been designed for optical applications.¹⁸¹

Magpol is also useful for adaptive optics applications where the focal length of a lens is continuously tuned to correct aberrations. This concept was used by Liebetraut et al., Qian et al. and Buguin et al. to design a Magpol based lens for adaptive optics applications.^{176 144, 182}

Von Lockette et al. developed magneto-active elastomer (MAE) composite structures for use in origami engineering applications.¹⁸³⁻¹⁸⁴ Most previous work described a single mode of deformation e.g. bending, elongation, and contraction. Higher degrees of actuation can be obtained by programming anisotropy into the composite during synthesis, e.g., in the form of chains. This will enable predetermined activation of selected regions of the composite.¹⁸⁵ A suitable sample constrain can also generate new modes of actuation as shown by Nguyen et al.⁴⁵ They showed that deformation could be changed from the commonly observed axial contraction to a novel coiling

mechanism by changing the boundary conditions. The coiling behaviour closely resembled Euler buckling which occurs in a long homogenous rod under compression.¹⁸⁶ The buckled rod exhibited a helical shape and showed promising properties for the development of artificial muscles.

The following sections discuss the models used to describe the behaviour of the magnetic nanoparticles, the polymer matrix and the composite Magpol for each of the functionalities.

2.5. Magpol

To achieve simultaneous self healing, damage sensing and actuation in Magpol requires material design that can use different triggers to achieve a specific function. In order to develop self healing and damage sensing, a thermal trigger should be present. This thermal trigger can be supplied by heating the magnetic particles present in the Magpol by an alternating magnetic field, which can then transfer the heat to the polymer matrix.^{35, 47-48, 187-188} On the other hand; actuation requires the application of a force. This force is generated through the application of a magnetic field gradient which will act on the nanoparticles embedded in the matrix, resulting in displacement of the entire composite.^{162, 181} The following sections describe the theoretical basis for magnetic heating and force generation needed for tri-functional Magpol.

2.5.1. Magnetic Heating of Magpol

When magnetic nanoparticles are exposed to an AMF, they undergo relaxation losses which results in heat generation. Rosensweig, Purushotham et al and McHenry et al proposed a model to calculate the amount of heat such losses could generate. The losses considered in the model are of two types; Néel and Brownian.^{48, 189-196} As the magnetic nanoparticles are embedded in Magpol, Brownian relaxation is much slower than Néel and hence, in this case, we only consider Néel relaxation as the primary source of heating. Volumetric power dissipation (P) of the nanoparticles is calculated from equation (1):

$$P = \pi\mu_0\chi_0 H_0^2 f \frac{2\pi f\tau}{1+(2\pi f\tau)^2} \quad (1)$$

Where μ_0 is the permeability of free space, f is the frequency of the applied field and H_0 is the magnetic field strength, χ_0 is the particle equilibrium susceptibility which is calculated using the Langevin equation (2):

$$\chi_0 = \chi_i \frac{3}{\xi} \left(\coth \xi - \frac{1}{\xi} \right) \quad (2)$$

initial susceptibility χ_i is calculated from equation (3):

$$\chi_i = \frac{\mu_0 \phi M_d^2 V_M}{3 k_B T} \quad (3)$$

where ϕ represents the volume fraction and M_d , the domain magnetization of nanoparticles. k_B is Boltzmann's constant ξ , (Langevin function parameter) can be calculated from equation (4):

$$\xi = \frac{\mu_0 M_d H_0 V_M}{k_B T} \quad (4)$$

The Néel relaxation time can be calculated by the expression in equation (5):

$$\tau_N = \frac{\sqrt{\pi}}{2} \tau_0 \frac{\exp\left(\frac{KV_M}{k_B T}\right)}{\sqrt{\frac{KV_M}{k_B T}}} \quad (5)$$

Where V_M is the magnetic volume, K is the anisotropy constant for the magnetic nanoparticles. τ_0 is $\sim 10^{-9}$ s.

Experimentally, quantification of heat generation from magnetic particles is given by the specific absorption rate (SAR) which can be calculated as ¹⁹⁰

$$SAR = C \left(\frac{\Delta T}{\Delta t} \right) \frac{Mass_{composite}}{Mass_{nanoparticles}} \quad (6)$$

where C is the mass weighted heat capacity of the ferrofluid and $(\Delta T / \Delta t)$ is the slope of the initial section of the temperature v/s time curve . Most ferromagnetic materials require applied field strengths of at least 100 kA.m^{-1} or more before they can generate maximum heating via hysteresis losses. In contrast, superparamagnetic particles are capable of generating high SAR values at lower fields, e.g., of about 15 kA.m^{-1} , which is utilized in this study.

2.5.2. Magnetic Force

Magnetic Field

Metallic magnetic materials can possess an incomplete 3d electron shell. The free electrons in this 3d shell are therefore free to contribute to the magnetic moment of the atom. At the local level, these magnetic atoms will interact with each other to generate regions with a common spin direction, known as domains. Therefore a bulk magnetic

material usually consists of several domains, each with its own orientation. The higher the percentage of oriented domains, the stronger the magnet.¹⁹⁷

The theoretical basis of the electromagnetic field was developed by Maxwell.¹⁹⁷ According to Maxwell's equations, an electromagnetic field has four vectors associated with it, the E (electric field) and B (magnetic flux density) vectors, and the D (electric flux density) and H (magnetic field) vectors. The B and H vectors are responsible for the existence of a magnetic field, and can be denoted as.¹⁹⁷

$$\nabla \cdot B = 0$$

$$\nabla \times H = 0 \quad (7)$$

These equations define the behavior of the vectors within the magnetic field. The H vector determines the orientation of the magnetic domains in bulk magnetic materials. The magnetic flux density and the magnetic field are related by the permeability coefficient, μ through the equation $B = \mu H$. The permeability is a material property and can be defined as the ratio of the material permeability

(μ_r) to the permeability of air (μ_a). The value of μ_a is $4\pi \times 10^{-7}$ H/m. The B and H values can be plotted as a hysteresis curve. As H is increased, B also increases. Because μ is not always linear for the entire range of the curve, the curve itself has linear and curved portions. There is a limit where increasing H no longer increases B, otherwise known as the saturation limit. However, when H is decreased, the curve of B does not retrace the path of curve corresponding to the initial increase in H, instead it follows a different path. However, once H is again increased, the curve returns to its original starting point, thereby forming a closed hysteresis loop. The shape of this hysteresis curve is useful to determine the appropriate usage conditions for any given magnetic system. In the case of a material that is already exhibiting magnetism, the presence of an applied field H causes an additional term to be added to the BH equation. The magnetization m in permanent magnets is independent of the applied fields, and therefore the equation relating B to H changes to $B = \mu(H + m)$.

Finally, a measure of a magnet's power comes from its maximum energy product, a value defined as the amount of energy a magnetic material can supply when it is a part of a magnetic circuit with minimal magnetic material. It is a way of evaluating the efficiency of a magnet. Understanding the magnet's maximum energy product can be useful in determining the size of the magnet necessary for a specific application while

still providing enough magnetic strength for that application.

The magnetic energy density for a constant permeability material is expressed as:³³

$$w_{mag} = \frac{B^2}{2\mu} = \left(\frac{1}{2}\right) BH \quad (8)$$

For materials with a nonlinear B - H curve, the energy density can be expressed as:

$$w_{mag} = \int H \cdot dB \quad (9)$$

This energy density is the area to the left of the B - H curve. The area under the B-H curve is called the co-energy density w_{co} . The sum of co-energy density and energy density is constant and equals to HB (Figure 2-14)

$$w_{mag} + w_{co} = HB \quad (10)$$

Figure 2-14: Energy density and co-energy density for a material with nonlinear B - H curve¹⁹⁷

For constant permeability materials, energy density and co-energy density are equal and have the value of $0.5BH$. Since the energy density w_{mag} is the magnetic energy per unit volume in a magnetic field, the total energy stored is the integral of w_{mag} over a volume:

$$W_{mag} = \int w_{mag} dV$$

For constant permeability materials, the stored magnetic energy is given by equation (11):

$$W_{mag} = \int \frac{B^2}{2\mu} dV \quad (11)$$

2.5.3. Magnetic Force Acting on Particles

In Magpol, the magnetic filler is in the form of nanoparticles. Hence it is necessary to

understand the force that will act on the magnetic nanoparticles in the presence of a magnetic field gradient. This response will influence actuation of Magpol.¹⁹⁸

The force acting on a small magnetic particle with a magnetic moment M due to a magnetic field gradient ∇B is

$$F_m = V_{particle} \cdot M(\nabla B) \quad (12)$$

When a small magnetic particle with volume V_P is embedded in a matrix, its magnetic energy density in a linear isotropic medium is expressed as $1/2BH$. The magnetic energy of the fluid enclosed in this volume is

$$\frac{1}{2}HB_mV_m = \frac{1}{2}\mu_mV_mH^2 \quad (13)$$

where $B_m = \mu_m H$ and $\mu_m = \mu_0(1 + \chi_m)$ is the permeability of the matrix. If the matrix material enclosed in this volume V_P is replaced by the particle, the energy associated with the particle is now

$$\frac{1}{2}HB_pV_p = \frac{1}{2}\mu_pV_pH^2$$

where

$$B_p = \mu_p H$$

$$\mu_p = \mu_0(1 + \chi_p)$$

And μ_p is the permeability of the particle. The energy gain of the system U is the difference between these two energies and for a constant permeability material, this is a good approximation. Thus

$$U = \frac{1}{2}(\mu_p - \mu_m)V_pH^2$$

Hence, the magnetic force can be written as:

$$\vec{F}_m = \frac{1}{2}\mu_0\chi V_p \nabla(H^2) \quad (14)$$

where $\chi = \chi_p - \chi_m$ is the difference between susceptibilities of the particle and the matrix. Therefore, effective ways of enhancing the magnetic force on particles include (i) increasing the susceptibility of the particle, (ii) increasing the magnetic field gradient

and (iii) using a strong magnetic field. Particle size also plays an important role since the force is proportional to the particle volume.

2.5.4. Buckling Analysis of Magpol

The actuation of Magpol is similar to buckling in a column. Thus, using the equations for magnetic force acting on a particle and the material properties of the matrix, we can calculate the critical magnetic field required for buckling to occur. The buckling can be analyzed through a force-load relationship acting on the composite samples, an equilibrium is established between the applied magnetic force and the weight of the sample to give the final load P (equation 15):⁴⁵

$$P = F_{\text{magnetic}} - W_{\text{weight}} \quad (15)$$

where F_{magnetic} is the force generated by the applied magnetic field acting on Magpol and can be calculated from equation 16 as:

$$F_{\text{magnetic}} = \int_V M \cdot \nabla B \cdot dV = \int_{z_{\text{bottom}}}^{z_{\text{top}}} M \cdot \frac{\delta B}{\delta z} \cdot a \cdot dz = \int_{B_{\text{bottom}}}^{B_{\text{top}}} a \cdot M(B) \cdot dB \quad (16)$$

The weight of the sample (W_{weight}) is given by:

$$W_{\text{weight}} = \int g \cdot dm = \int_V \rho \cdot dV \cdot g = \int_{z_{\text{bottom}}}^{z_{\text{top}}} \rho \cdot g \cdot a \cdot dz \quad (17)$$

Considering the cross-sectional area (a) to be constant, the load can be expressed as:

$$P = a \cdot \int_{B_{\text{bottom}}}^{B_{\text{top}}} M(B) \cdot dB - a \cdot \int_{z_{\text{bottom}}}^{z_{\text{top}}} \rho \cdot g \cdot dz \quad (18)$$

The $M(B)$ function can be fitted to experimental values and the magnetic force can be computed from Equation (16). B_{bottom} (at z_{bottom}) and B_{top} (at z_{top}) indicated the magnitude of the applied field acting on the sample at each end. This is calculated from the model proposed by Zrinyi et al.¹⁹⁹ and using the specifications given by Snyder et al.²⁰⁰⁻²⁰¹ The magnetic field strength (B) at a given distance z from the electromagnet pole center, can be determined using Equations 16-18.

$$B(z) = B_{\text{max}} f(z) \quad (19)$$

$$f(z) = 1 - kz^2 \text{ if } |z| < \delta \quad (20)$$

and

$$f(z) = (1 - k\delta^2) \exp[-\gamma(|z| - \delta)] \text{ if } |z| \geq \delta \quad (21)$$

Where $B_{\max}$ is the maximum field measured experimentally at $z=0$. The field decay (k) is dependent on the electromagnet pole radius (δ) and can be calculated by $k=\gamma/(2\delta + \gamma\delta^2)$. γ is a characteristic constant of the electromagnet and is taken to be ~ 40 for this calculation.

Euler's formula states that buckling of a long sample occurs when the load acting on it is equal or more than a critical value (P_{cr}), is applied. P_{cr} is expressed as

$$P_{cr} = \frac{n^2 \pi^2 EI}{(KL)^2} \quad (22)$$

Where n is the mode number, E is the Young's modulus, I is the area moment of inertia, K is the effective length factor, and L is the unsupported length of the sample.

2.5.5. Properties of the polymer matrix

Thermoplastic and amorphous polymers are viscoelastic materials. The behaviour of such materials can be determined via constitutive models; linear differential equations can be used to connect the stress and strain at a given point in time. Viscoelastic models must by definition consider both elastic and viscous elements, usually modelled as springs and dashpots respectively.²⁰²

The elastic element can be modelled as a linear spring which obeys Hooke's law:

$$\sigma = E\epsilon \quad (23)$$

Where σ is the stress, E is the modulus of the polymer and ϵ is the resulting strain. The viscosity of the polymer will follow Newton's law and can be modelled as a dashpot and is related by the expression:

$$\sigma = \eta \frac{d\epsilon}{dt} \quad (24)$$

where η is the viscosity of the fluid.

Therefore, to build a rheological model, these two systems must be connected with each other. The connection can be either in series or parallel, with each having a different outcome. For example, if the elements are connected in parallel, the strain will also act

in parallel, while the stresses will add together. On the other hand, a series connection will result in the strains being added together, while the stresses remain constant.

Maxwell's model considers elastic and viscous elements to be connected in series and the resulting constitutive equation is given by:

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad (25)$$

The Maxwell model is used to calculate the best approximation of the modulus of the polymer and its stress relaxation properties. An alternate model, called the Kelvin-Voight model is more suited for calculating creep and strain recovery. In this model the elements are connected in parallel and the relevant equation is:

$$\sigma = E\epsilon + \eta \frac{d\epsilon}{dt} \quad (26)$$

It is difficult to describe the behaviour of real materials using these models. Better estimates can be obtained by combining several elements as well as models. A multi-element model which is particularly suitable for modulus modeling is the Maxwell - Weichert (or generalized Maxwell) model, which consists of multiple Maxwell elements coupled in parallel. The Zener model is a standard viscoelastic model which combines a Maxwell element in parallel with a spring to explain material deformation.²⁰²

2.5.6. Shape memory behaviour of poly (ethylene-co-vinyl acetate) EVA

Currently there is high interest in research on active and responsive smart polymers. This is partly due to the discovery of the shape memory effect (SME) in certain polymers.²⁰³ This effect is characterized by the ability of the polymer to regain its original dimensions after it has undergone plastic deformation. This recovery can only occur in the presence of a certain stimulus that provides the energy necessary for recovery.²⁰⁴ Thus Shape-memory polymers (SMPs) can be defined as polymeric smart materials that have the ability to return from a deformed state (temporary shape) to their original (permanent) shape induced by an external stimulus (trigger), such as temperature change. This process differs from the elastic shape changing effect (SCE), where energy is stored within the material during deformation and subsequently used to recover the original shape.²⁰⁵ Suppose that a material can exist in either state A or B. SCE materials do not have an energy barrier between the two states, while SME

materials do. If the energy barrier (H) is high enough, a deformed SME material will retain shape B until sufficient energy is supplied to the system to overcome the energy barrier and allow the recovery of shape A. This energy can be in several different forms. Temperature, chemical, light and mechanical force have all been used to trigger shape change in SME materials.²⁰⁶ Thermoresponsive shape memory polymers (SMPs) can be triggered by direct and indirect application of heat, while chemoresponsive polymers can be affected by a change in water content, pH, solvents, etc. Light can be used to trigger shape change, by either indirectly heating the polymer or through inducing a chemical reaction. Mechanical force like pressure or impact force can also be used for shape recovery.

2.5.7. Mechanism of Shape memory polymers

The shape memory effect is caused by the existence of two distinct phases in the polymer. The first phase consists of a hard segment that retains its elastic nature. The second, soft, phase can reversibly change its stiffness by the application of a force. Thus, the soft segment will undergo plastic deformation, when the SMP is placed under tensile loading. After this plastic deformation, if adequate energy is, the soft phase will regain its original shape, resulting in shape recovery of the sample.²⁰⁷ For thermoresponsive polymers, the energy is supplied in the form of heat which must exceed either the glass transition (T_g) temperature or the melting point (T_m) of the polymer. These temperatures are the most common transition points in shape memory polymers. Figure 2-15 shows a schematic stress strain curve that is observed during strain and recovery in a thermoresponsive SMP.²⁰⁸

According to Figure 2-15, the SMP will first trace path “a” when it undergoes deformation. The material is deformed upto the strain ϵ_m . This can be done either above or below the transition temperature. After deformation, the load is removed and the material traces the path “b”, where some of the strain is recovered due to elasticity of the material.

Figure 2-15: Schematic of the stress and strain values obtained during a typical thermoresponsive shape memory polymer cycle of deformation and shape recovery.²⁰⁸

The strain obtained after unloading is used to calculate the shape fixity of the material. Shape fixity is an indication of how well the material can retain a programmed shape after the programming load is removed. The shape fixity can be calculated by the equation:

$$Rf = \frac{\varepsilon_u}{\varepsilon_m} \quad (27)$$

Where ε_u is the residual strain and ε_m is the maximum strain that the SMP is subjected to. The original shape can be recovered either partially or completely, by heating the SMP above its transition temperature, such that it follows path “c”. The Shape recovery ratio (Rr) determines the efficiency of the recovery process and can be calculated by the equation

$$R_f = \frac{\varepsilon_u - \varepsilon_h}{\varepsilon_u} \quad (28)$$

Where ε_h is the remnant strain after shape recovery.

For polymers like EVA, it has been observed that shape fixity is quite low. During unloading at low temperatures, the material may regain a large percentage of its original shape. This can be explained by the nature of EVA polymers, which show a large viscoelastic effect.²⁰⁵

Depending on the mechanistic behaviour, thermoresponsive shape memory polymers are classified into three groups. The dual-state mechanism (DSM), dual-composite mechanism (DCM), and partial-transition mechanism (PTM) are explained in the

schematic below (Figure 2-16).²⁰⁵⁻²⁰⁶

The dual state mechanism (Figure 2-16 I) is applicable to rubbery materials like silicone that have a T_g below room temperature. The material must be deformed and held in that state as the temperature is reduced below the T_g . On returning to room temperature, the original shape is recovered. This mechanism relies on the existence of cross links within the polymer.

Dual-Component Mechanism (DCM) (Figure 2-16 II) is applicable to the polymer matrix used in Magpol, (EVA) as well as other thermoplastics like and polyurethane (PU).²⁰⁸ Thermoplastics are usually semicrystalline in nature, and have both hard and soft segment phases. The hard phase retains its elasticity; the soft phase can change its stiffness depending on the ambient temperature and its transition temperature (either T_g or T_m). The hard phase is referred to as the elastic component, and the soft phase as the transition component. When the material is strained, the elastic component will store deformation energy. The plastically distorted and (re-)hardened transition component does not allow for shape recovery below the transition temperature. Heating above the transition temperature reduces the energy barrier and shape recovery is driven by the stored elastic energy in the elastic component, returning the polymer to its original shape.

In the partial transition mechanism, (Figure 2-16 III), the material is homogenous. The energy supplied for shape recovery does not exceed the transition temperature. Therefore, strain causes some sections to act as transition components while others act as elastic components.

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Figure 2-16: Schematic of the types of shape memory effects occurring in SMPs. (I) Dual-state mechanism (DSM); (II) dual-component mechanism (DCM); (III) partial-transition mechanism (PTM). (a) Original sample at temperature below T_g ; (b) after heating and shape fixing; (c) Constrained cooling; and (d) unconstrained heating induces shape recovery.²⁰⁸

2.5.8. Model for Healing in Magpol

Healing in thermoplastics can be achieved when the damaged surfaces undergo welding at the interface. Based on theoretical models, the factors influencing the degree of healing can be deduced. This will serve as an important component in material selection.

The healing behaviour of the thermoplastic composites has been modelled by several groups using the reptation theory as a basis for polymer chain mobility.²⁰⁹⁻²¹¹ The reptation theory describes the behaviour of polymer chains present at an interface and above their transition temperature. The model assumes that at time $t=0$ the movement of a polymer chain (length L) is restricted to the confines of a tube. For every time step t , the chain is subjected to Brownian motion, which causes the end of the chain to escape

from the tube. This escaped region is referred to as the minor chain. The minor chain length increases with time (reptation time t_{rep}) till it encompasses the entire length L . This minor chain is responsible for interacting with other polymer chains in the region resulting in interpenetration of chains across the interface. Higher chain interpenetration will result in stronger bonds and more efficient healing. Yang and Pitchumani developed a model to calculate the degree of healing based on the polymer chain movement across the interface and is calculated using equation (30):

$$D_h(t) = \left(\frac{1}{L}\right)^{1/2} = \left[\int_0^t \frac{1}{t_{rep}(T)} dt\right]^{1/4} \quad (29)$$

It can be seen that the reptation time (t_{rep}) and temperature (T) will influence the degree of healing. In turn, t_{rep} depends on the interactions between adjacent polymer chains and also with neighboring nanoparticles. Taking into account these interactions, the t_{rep} can be calculated from equation 31:^{212,213}

$$t_{rep} = \frac{b^2 N^{5/2}}{2\pi^2 k_B T N_e} [\xi_0 N^{1/2} + \xi_a] \quad (30)$$

ξ_0 and ξ_a are the friction coefficients of the isolated monomer and nanoparticle absorbed monomers respectively, b is the statistical length of a segment, N is the number of monomer units in a chain and N_e is the number of monomer units per entanglement strand. We assume that the polymer is composed entirely of vinyl acetate.

ξ_a can be calculated based on the theoretical model given by Subbotin et al. (equation 32):

$$\xi_a = \frac{k_B T \tau}{b^2} \quad (31)$$

where

$$\tau = \tau^* \exp\left(\frac{U}{k_B T}\right)$$

and

$$\tau^* = b \left(\frac{m}{k_B T}\right)^{1/2}$$

M is the weight of one monomer unit, U is the activation energy.

2.6. Applications of Trifunctional Magpol

There is a significant need for multifunctional sensing and self healing in polymeric

materials that undergo continuous actuation during service resulting in severe plastic deformation and failure. Examples include polymer composite skins used in morphing aircraft wings^{14, 18, 148, 214} and biomedical coatings used in catheters and guidewires during minimally invasive surgery.²¹⁵ Both these areas can greatly benefit from the introduction of a multifunctional polymer composite material. Wlezien et al.²¹⁶ stated that by using a lighter wing that could adapt to real time aerodynamic requirements, instead of complex high lift systems, the cost of an aircraft could be reduced by 50%. In addition, the weight of the aircraft could also be reduced by 8% when a morphing wing is used.²¹⁷ The development of such morphing wings requires durable outer skins to make this technology feasible. Kikuta and Thill et al.^{14, 54} outlined some of the requirements for a morphing skin to include: elasticity, flexibility, abrasion, weather and chemical resistance, high strain capability, high strain recovery rate, and fatigue resistance.

In case of biomedical catheter and guide wire coatings, the recent U.S. Environmental Protection Agency requirement that manufacturers eliminate the suspected carcinogen perfluorooctanoic acid (PFOA) from their PTFE formulations by 2015, is causing a serious problem with regards to flaking and delamination of PTFE coatings. This has resulted in FDA recalls of several types of guidewires from different companies.²⁴ Thus, there is a significant demand for the development of a new reusable coating material capable of healing and damage detection before each use.

Considering the requirements for the development of damage sensing and self healing for both large structure morphing wing skins and small scale biocompatible guidewire coatings, magnet-polymer composite (Magpol) materials are ideally suited for the development of multifunctionality. Prior work has shown that due to the flexibility in the choice of polymer matrix and magnetic fillers, Magpol is capable of remote contactless actuation, high actuation strain and strain rate, self-sensing and quick response, which provide diverse stimuli for triggering functions such as actuation, sensing or healing.

Chapter 3

3. Materials Selection and Experimental Methodology

This chapter describes the procedure used to select the matrix and filler components of Magpol based on the property requirements. Appropriate synthesis techniques were chosen for the nanoparticle and the composite based and are described in the text. The different experimental procedures used for characterization, and property evaluation of self healing, sensing and actuation in Magpol are also described.

3.1. Material selection

Throughout the literature a common thread emerges in relation to the development of bioinspired soft materials: A composite material consisting of a polymer matrix with various fillers is the most flexible with regards to incorporation of multifunctionality. To obtain multifunctionality in a composite material selection plays an important part, as multiple material parameters will determine the composite's efficiency in each function. Therefore tradeoffs are needed to improve the functions.

3.1.1. Magnetic filler

The simultaneous strain sensing, self healing and actuation properties can only be achieved in Magpol due to the incorporation of a magnetic filler. Under the influence of a magnetic field, the polymer is able to actuate, as described by Nguyen et al.⁷⁰ Induced heating of the magnetic filler by the application of an AC magnetic field is responsible for self healing and the formation of the dye aggregates required for strain sensing. The heating produced by the filler must be controlled to prevent pyrolysis of the polymer matrix and decomposition of the dye molecules. In the case of acid copolymers, the temperature must remain below $\sim 150^{\circ}\text{C}$ to prevent anhydride formation. Thus the filler plays the most important role in the multifunctional composite. The filler must have a low Curie temperature to prevent degradation of the composite by regulating the temperature. It must also possess high M_s and permeability to produce actuation. Thus, there must be a trade-off between these two properties while selecting an appropriate filler.

Additionally, filler size also plays an important. To prevent additional heating via eddy currents, the particles must be superparamagnetic. Superparamagnetic particles are also necessary to prevent large scale aggregate formation during film casting. Inductive heating is a volumetric effect, induced currents in the particle create a magnetic field which opposes the applied magnetic field, a phenomenon known as shielding effect. Typically, the magnetic field is highest at the surface of the susceptor and decreases exponentially with depth. Such shielding effects disappear for nano sized particles, which is another reason to control filler size.

Figure 3-1 and Table 3.1 gives a list of the available T_c controlled magnetic materials used in current research.

Figure 3-1: Selection of Tc (80°C-200°C) controlled magnetic materials with respect to Magnetic Saturation (Ms) and Permeability (μ) using Cambridge Engineering Selector (Granta Design)

Table 3-1: Tc tuned magnetic metal oxide nanoparticles^{193, 218-225}

Composition	Size (nm)	Tc °C	Ms(emu/g)	Processing technique	Reference
$\text{Fe}_x\text{Ni}_{1-x}$	12	78-112	80-117	Thermal decomposition	McNerny et al. ¹⁹³
$\text{Zn}_x\text{Gd}_{1-x}\text{Fe}_2\text{O}_4$	6	25	67	Co-precipitation	Al Hayek et al. ²¹⁹
$\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$	100	50	60	Microwave sol gel	Bahadthur et al. ²²¹
$\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$	7-10	60-105	38-54	Hydrothermal	Hejase et al. ²¹⁸
$\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$	8	267-415	39-54	Co-precipitation	Sendhilnathan et al. ²²³
$\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$	60	77-140	50-80	Hydrothermal	Zheng et al. ²²⁵

Figure 3-1 shows that the best Ms and μ for the Curie temperature range between 80°C - 200°C will be obtained from Mn-Zn ferrites. Recently Curie temperature engineering

has been studied in metallic nanoparticles.²⁵¹ Metallic nanoparticles have larger M_s values and fine control over the Curie temperature which can theoretically lead to higher heating rates. This would be beneficial in obtaining more efficient self healing. In practice, metallic nanomagnets are synthesized by physical methods leading to large particle size distributions as compared to chemical methods. This is counter productive for RF heating as there is a strong correlation between the applied frequency of the magnetic field and the size of the nanoparticles for optimum heating (section 2.5.1). Thus the large particle size distribution results in reduced heating rates leading to a preference for chemically synthesized ferrites which show almost comparable M_s values, but with more efficient heating. As narrow particle size distribution on the nanoscale is preferred, a review of literature presents several possibilities for synthesizing Mn-Zn ferrites (Table 3.1)

The Mn-Zn ferrites are desirable as there is the possibility of tuning M_s and Curie temperature by changing the composition by tuning the Mn:Zn ratio of the nanoparticles. *Thus, Mn-Zn ferrites are chosen as the magnetic filler in the Magpol composite.*

3.1.2. Polymer Selection

The polymer must be able to incorporate actuation, damage sensing and self healing; hence there are certain restrictions on the choice of materials. Firstly, to incorporate strain sensing, the polymer must be semicrystalline. This allows formation of dye aggregates in the amorphous regions. Also, the polymer must show large plastic strain before fracture. This is a beneficial property, as it gives time for a repair cycle.

Secondly, for actuation, the material must have low elastic modulus, enabling the material to undergo large deflection in magnetic fields. The two properties described are contraindicative as a semicrystalline polymer will typically have a larger elastic modulus as compared to an amorphous elastomer like silicone. Thus, there is another trade-off while selecting the matrix.

An Ashby plot shows the properties of semicrystalline polymers in relation to other materials with reference to their Elongation v/s Young's Modulus (Figure 3-2)

Semicrystalline polymers are highlighted in dark blue, while other materials are grayed out. Here we consider materials in the top left corner, which have the lowest modulus and can withstand the highest strain.

Figure 3-2: Ashby plot of Modulus vs. elongation strain showing possible candidates for Magpol matrix material

Additionally, for self healing via localized melting of the nanocomposite, we choose polymers with lower T_m to obtain better healing properties with low loading of nanoparticles.

Three different polymer systems were selected as possible candidates in developing a proof of concept multifunctional composite. The properties of the polymer are listed in Table 3.2

Tensile stress at break or ultimate tensile strength is the tensile stress at the moment at which a test specimen fails. Elongation at break, also known as fracture strain, is the ratio between changed length and initial length after breakage of the test specimen.

Out of the three available candidates, EVA has previously been reported to have shape memory properties. This shape memory response can be adapted for use in the strain sensing and self healing functionalities. The ability for shape recovery after damage can be used to develop a multicycle strain sensor as well as for shape memory assisted self healing (SMASH). *Thus, EVA is chosen as the Magpol matrix.*

Table 3-2 Relevant properties of the polymer chosen to synthesize the Magpol composite

Polymer	Melting point (°C)	Elastic Modulus (MPa)	Tensile Stress at break (MPa)	Strain at break (%)
PEAA	85	6-100	13-34	400-700
EVA	86	15	3-35	300-800
(Cosmothane[®])				
Ionomer Na⁺	98	200	10-37	350
(Surllyn[®])				

3.2. Material preparation

3.2.1. Synthesis of Magnetic Nanoparticles

The magnetic material chosen as a filler for Magpol are the Mn Zn ferrites. Nanomagnets can be synthesized by both physical and chemical methods.²⁵³ For physical methods based synthesis, a typical top down approach is high energy ball milling, which can yield sub-10nm particles. But the major drawbacks are surface contamination and introduction of structural defects. Bottom up techniques include spray techniques and PVD-based techniques. From a practical standpoint, chemical techniques are better as they are cheaper, provide a large yield and do not require sophisticated instrumentation. Numerous chemical methods can be used to synthesize magnetic nanoparticles including coprecipitation, microemulsions, sol-gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow injection syntheses, and electrospray .syntheses.²⁵³ Narrow size distribution and crystallinity are the most important requirements to obtain efficient RF heating (section 4.2.4). Therefore the synthesis method should provide these properties in the nanoparticles along with a high yield. While microemulsions and polyol methods form nanoparticles with the narrowest size distribution, the yield is not sufficient to obtain Magpol films. High yield is obtained through co-precipitation technique, but with a larger size distribution. High yield, narrow size distribution and high crystallinity are obtained through hydrothermal methods.²⁵³ Hence the Mn Zn ferrites in this thesis were synthesized by 2 methods:

1. $\text{Mn}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$ prepared by co-precipitation technique
2. $\text{Mn}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$ prepared by hydrothermal method

The nanosize manganese zinc iron oxide particles were synthesized via co-precipitation methods. Manganese (MnCl_2), Zinc (ZnCl_2) and Iron chloride salts (FeCl_3) were each dissolved separately in appropriate molar quantities in MilliQ water. The salt solutions were then combined in one container equipped with a mechanical stirrer. The aqueous solution was vigorously stirred while adding sodium hydroxide until the reaction mixture reached pH 12. The solution was heated to 90°C for 30 minutes. The final mixture was then washed repeatedly with deionized water and ethanol to remove byproducts and remaining reactants. The magnetic particles were then collected using magnetic separation and stored in a vacuum chamber for a few days for complete drying.

For hydrothermal synthesis, the same precursors were used. NaCl was removed to prevent the Mn and Zn hydroxides, formed during the addition of NaOH, from redissolving and complexing with the sodium salts, changing the stoichiometries. This was achieved by precipitating the FeCl_3 separately. NaOH was added to FeCl_3 to precipitate the Fe ions and remove excess Cl^- . This occurred when the pH of the solution reached ~8. The precipitated Fe sludge was washed with MilliQ water, re-suspended in water and added to Mn and Zn salt solutions. The pH was further adjusted to ~10 to 11 by adding NaOH. The volume of the solution was adjusted to 80% of the hydrothermal reactor volume and placed in an oven at 190°C for 4 hours. The product obtained from the reaction was then magnetically separated, washed and dried for further complexing or characterization. The characterization of the nanoparticles and their size determination through XRD and TEM is discussed in chapter 4.

3.2.2. Polymer coating of Magnetic Nanoparticles

In order to obtain a stable dispersion, the nanoparticles were then coated with Poly (ethylene-co-acrylic acid) PEAA. The slurry resulting from hydrothermal synthesis was transferred into tetrahydrofuran through continuous washing and sonication for 10 minutes. PEAA (40 mg/ml) was added to the nanoparticle slurry in a 1:1 wt/wt ratio. The solution was subjected to continuous ultrasonication for 4 h in a bath. Following ultrasonication, the solution was kept standing for 12 h to enable large particle aggregates to settle under gravity. The non-settling colloidal particles remained in

suspension and were magnetically separated and washed with THF to remove excess PEAA. The particles obtained were then further characterized to determine the amount of PEAA coating.

3.2.3. Polymer film preparation

Polymer films were prepared by both compression molding and solution casting. For compression molding, polymer pellets were heated to 150°C for 20 min and allowed to cool down to room temperature under ~1000 psi pressure. The resulting films were around 300 µm thick.

Organic solvent 1,1,2,2 tetrachloroethane (TCE) was used for solution casting Magpol films. EVA pellets were dissolved in TCE at ~120°C and cast into petri dishes placed in a preheated oven. Solvent evaporation was carried out for 4 h at 115°C following which the films were removed and allowed to cool to ambient temperature. Residual solvent was removed by placing the films in a vacuum oven for 24 h at ambient temperature. The films obtained through solution casting method were ~150 to 200 µm thick.

Composite films containing BSS dye and magnetic nanoparticles were prepared by solution casting in a manner similar to the procedure described above. The required amount of BSS and Mn-Zn ferrite were added to the TCE solution and mechanically stirred until a homogenous solution was obtained. The solution was then poured into a petri dish and placed in an oven, as mentioned above. Depending upon the requirement for the dispersion of the dye, the films were either rapidly quenched in an ice bath or slowly cooled to room temperature.

3.3. Characterization

3.3.1. Characterization of the Magnetic Phase

The magnetic nanoparticles were characterized to determine their composition and crystal structure using a Shimadzu Lab X XRD-6000 X-ray diffractometer with Cu K α radiation of wavelength $\lambda = 1.54056 \text{ \AA}$. The scan speed used was 1.0 – 2.0 °/min and the 2θ scans range at least 25 – 90 °. *MATCH!* software (version 1.11c created 1/11/2012) was used to identify the phases present by matching peak positions and relative intensities to JCPDS reference files. Lakeshore 7404 Vibrating Sample Magnetometer (VSM) was used to measure the magnetic properties of the nanoparticles

at room temperature in an applied magnetic field range of 0 to 1T. T_c was measured at 500Oe from 295K to 773K.

The nanoparticle morphology was studied using a JEOL 2010 Transmission Electron Microscope under an operating voltage of 200kV and a LaB_6 cathode

The heat generated by the magnetic nanoparticles in an RF field was measured by using a 10mg/ml solution of the particles in a high boiling point solvent. 5 ml of the stable magnetic nanoparticle suspension was placed inside a five loop copper induction coil and covered with insulating ceramic wool. The coil was energized by an AC generator (Inductelec,UK) and frequency of 475 kHz. Temperature changes were recorded using a Luxtron MD600 fiber optic thermometry probe.

The polymer coating on the nanoparticles was estimated using thermo gravimetric analysis (TGA), (TA instruments TGA Q500 thermo gravimetric analyzer). About 5 to 10 mg of the dried sample was placed in a platinum pan and heated to 600 °C at a rate of 10 °C/min under nitrogen flow.

3.3.2. Characterization of Polymer Phase

The mechanical properties are studied using a tensile tester (Instron 5567) following the ASTM D 882 standard for thin films. Differential Scanning Calorimetry (DSC) (TA DSC Q10 and DSC 2010) with a heating rate of 5°C/min under nitrogen flow was used to study the thermal properties of the polymers.

3.3.2.1. Shape memory characterization

Dynamic mechanical analysis (DMA) was used to determine the glass transition temperature (T_g) and study the effect of the nanoparticle filler on the shape memory performance of Magpol. All samples were run using a TA Instruments Q800 Dynamic Mechanical Analyzer with a film tension accessory. The test was run in Multi-frequency Strain mode to obtain information about T_g at a maximum frequency of 0.1 Hz. To monitor shape memory strain, the instrument was run using Controlled Force mode. Two cycles of heating and cooling were carried out; stress and resulting deformation were measured from the nanocomposites.

3.3.3. Evaluation of Strain Sensing

To evaluate strain sensing properties of Magpol, the film was cut into dog-bone shaped

samples and strained under different crosshead speeds in a tensile tester (Instron 5567). A draw ratio of ~ 3 was used in each case. This was measured by marking a fixed distance (1cm) on the specimen with a marker and measuring the length before and after deformation. The fluorescence of the film was measured by a spectrofluorophotometer (Shimadzu RF-5301) at an excitation wavelength of 277 nm. The fluorescence measurement was carried out before and immediately after straining the film.

3.3.4. Evaluation of Self Healing property

The degree of self healing was measured for different types of damage. Magpol was damaged by subjecting the composite film to tear testing (ASTM standard D1938-08) using a mechanical tester. (Instron 5567) and 50mm/min crosshead speed. The healing process involved holding the torn edges of the sample between glass slides. The slides were then placed within the insulated induction coil and exposed to an AMF of strength 4 kAm^{-1} for varying time interval between 5 min. to 30 min. After exposure, the specimens were tested again to measure healing efficiency which was determined using the equation.

$$\% \text{Healing Efficiency} = [\text{Max. Tear strength (virgin)} / \text{Max. Tear strength (Healed)}] \times 100$$

The wear resistance properties of Magpol before and after damage were measured via its tribological performance. Samples were slid against a 6 mm steel ball (Cr6) using a ball-on-disk tribometer (CSEM 15-208) for 150 m under a normal load of 2 at ambient temperature (22°C). Velocity of 5 cm/s and sliding path of 2 mm (radius) and was used.

Cut-through damage was simulated by cutting the polymer film with a razor blade. Healing was achieved by placing the cut edges together within the induction coil and heating for 1 h. The morphology of the cut section was observed under the Scanning Electron Microscope JSM-5410 with accelerating voltage in the range of 5 to 15 keV.

3.3.5. Actuation Measurements

3.3.5.1. Bending Actuation

Bending actuation involved placing the Magpol film, one end of which is clamped, away from the electromagnetic poles and measuring the deflection when the current is applied to the electromagnetic coils towards the region of the higher magnetic field

gradient.

3.3.5.2. Displacement Measurements

The magnetic field was generated using a Lakeshore CM-4 dipolar electromagnet. The pole distance was set to 2.5 cm in all experiments. The sample was secured at one end using a non-magnetic clamp. The free end was connected to a Vernier dual range force sensor (resolution 0.01N) *via* a string. Displacement of the free end of the sample was recorded on a laser triangulation system (Acuity AR600). The sample was placed at varying distances from the electromagnet poles and the displacement of the free end towards the poles was measured.

3.3.5.3. Work loop

The work capacity of Magpol was measured using the Work-Loop technique. The sample was displaced up to $\pm 50\%$ strain, while simultaneously measuring force generated for every 0.5 cm of elongation. At 50% strain, magnetic field of 1T was applied and the increase in force measured. The sample was then released in 0.5 cm increments in the presence of the maximum magnetic field while measuring the force. The change of force for strain levels of 0% to 50% and back to 0% forms a loop; the area of the loop yields the work output of Magpol.

3.3.5.4. Buckling actuation

Figure 3-3 shows a schematic of the experimental setup used to measure stress and strain values generated by Magpol in an applied magnetic field. The setup was similar to that used for displacement measurements; except that the sample was placed between the electromagnet poles. A glass cylinder was also used to constrain the sample between the poles.

3.4. Finite Element Simulations

3.4.1. Magpol film heating in RF field

The temperature rise of Magpol as a function of time on application of the AMF was calculated using the values obtained from equation (1) which determines the volumetric power output of Magpol in an AMF. Using heat transfer in solids module (COMSOL Multiphysics 4.3b) the temperature rise of the sample could be predicted using the inbuilt equation (32):

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \cdot \nabla T = \nabla \cdot (k \nabla T + Q) \quad (32)$$

Where ρ is the density, k is the thermal conductivity, C_p is the heat capacity of the polymer and Q is the volumetric power output from the magnetic nanoparticles, as calculated from equation (1). Fine triangular meshing was used for the model. Initial and boundary conditions include T_0 = room temperature and convective cooling at the outer boundaries. The heat generated was also measured experimentally using a fiber optic thermometer.

Figure 3-3 Schematic of experimental setup to measure buckling actuation mode. The sample film is clamped at one end above the pole, while the free end is placed between the poles in a glass cylinder. Buckling occurred within the pole diameter.

3.4.2. Buckling actuation

The buckling behaviour of Magpol was studied using finite element analysis (FEA) in the COMSOL Multiphysics solid mechanics module. The sample was modelled as a 3 dimensional cantilever beam placed in a magnetic field. Experimental values of sample dimensions, material properties and magnetic field were used. The Magpol beam was secured at one end, while the other end was free to deflect in the field. The magnetic force acting on the sample was calculated for a magnetic field strength of 750 kA/m. Linear buckling analysis was performed on the sample and the first 2 buckling modes were calculated. Relative permeability of 1.3 and sample modulus of 14 MPa were used in the simulation.

Chapter 4

4. Results and Discussion: Material Characterization

This chapter describes the properties of the magnetic nanoparticles that function as the filler in Magpol, as well as the properties of the matrix thermoplastic EVA. When combined into Magpol as a composite, the material properties were again characterized for different filler loadings (weight percentages). Physical, magnetic, mechanical and thermal properties of Magpol were measured and their effect on self healing, sensing and actuation behaviour is discussed. Through these experiments, it was observed that hydrothermal wet chemical method produced the most suitable magnetic nanoparticles while solution casting produced homogenous Magpol films. The modulus, magnetic properties, heating rate, T_g and shape memory properties of Magpol improved with increased nanoparticle filler loading.

4.1 Physical properties of Magnetic Nanoparticle fillers

MnZn ferrite nanoparticles of different stoichiometries were synthesized by co-precipitation and hydrothermal methods. Both these methods utilize the wet chemical approach and have common precursors, but have different outcomes in relation to the crystallinity and size distribution of the sample. Additionally, changing the Mn:Zn ratio leads to changes in particle size, magnetic properties and most importantly, can be used to tune Curie temperature. Both the chemical co-precipitation technique and the hydrothermal synthesis method have been previously shown to yield large amounts of crystalline nanoparticles with a reasonably narrow size distribution. Hence the following nanoparticles were synthesized using these two methods

- Co-precipitation
 - $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$
 - $\text{Mn}_{0.8}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$
- Hydrothermal synthesis
 - $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$
 - $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$
 - $\text{Mn}_{0.8}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$
 - $\text{Mn}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$

The crystallographic structure of the synthesized particles was determined through X-ray diffraction patterns. Figure 4-1 shows the XRD patterns for the particles synthesized via chemical co-precipitation. The peaks correspond to the spinel franklinite, while the broadening of all the peaks suggests the formation of nanosize crystallites.

Figure 4-3 shows the XRD patterns for the particles synthesized via hydrothermal reaction. The peaks observed in these patterns were sharper compared to those of the co-precipitated particles indicating much higher degree of crystallinity.

Figure 4-2: XRD pattern for (a) $\text{Mn}_{0.4}$ and (b) $\text{Mn}_{0.8}$ nanoparticles synthesized by co-precipitation; showing the spinel crystal structure

Figure 4-3: XRD pattern for (a) $\text{Mn}_{0.4}$, (b) $\text{Mn}_{0.7}$, (c) $\text{Mn}_{0.8}$ and (d) $\text{Mn}_{0.9}$ nanoparticles synthesized by hydrothermal method. Note the sharper peaks as compared to Figure 4-2

In both cases, the 2θ peaks were observed at 29.9° , 35.2° , 42.6° , 52.9° , 56.3° and 61.9° . These peaks were matched to franklinite spinel structure (JCPDS card No. 10-0467), confirming the existence of $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ in all the samples (Figure 4-4). Small differences between the 2θ values denote differences in unit cell parameters. A small shift in the 2θ peaks was observed with increasing Mn content. This is explained by the larger divalent ion radius of Mn (.80 Å) compared to Zn (0.74 Å) which causes the lattice parameter to shrink when Fe^{2+} is replaced by Mn.

Figure 4-4: Peaks of synthesized magnetic nanoparticles match that of franklinite Mn-Zn ferrites.

Minor peaks observed at 2θ values of 33.15° , 35.61° , 40.85° , 49.48° , 54.09° and 63.99° indicate the presence of hematite ($\alpha\text{-Fe}_2\text{O}_3$). (JCPDS card No. 33-0664). Hematite was formed in small amounts during the hydrothermal reaction due to precipitated Mn and Zn hydroxides re-dissolving and complexing with sodium salts (from NaOH). This caused preferential formation of iron hydroxides and hence $\alpha\text{-Fe}_2\text{O}_3$.

The average crystallite size was calculated using the Scherrer equation (33)

$$d_{XRD} = \frac{k\lambda}{\beta \sin\theta} \quad (33)$$

Where d_{XRD} is the average crystallite size, λ is the X ray wavelength, k is the shape factor of 0.94 and β is the full width at half maximum of the peak at θ . To avoid interference of $\alpha\text{-Fe}_2\text{O}_3$ peaks in the size calculation the 29.78° peak was used to measure the full width at half maxima. It was observed that increasing Mn content increased crystallite size. The average size increased from 12.4 nm for Mn_{0.7} nanoparticles to 13.2 nm for Mn_{0.8} and 15 nm for Mn_{0.9} nanoparticles. The Mn^{2+} cations have a lower affinity for tetrahedral lattice sites in the spinel structure which results in larger particle size.

4.1.1 Transmission Electron Microscopy

TEM images were obtained for the Mn_{0.7}Zn_{0.3}Fe₂O₄ and Mn_{0.8}Zn_{0.4}Fe₂O₄ nanoparticles, used as a filler in Magpol in the thesis. Figure 4-5 shows the bright field TEM images of the bare nanoparticles.

TEM images showed that the particles were roughly equiaxial and aggregated. Kim et al. suggested that the existence of van der Waals interactions between the particles results in aggregation.²²⁶ Alternatively, magnetic nanoparticle aggregation could be due

to magnetostatic interactions caused by dipole–dipole interactions. Larger and more well defined particle shapes were observed in samples synthesized *via* the hydrothermal process. The supercritical fluid present in the hydrothermal reactor causes recrystallization driven by dissolution of thermodynamically unstable iron oxyhydroxides to occur resulting in larger particles and more well-defined crystals.²²⁷

A selected area electron diffraction (SAD) pattern, obtained from the area shown in Figure 4-5a, is presented in Figure 4-5c. The diffuse intensity distribution in the SAD individual pattern verifies the nanocrystallinity of the material. The ring spacing on the diffraction pattern matched the spinel manganese zinc ferrite crystal structure.

Figure 4-5: Bright field TEM images of (a) Mn_{0.7} and (b) Mn_{0.8} nanoparticles and associated SAD pattern of Mn_{0.7} nanoparticles

The average particle size was also calculated from the TEM images (Figure 4-6). The average particle size of 12.5 for Mn_{0.7} and 13.6 nm for Mn_{0.8} matches the values of 12.4 nm and 13.2 nm obtained through XRD data. Aggregation was observed in all samples due to magnetic interactions. Narrower size distribution (9 nm to 18 nm) was seen for the Mn_{0.7} particles as compared to Mn_{0.8} nanoparticles which had a wider

size distribution (9 nm to 19 nm).

Figure 4-6: size distribution of Mn_{0.7} and Mn_{0.8} nanoparticles.

4.2 Magnetic properties of nanoparticle filler

4.2.1 Saturation Magnetization

Saturation magnetization (M_s) at room temperature, and the Curie temperature were measured. The ability of the magnetic filler to respond to, both direct and alternating applied magnetic fields depends on these values of M_s and T_c . Figure 4-7 plots the magnetic moment per gram of the nanoparticles vs. the applied magnetic field (B-H curve) for the nanoparticles synthesized by both the co-precipitation and hydrothermal methods.

In both cases, the particles retrace the loop through the origin, exhibiting a sigmoidal magnetization curve. Experimentally, due to size distribution and clustering effects, a small amount of hysteresis may be observed. In both cases, it was observed that the M_s value increases with the Mn content. The manganese ions in the cubic spinel structure increase the magnetic moment of the sublattice consisting of tetrahedrally coordinated ions. Figure 4-7 also shows that at low fields, magnetic permeability increases with manganese content, in agreement with literature on Mn-Zn ferrites.^{222-223, 225}

Figure 4-7: Room temperature VSM curves of Mn-Zn ferrites synthesized via (a) co-precipitation and (b) Hydrothermal methods

The small coercive fields indicate low hysteresis losses. On closer examination, it was observed that the Mn0.9 particles did not show superparamagnetic behavior (coercive field ~ 50 Oe) (Figure 4-8). The high Mn content results in an increase in particle size above the critical domain size, causing the emergence of ferromagnetic behaviour in the Mn0.9 nanoparticles.

Figure 4-8: Hysteresis behaviour of Mn_{0.9} magnetic nanoparticles

M_s increases with increasing Mn:Zn ratio. For Mn 0.4, the M_s is only 22 emu/g, but this increase for Mn 0.4 to 35 emu/g for Mn 0.8 co-precipitated nanoparticles. For hydrothermally synthesized particles, the M_s value increased from 45 emu/g for Mn 0.4 to 55 emu/g for Mn_{0.7} to 62 emu/g for Mn_{0.8} and 65 emu/g for Mn_{0.9}. The hysteresis curves show that for the same stoichiometry, the particles synthesized by the hydrothermal method have higher M_s than those from the co-precipitation method. The longer reaction times, higher temperature and pressure of the hydrothermal method contribute toward the higher crystallinity of the particles produced in the hydrothermal method, resulting in improved magnetic properties. Thus, only hydrothermally synthesized nanoparticles were used as fillers in Magpol.

4.2.2 Curie temperature (T_c)

The T_c (or more specifically the Néel temperature as ferrites are antiferromagnetic) is an important magnetic property when considering controlled heating of magnetic nanoparticles. To prevent excess heating and thermal damage to the matrix, the T_c must be tuned to the processing temperature of thermoplastic EVA. We therefore measured the T_c of the magnetic nanoparticles Mn_{0.7}, Mn_{0.8} and Mn_{0.9} (Figure 4-9)

Figure 4-9: Magnetization vs. temperature curves of (a) Mn0.9, (b) Mn0.8 and (c) Mn0.7 nanoparticles

A magnetization v/s temperature (M-T) curve was also plotted For the Mn0.7, Mn0.8 and Mn0.9 samples to determine their T_c . Sharp transition temperatures were not observed. In such cases, the T_c can be calculated from the relationship between spontaneous magnetization (M_s) and $(T_c - T)^\beta$ which scales when the critical exponent $\beta = 1/3$.¹⁹³ The T_c can then be determined by extrapolating M^3 to 0. Using this relation, the T_c was calculated for each sample. Mn0.7 had the lowest T_c of 190°C, while Mn0.8 had a T_c of 230°C and T_c of Mn0.9 sample was 280°C.

The effect of the Mn and Zn content on saturation magnetization and Curie temperature can be explained on the basis of the exchange interactions occurring in the sublattices of the nanomagnets. Spinel ferrites with a cubic crystal structure show two different crystallographic sublattices, composed of tetrahedral (A) and octahedral (B) sites. In the undisturbed case of magnetite Fe_3O_4 , the ferrimagnetic structure results from an antiferromagnetic superexchange interaction between the ions on the A and B sites mediated by oxygen ions as well as a ferromagnetic double exchange interaction between the B site ions.

For $Mn_xZn_{1-x}Fe_2O_4$ nanoparticles, the observed tendency of the saturation magnetization can be explained on the basis of the cation distribution, which influences the exchange interaction between the ions at the tetrahedral and octahedral sites. Zn^{2+} ions and Fe^{3+} ions have the preference to occupy the tetrahedral sites. Mn^{2+} and Fe^{2+} do not show this tendency; hence, they are supposed to be equally distributed over all three

possible sites. As more non-magnetic Zn^{2+} ions occupy the tetrahedral A site, its average magnetic moment decreases and no magnetic interaction between the magnetic ions of the sublattices takes place. Furthermore, due to the presence of Zn ions on the tetrahedral sites the regular distribution of Fe^{2+} and Fe^{3+} on the octahedral sites is distorted. This effect is strengthened by the presence of Mn^{2+} ions on the B sites, whose electron configuration equals that of Fe^{3+} ions. Therefore, the ferromagnetic double exchange interaction between Fe^{2+} and Fe^{3+} ions on the B sites is replaced by an antiferromagnetic superexchange interaction between Fe^{3+} with Fe^{2+} and Mn^{2+} , resulting in a distorted antiferromagnetic structure on the B sites.

In conclusion, the disturbed superexchange interaction as well as the canted (non-collinear) spins lead to a decrease in the magnetic moment with increased Zn concentrations. This reduced interaction between the A sites and the B sites results concurrently in a lower value for the Curie temperature. Even though the Curie temperature and the saturation magnetization of the particles are mutually dependent, the saturation magnetization is not the only factor influencing the Curie temperature but for example also the inversion parameter has an impact. In addition, surface anisotropy like the formation of a dead layer on the particle surface, existence of random canting of particle surface spins, and non-saturation effects due to broad distribution of particle size or deviation from the normal cation distribution influence the magnetic properties of nanosized particles. In conclusion, even though the general magnetic behavior of the particles can be explained, a full understanding of all observed properties will require further investigations.²⁵²

4.2.3 Heating in a Radio Frequency Alternating Magnetic Field (AMF)

The ability of the nanoparticles to respond to an alternating radio frequency field and thereby generate heat is essential for the self healing ability of the composite. This ability is characterized by the Specific Absorption Rate (SAR) which depends upon the size of the particles as well as the field frequency. The heating of the particles is regulated by their T_c , and hence the heating rate slows down as the ferrofluid approaches the T_c of the particles and eventually the temperature reaches a steady state (Figure 4-10).

Figure 4-10: (a) Temperature rise of magnetic ferrofluid v/s time (b) Relative temperature rise v/s time showing change in temperature during heating

The particles synthesized via the co-precipitation technique do not show adequate heating characteristics as compared to similar stoichiometry particles synthesized *via* the hydrothermal method. The maximum temperature obtained by the ferrofluid also gives us an indication of the particle's T_c , which roughly matches values from VSM experiments and literature, assuming some heat loss. Particles with Mn concentration above 0.7 could not be used, as the maximum temperature reached by the Mn 0.7 particles matched the boiling point of the suspending liquid. The discrepancy between heating rates for co-precipitated and hydrothermal particles can be explained by the difference in particle size and reduced magnetization of co-precipitated nanoparticles. The influence of size on heating power of the nanoparticles at a fixed AMF frequency

is discussed in the next section.

4.2.4 Calculation of power output from magnetic nanoparticles

Experimentally, the heat generated by the magnetic nanoparticles is given by the specific absorption rate (SAR). The specific absorption rate (SAR) determines the efficiency of the particles in converting the applied AMF into heat and is calculated by the formula:

$$SAR = C \left(\frac{\Delta T}{\Delta t} \right) \frac{mass_{matrix}}{mass_{nanoparticles}} \quad (34)$$

Where $(\Delta T/\Delta t)$ is the initial slope of the temperature vs. time plot. and C is the heat capacity of Magpol

The heating efficiency for individual monodisperse nanoparticles has a single maximum at the peak frequency f_p given by:

$$2\pi f_p = \tau^{-1} \quad (35)$$

Thus, to obtain a maximum heating rate, the particle size must correlate with the field frequency. There is a flexibility to tune particle size for a given frequency, or alternatively, tune the frequency to suit particle size to obtain maximum heating rate. This relation is important when selecting the method for filler synthesis, as it allows us to fix particle size. Theoretically, the power (P) generated by the nanoparticles under fixed AMF field depends on the relaxation time and permeability of the magnetic nanoparticles.²²⁸

$$SAR = P/D \quad (36)$$

Where D is the density of the material and P is obtained from equation 1. The optimum size of the nanoparticles required for maximum SAR can be calculated from the equation 36.

AMF frequency and field strength, and particle size and anisotropy constant influence SAR: narrow particle size range will generate higher SAR. Optimum particle sizes for heating were found to be in the size range of 14 to 16 nm for both Mn_{0.7} and Mn_{0.8} nanoparticles for a frequency of 475 kHz and field strength of 4 kA/m. (Figure 4-11) This corresponds to the size of the particles synthesized by the hydrothermal method. Thus optimal heating will be achieved with the as synthesized particles.

Table 4-1: Data used to model SAR of Mn-Zn ferrites

Parameter	Mn0.7	Mn0.8
Domain Magnetization (M_d)	400 kAm ⁻¹	460 kAm ⁻¹
Anisotropy constant (K)	1800	1800
Volume Fraction ϕ	12 wt% and 16 wt%	12 wt% and 16 wt%
Temperature (K)	310	310
Frequency (kHz)	475	475
Field Strength (H_0)	4 kAm ⁻¹	4 kAm ⁻¹
Saturation Magnetization (M_s)	50 emu/g	65 emu/g

Figure 4-11: SAR vs. particle size for optimum heating

4.3 Colloidal stabilization of Magnetic nanoparticles

Homogenous distribution of magnetic nanoparticles within a polymer matrix is a challenge due to the tendency of the particles to aggregate within the matrix. Aggregation occurs either to minimize the surface energy of the particles, through van der Waals interactions or because of dipole interactions between the magnetic nanoparticles. This is especially problematic when dispersing nanoparticle powder into the thermoplastic through melt mixing. Synthesis of the composite by solution casting

is a viable option to avoid mixing. By dissolving the components in an appropriate solvent, it is easier to achieve homogenous mixing. Stabilizing the nanoparticles in a suspension of the solvent compatible with a casting solvent will ensure good mixing.

EVA is soluble in only a limited number of organic solvents; hence the nanoparticle colloidal suspension must also be in an organic solvent. Tetracholoethane was chosen for a solvent exchange reaction, between the magnetic nanoparticles, which are synthesized in an aqueous solution, and EVA which is cast in organic TCE.

Polyethylene-co-acrylic acid (15 wt% acrylic acid) was used to stabilize the magnetic nanoparticles. The Fe^{3+} ions on the nanoparticle surface can bind to the polar carboxyl group of the acrylic acid in the PEAA chains. The polyethylene segments then act as the stabilizing agents or tails to keep the particles in the colloidal state. (Figure 4-12)¹⁸⁹

Figure 4-12: Ionic bond formation between carboxylic acid groups of PEAA and Fe ions on the surface of magnetic nanoparticles for colloidal stability

The amount of PEAA coated onto the nanoparticles was measured using TGA (

Figure 4-13). The total amount of PEAA coating the particles was calculated to be 11.4% (starting weight % at room temperature – end weight % at 600°C). The weight of PEAA was subtracted from the total weight during synthesis of the composite so that only the weight of the nanoparticles is considered when calculating the final weight percent of nanoparticles in the films. PEAA shows a single temperature region of weight loss. The major decomposition region lies at ~425°C where the polymer backbone undergoes decomposition resulting in a majority of the observed weight loss. The acrylic acid side groups are stable and decompose simultaneously with the rest of

the polymer chains, as observed from the single step curve.

Figure 4-13: TGA of PEAA coated Mn0.8 magnetic nanoparticles.

4.4 Magnetic nanoparticle filler dispersion in EVA matrix

Mn07, Mn08 and Mn09 nanoparticles were used as fillers in the synthesis of Magpol. Mn07 and Mn08 are superparamagnetic and hence show minimal aggregation after colloidal stabilization. Mn09 has a coercive field of -50Oe , and showed significant aggregation in both the colloidal solvent and in the Magpol samples. SEM micrographs and optical photographs were used to observe the aggregation of magnetic nanoparticles in the Magpol matrix. Figure 4.14 shows particle distribution in Mn07, 08 and 09 films (SEM micrographs and photographs). Mn09 shows visible aggregates which are also seen in the SEM images, while Mn07 and Mn08 show relatively homogenous distribution of nanoparticles in the SEM micrographs, and a smooth appearance in the optical photos.

Figure 4-14: SEM micrographs and photos of Magpol films showing particle distribution. a) Mn07 and b) Mn08 show homogenous distribution while c) Mn09 shows particle aggregation

4.5 Mechanical Properties of the polymer matrix and Magpol composite

The addition of the magnetic nanoparticles to EVA enhances the properties of the polymer, the same mechanical and thermal tests are carried out on both the original EVA as well as Magpol.

Figure 4-15: stress strain curve of EVA

For efficient actuation and strain sensing, the modulus of EVA must be low and it must show large plastic deformation before break. The tensile properties of EVA and Magpol with different loadings are given in Figure 4-15 and Figure 4-16.

Figure 4-16: stress vs. strain curve of EVA containing 2wt% to 60 wt% of magnetic nanoparticle filler

Table 4.2 gives an overview of the change in modulus with increasing filler concentration.

Table 4-2: Elastic modulus of Magpol with 2 to 60 wt% nanoparticle filler

Nanoparticle loading (wt%)	Modulus (MPa)
0	5.8
2	7.5
5	8.3
10	9
20	10
40	12.3
60	14

The addition of nanoparticle fillers increased material stiffness. The increased modulus is caused by interactions between the magnetic nanoparticles and polymer matrix chains. The interaction is facilitated by the presence of the PEAA coating on the magnetic nanoparticle surface. The interaction between the filler and matrix results in greater force transfer between the nanoparticles and matrix resulting in increased actuation response. However, higher modulus will necessitate greater force to obtain

actuation. Therefore there exists a trade-off when selecting the optimal filler concentration.

4.6 Thermal properties of EVA and Magpol

The multicycle self healing and sensing properties of Magpol depend on the transition temperatures of EVA. A low melting temperature and melt viscosity is ideal for reptation based self healing, while the shape memory properties will determine Magpol recovery after damage. Figure 4-17 shows a DSC thermogram of EVA over a second cycle to remove the thermal history of the sample.

Figure 4-17: DSC thermogram of EVA

The low melting temperature of 86°C is suited for self healing via magnetic nanoparticle heating. The processing temperature of EVA is also between 140°C to 160°C. This temperature can be achieved by the Mn0.7 and Mn0.8 nanoparticles. The crystallinity of EVA was also calculated using the formula

$$\% \text{ Crystallinity} = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^\circ} \quad (37)$$

Where ΔH_m represent the latent heat of melting, ΔH_c the heat of cold crystallization and ΔH_m° is a reference value which represents the heat of melting if the polymer is in a 100% crystalline state. For EVA, ΔH_m° is approximately 293.6 J/g. The crystalline nature of EVA is required for efficient strain sensing, as phase separation is an integral part of the sensing process.

The glass transition temperature of Magpol was also determined through dynamic mechanical analysis. DMA results (Figure 4-18) show that there is little change in T_g with increased filler loading.

Figure 4-18: DMA analysis of EVA with 12, 16 and 20 wt% loading showing a) the Storage modulus vs. temperature and b) Glass transition temperatures obtained from Tan Delta curves

T_g ranges between -7 $^{\circ}\text{C}$ for 0 wt % loading to -9 $^{\circ}\text{C}$ for 20 wt% loading. At -80 $^{\circ}\text{C}$, there is an increase in storage modulus with loading. The storage modulus was found to be 1.5 GPa, 1.8 GPa, 2 GPa and 2.6 GPa for 0 wt%, 12 wt%, 16 wt% and 20 wt% loading respectively. This is consistent with the increase in elastic modulus with increasing filler loading.

The shape memory properties were measured by unconstrained strain recovery. It was observed that increasing amount of stress was required to achieve the same strain with increased filler loading, while shape recovery improved with increased loading. Complete shape recovery can be observed when Magpol is heated above 86 $^{\circ}\text{C}$, but due

to experimental constraints, maximum recovery temperature was fixed at 70°C. At this temperature there is a small difference in the shape recovery properties of Magpol; increasing loading enables higher shape recovery, EVA 0 wt% filler shows lowest shape recovery. (Figure 4-19)

Figure 4-19: DMA analysis of Magpol with 12, 16 and 20 wt% loading over two constrained shape recovery cycles

This increase in storage modulus and shape memory properties can be ascribed to the magnetic nanoparticles acting as crosslinks. These crosslinks store energy during the deformation process and act as a guide to restore the original sample dimensions during recovery.²⁰⁸

4.7 Magnetic properties of Magpol

The saturation magnetization of the Mn0.7 and Mn0.8 films containing 2 to 60 wt% loadings were measured (Figure 4-20).

It was observed that the coercivity of the samples decreased with increasing nanoparticle loading in both Mn0.7 (51.4 G for 2 wt % to 18 G for 60 wt %) and Mn0.8 (55.8 G for 2 wt% to 45 G for 60 wt %) samples. Conversely the M_s increased with increasing loading – (2 emu/g to 15.2 emu/g for Mn0.7 and 2.1 emu/g to 21.2 emu/g for

Mn_{0.8}).

Figure 4-20: room temperature VSM curves of (a) Mn_{0.7} and (b) Mn_{0.8} Magpol composites with different nanoparticle loadings

The magnetic properties of Magpol determine the extent of actuation in an applied magnetic field. The force acting on Magpol and hence the work output depend on the magnetization of Magpol.

Chapter 5

5. Results and Discussion: Self Healing in Magpol

This chapter describes the self healing functionality of Magpol. As covered in the literature review, there are various methods to develop self healing soft material. In the framework of a multifunctional composite material, we select a reptation based healing mechanism. This chapter will focus on the different types of damage that Magpol is capable of healing, the role of magnetic nanoparticles in healing and compares the experimental healing efficiency with theoretical models.

In order to determine the self healing ability of Magpol, the composite was subjected to different damage modes, such as chaffing and tear. Greater healing efficiency was obtained at lower filler loading compared to other relevant systems. Efficient healing was obtained without any thermal degradation. Good agreement was observed between experimental results and theoretical models of polymer healing. Thus, a Curie temperature controlled magnetic nanocomposite system was developed with improved self healing capabilities.

5.1. Introduction

One of the motivations behind the synthesis of self healing Magpol is to use it as a self healing wire coating material, both for electrical as well as biomedical applications.²²⁹⁻²³⁰ In certain application spaces like aerospace, automotive industries etc., polymer coatings are exposed to aggressive working conditions, such as repeated mechanical damage, flexing, vibration, environmental factors, handling etc. The ability to achieve healing of damaged insulation, *in situ* and at greater penetration depths in a localized region than currently possible is of immense commercial interest. Thus, this work is designed to optimize self healing of common forms of wire coating damage with high efficiency and in less time.

Figure 5-1 illustrates the processes occurring during healing, as described in the literature review. The damaged sections of Magpol are held together and exposed to an AMF. Nanoparticles embedded in the composite generate heat on exposure to the AMF. The maximum heat that is generated by the nanoparticles is controlled by their T_c . Heat transfer occurs between the nanoparticles and the matrix triggering the self healing reaction. Self healing involves movement of polymer chains across the damaged interface, resulting in chain entanglement and ultimately welding of the damaged sections resulting in self healing.

Figure 5-1 Schematic showing the mechanism of self healing in Magpol. On exposure to the AMF, the nanoparticles transfer heat to the matrix, which causes enhanced polymer chain mobility and reptation based healing.

5.2. Magnetic nanoparticle heating and heat transfer

First, the heat generated by the particles is calculated *via* equation (1) using the same parameters as chapter 4. The contribution due to Brownian relaxation is omitted from the calculation as the relaxation time is several orders of magnitude higher than the Néel relaxation. The difference is because of the nanoparticles are embedded in the polymer matrix. Even when the polymer melts, the viscosity is too large to appreciably reduce the Brownian relaxation time as compared to a more common ferrofluid, where the suspending liquid is water.

Figure 5-2 shows the calculated Brownian and Néel relaxation times for magnetic nanoparticles of different sizes.

The power output of 10 wt%, 12 wt% and 16 wt% loadings for Mn_{0.7} and Mn_{0.8} samples is calculated in Table 5.1.

Using the calculated power output as the heat source in COMSOL, heating behaviour of the samples was modelled. Figure 5-3 shows the theoretical model used to determine heat generated on the sample surface due to AMF exposure. COMSOL heat transfer module was used to determine the temperature rise over time in the Magpol film (details in section 3.4.1).

The temperature was recorded until equilibrium was reached due to heat loss to the environment. The simulation was continued until the temperature equilibrated and a graph of temperature vs. time was plotted. This theoretical temperature rise was then compared to experimentally obtained values.

Figure 5-2: Néel and Brownian relaxation times of magnetic nanoparticles embedded in Magpol

Table 5-1 Total power output calculated for Mn0.7 and Mn0.8 samples for different loadings.

Nanoparticle filler Loading (Wt%)	Volumetric power output (kW/m ³)	
	Mn0.7	Mn0.8
10	843	1175
12	1014	1413
16	1334	1859

Figure 5-3: COMSOL model of the Magpol film used to study temperature rise over time in an AMF

The experimental temperature rise is more rapid than that predicted by the model. (Figure 5-4) A sharp temperature cut-off is also observed in the experimental samples which are not represented by the model. This sharp cut-off is a self regulating mechanism, wherein the particle ceases to generate heat once the temperature of the system approaches the T_c of the magnetic nanoparticles. The model considered heat loss to the environment to reach the equilibrium temperature. Mn0.8 films with higher T_c can achieve higher temperatures compared to Mn0.7 before the self regulating mechanism is activated. The nanoparticle loading also influences heating of Magpol. Higher equilibrium temperatures are achieved with increased loading; but the temperature is controlled by the “failsafe” T_c of the nanoparticles which ensures that

the maximum temperature does not cross the T_c .¹⁹⁵ This “failsafe” prevents damage to the matrix due to uncontrolled heating. The average processing temperature for EVA (between 150°C and 220°C) could be obtained in all the Mn0.8 samples and the 16 wt% loading Mn0.7 samples.²³¹

Figure 5-4: Observed and modelled heating of [a] Mn0.8 and [b] Mn0.7 Magpol samples with increasing filler loadings.

5.3. Tear Tests damage and repair

Magpol samples were subjected to a tear test to mimic damage that can occur in guidewires when the coating is notched or cut. This is a common cause of failure in wire insulation. The healing efficiency of Magpol in the AMF was determined for varying time intervals (5 min.-30 min.). The healing efficiency for Mn0.8 and Mn0.7 samples with 10 wt%, 12wt% and 16 wt% are given in Figure 5-5.

Figure 5-5: Experimental and predicted healing efficiency of Mn0.7 and Mn0.8 films with [a] 10wt% [b] 12 wt% and [c] 16 wt% nanoparticle loadings

It was observed that the interfacial temperature determined healing efficiency. Higher interface temperatures resulted in greater healing efficiency. Initially, high % healing was observed between 0 to 5 min. During this period, the polymer chains undergo surface rearrangement and wetting.^{212, 232} The second half of the healing reaction is dominated by chain diffusion and randomization which are time dependent properties.

Hence longer AMF exposure times resulted in increased healing efficiency. Mn0.7 samples did not show 100% healing even after 30 min. This was due to insufficient temperature rise in the sample hindering polymer chain motion and entanglement. The Mn0.8 samples were able to heal upto 100% in all cases; but increased loading enhanced healing efficiency by decreasing time required for complete healing. The experimental % healing values were greater than the predicted values. This could be explained by the additional pressure generated by the glass slides which were used to hold the sample during healing. The pressure results in increased entanglement amongst the polymer chains, resulting in stronger bonds, which is not accounted for by the model.

5.4. Multicycle healing

In order to mimic biological systems, Magpol must be capable of undergoing multiple cycles of self healing without a reduction in mechanical properties. This was studied by subjecting 12wt% Mn0.8 films to repeated cycles of damage followed by a healing reaction. The samples were subjected to ten cycles of repeated damage and healing (Figure 5-6). The sample was repeatedly damaged *via* the tear test followed by AMF exposure for 20 min to induce healing.

The tear strength for 50mm extension was similar for the initial recovery cycles and decreased slightly for the next seven cycles. The direction of the tear followed the same path, resulting in reduced maximum tear strength from the third cycle onwards. The sample failed completely after the tenth cycle and did not heal sufficiently. This experiment showed that Magpol is similar to a biological system in the sense that it can undergo multiple cycles of damage and still be able to self heal.

5.5. Cut through test and repair

The ability of Magpol to heal cut through damage was studied using a razorblade to cut the sample through its entire volume. Healing on the microscopic level in Mn0.8 12wt.% samples over different time periods in the AMF was studied using SEM. (Figure 5-7) show the sample morphology in the damaged region. Surface rearrangement and wetting occurs at the interface within 60 s. This is followed by chain entanglement and bridge formation at 2 min. Interpenetration and randomization then occurred till 20 min where complete healing is observed without scar formation. The

high healing efficiency and absence of scarring is ideal for applications where surface morphology is important for preventing friction or drag.

Figure 5-6: Load vs. Peel extension plotted for 12wt% Mn_{0.8} sample subjected to 10 cycles of damage and healing.

5.6. Wear damage and repair

Wear occurring during operation can cause volume damage to the coating and generate debris which can cause embolization. The recovery of tribological properties of Magpol is also an important aspect of self healing.

Wear testing was carried out using a pin on disc tribometer. Mn_{0.8} 12 wt% samples were damaged to varying degrees by increasing the path length of the sliding pin. Samples were worn through 10% to 50% of the sample volume. Healing was then carried out as described above. Healing efficiency was calculated by comparing the wear path length of the original and healed samples. Upto 10% of wear, Magpol could recover completely through redistribution of the matrix over the damaged area. Beyond 10%, polymer chain movement could not compensate for the large damage volume resulting in only partial recovery.

Figure 5-7: Different stages of self healing observed in SEM micrographs in Mn_{0.8} 12 wt% film on exposure to an AMF for A] 0 mins, B] 1 min, C] 2mins, D] 5 mins, E] 10 mins and F] 20 mins

Table 5.2 shows the % healing corresponding to a given damage volume.

Table 5-2 % Healing measured for different damage volumes

Damage volume %	Healing efficiency %
10	100
20	97
30	90
50	51

The low melt flow index of the EVA matrix resulted in slower chain movement across the damaged region and decreased healing efficiency. This problem can be overcome by choosing a matrix material with higher chain mobility and melt flow index.

The sample morphology during wear damage and after healing is shown in Figure 5-8. SEM images show the sample surface after 10% wear of Mn08 12wt% Magpol and after 20 min healing. Due to the shape memory effect, the worn surface is restored to the original topology and no scarring was observed. This is significant as healing restores the tribological properties of Magpol, decreasing the probability of subsequent friction damage.

Figure 5-8: SEM micrographs of 12 wt% Mn08 sample after a) wear damage and b) healing.

5.7. Thermal degradation study

To enable long term use of self healing Magpol as a wire coating, the composite must not undergo degradation during exposure to the AMF. Thermal decomposition analysis

of Magpol was done by measuring the weight reduction in a 16 wt% sample before and after exposure to the AMF for 20 mins. Figure 5-9 shows the TGA curves for both the original and AMF exposed samples. During heating virgin EVA shows a two-step weight loss curve in which the first step corresponds to decomposition of the volatile acetate groups at $\sim 350^{\circ}\text{C}$ followed by the polymer backbone decomposition at 425°C . No change was observed in the decomposition behaviour after exposure to AMF in either the volatile ($<300^{\circ}\text{C}$) acetate groups or the polymer main chain ($>300^{\circ}\text{C}$) with weight loss equal in both samples. This is because the “failsafe” Tc regulation prevents the maximum temperature obtained via heating in the AMF (220°C) from crossing the temperature at which thermal degradation begins ($>300^{\circ}\text{C}$).

Figure 5-9: Weight loss observed through of Mn0.8 12 wt% Magpol in original sample and after AMF exposure during healing. Overlapping curves suggest absence of pyrolysis and sample degradation.

In this work, due to the geometry of the coil and the sample placement, the entire sample undergoes heating in the self healing reaction. In practice, it may not be possible to place entire components within an RF coil either due to geometrical constraints or because of thermally susceptible components in some areas. To overcome this problem, new coil geometries have been suggested. A promising geometry is the “pancake” coil used by Duenas et al. The planar coil was used to isolate the healing area as well as depth of heating in a proof of concept ballistic missile surface.^{29, 30}

5.8. Shape memory assisted self healing

It was observed that when plastically deformed Magpol was placed in an AMF, the sample tended to recover its original shape. This shape recovery can be applied to self healing, to recover the original sample dimensions before the damaged segments can be held together to undergo repair. This method is similar to SMASH described in the literature review. Figure 5-10 shows a Magpol sample that has been stretched until failure. This has resulted in a very large plastically deformed region. Simply trying to weld the damaged sections together is not feasible as the deformation is too large to obtain closely matched edges.

Figure 5-10: Shape memory assisted self healing (a) exposure to the AMF causes the plastically deformed regions to regain their original shape. The two sections are held together to enable full recovery. (b) Mechanical properties of the original and healed sample

Healing of Magpol occurred in two steps. (a) Shape recovery restored the original sample dimensions. This step reversed the plastic deformation that occurred before failure, resulting in two pieces with a defined edge (Figure 5-10 (a) the two halves were then held together in an AMF for 10 min. to achieve complete healing at the interface. Healing was achieved through entanglement of polymer chains along the interface. Figure 5-10 shows the recovery of mechanical properties of Magpol after failure. The yield stress was lower in the recovered sample, possibly due to lower crystalline content (consistent with the DSC analysis: chapter 4). Crystallites can act as fillers and as cross-links which are not completely recovered after failure.

5.9. Summary

Magnet-polymer (Magpol) based composites were adapted to possess self healing properties by improving and customizing the material system for use as wire insulation. Due to the choice of the Tc tuned magnetic nanoparticles, with optimized SAR and the use of low melting and melt index EVA, the healing efficiency of Magpol was optimized. Figure 5-11 gives an overview of currently available self healing polymers and composites based on their healing efficiency and time required for healing and compares it to Magpol. The high efficiency and low time required to obtain 100% healing thus makes Magpol an attractive system for wire coatings.

Figure 5-11: Comparison of the healing efficiency of Magpol and other self healing materials

Chapter 6

6. Results and Discussion: Damage Sensing in Magpol

To develop an artificial skin material, it is necessary to recognize or sense damage before catastrophic failure occurs. Just as the skin of certain living animals can change colour depending on the environment, it would be beneficial for soft composites to also possess a remote, lightweight sensing mechanism that does not require continuous energy input. This lightweight multicycle sensing in Magpol is useful for the development of morphing wing skins.¹⁴ as well as for wire coatings, as described in the previous chapter

This chapter describes the incorporation of strain sensing functionality into Magpol through the use of the bis(benzoxazolyl)stilbene (BBS) chromophore. The strain sensing ability of Magpol was optimized by changing the concentration of BBS and utilizing various processing methods. The colour change response was correlated to the applied strain. The ability of Magpol to undergo multiple cycles of strain sensing and recovery was also studied. The mechanism of strain sensing ability draws directly from the shape memory assisted self healing described in chapter 5. Thus the sensing and self healing functions are linked in a novel fashion in this work.

6.1. Introduction

Figure 6-1 is a schematic of strain sensing and self healing of Magpol.

Figure 6-1: Schematic of damage sensing and self healing in Magpol. The sample displays damage sensing by a colour change on plastic deformation. This colour change becomes more pronounced with increasing strain. The sample is strained until failure. Subsequently, healing is carried out in an AMF. Embedded nanoparticles generate heat, resulting in recovery of the original shape and healing of the damaged region along with a return to the original colour.

Plastic deformation causes color change from greenish blue to deep blue due to disaggregation of the bis(benzoxazoly)stilbene (BBS) chromophore. Further deformation can ultimately lead to failure. Following failure, Magpol is remotely and wirelessly exposed to a radio frequency alternating magnetic field (AMF). This AMF causes the nanoparticles embedded in Magpol to generate heat through Néel relaxation

losses. This heat is transferred to the shape memory polymer matrix (poly ethylene – co- vinyl acetate). The temperature rise acts as a trigger to recover the original component shape and the original chromophore aggregate structures. This causes the original colour to re-emerge. Once the damage has been visualized, self healing can be achieved as described in chapter 5.

The advantage of using magnetically triggered heating is twofold: firstly, heating can be triggered remotely and at greater penetration depths. Secondly, due to the distribution of the nanoparticles within the matrix acting as a heat source, chromophore aggregates present on the surface of the material are at a relatively lower temperature preventing their disaggregation, while the interface can achieve higher temperature required for polymer chain movement and thus ensuring efficient healing.

6.2. Optimization of bis(benzoxazolyl)stilbene concentration

The ability to sense plastic deformation in Magpol relies on dye aggregate formation and the ease of aggregate dissociation when force is applied. Aggregate formation is influenced by the properties of both the dye and the polymer matrix. The dye concentration required to form aggregates depends on the miscibility of the dye in EVA. Aggregates form when the concentration of the dye is above its solubility limit and the dye molecules can aggregate. In addition to this caveat, the size of the aggregates also influences the sensitivity of Magpol to applied strain. Smaller dye aggregates will be able to undergo rapid disassociation at low applied strains, increasing Magpol's sensitivity. Thus, BBS concentration must be optimized to ensure formation of responsive BBS aggregates.

Figure 6-2 compares the molecular dispersability of the dye in the polymer matrix by determining the change in the fluorescence spectrum with increasing BBS concentration. Peaks observed between wavelengths 410 to 450 nm indicate the presence of isolated BSS chromophores, while the broader peaks between 450 to 525 nm indicate the presence of molecular aggregates. (i.e. I_E to I_M ratio – ratio of green to blue emission peak).

For 0.02wt.% and 0.05wt.% BBS concentration, the higher intensity peak was observed at approximately 430nm. This indicates the presence of isolated BBS species, the lower intensity peak centred at approximately 460nm wavelength indicates the presence of BBS aggregates formed within the EVA matrix. The relative ratio between these two

peaks indicates the majority species present within the matrix and hence the colour of the Magpol. For 0.08 wt.% BBS, the peak ratio changes significantly, with green emission peak becoming increasingly prominent. This signifies the formation of BBS aggregates. The most prominent green aggregate peak is observed for a concentration of 0.1 wt%. From this result, it can be inferred that 0.1 wt.% BBS is the minimum concentration required for aggregate formation.

Figure 6-2: Fluorescence spectra of a) BBS in dilute solution of TCE showing majority species of isolated BBS molecules (430 nm) and small peak at 460nm showing aggregation.¹¹⁶ b) Magpol with varying BBS concentration showing increased aggregation with increasing BBS concentration

6.3. Optimization of Annealing Time

The ability of the molecular aggregates of BSS to break up during plastic deformation is essential to the strain sensing property of Magpol. This requires the formation of smaller sized/ finer aggregates. This can be achieved by quenching Magpol and then subjecting it to an annealing process. The mobility of the dye molecules in the matrix will allow the formation of finer aggregates.

The solution cast specimen was quenched in an ice bath after removal from the oven, as opposed to the slow cooling that was utilized for the earlier experiment above. A similar sample containing BBS 0.1wt% (as used in the previous experiment) was cast under the same conditions. After quenching, the film was cut into 5 sections and each section was annealed at 70°C for a time range of 15, 30, 45, 80 and 120 minutes respectively. The fluorescence spectrum of the five specimens was compared over increasing time intervals for annealing. Figure 6-3 shows the comparison of fluorescence spectra for different annealing times.

Figure 6-3: Fluorescence spectrum of different annealing time

Based on the fluorescence spectrum in Figure 6-3, the specimens that have been annealed for 15 and 30 minutes show higher intensity monomer blue peak (I_M) compared to the excimer emission green peak (I_E). the shorter annealing time (<45 mins) is not sufficient for excimer formation. At 45 mins, the relative intensities of the monomer and excimer peaks are similar, indicating equal amounts of aggregates and single molecules. However, with longer annealing time range of 80-120 minutes, the emission peak is significantly higher than the monomer peaks. Annealing beyond 120 mins did not affect the I_M/I_E ratio significantly, indicating that there is a maximum limit to the formation of dye aggregates.

6.4. Correlation of strain with colour change

Photoluminescent (PL) measurements were conducted to investigate the correlation between applied strain and the chromic properties of Magpol (Figure 6-4). 20 wt% Magpol was stretched to different strains at room temperature until failure. The emission spectrum in the center of the deformation region was measured for each strain value. Upon plastic deformation the chromophore aggregates (I_E) (525 nm) exhibited distinct changes in the absorption band compared to the monomeric species (I_M) (475 nm). There is an almost linear decrease in the I_E/I_M ratio up to 150 % strain, which then

begins to level out until failure of the sample. Therefore, in addition to gross colour change, the measured relative intensities of the I_M and I_E peaks can be correlated to the actual strain that Magpol has undergone.

While I_E/I_M ratio could not be measured during elastic deformation in this work due to experimental constraints; several studies have reported that the % change in I_E/I_M ratio corresponds closely to the tensile stress vs strain curve of the polymer matrix. This correlation has been observed in both elastic and plastic deformation regions, as well as in thermoplastics and elastomers.¹¹⁶⁻¹²¹ This indicates that deformation in amorphous regions can also be sensed via BBS. Thus mechanochromic dyes are a robust and versatile method of incorporating strain sensing into polymers.

6.5. Reversible strain sensing

Previous studies have demonstrated the use of mechanochromic molecules as strain sensors in polymers. However, a significant drawback is the single cycle use. In previous reports plastic deformation could not be reversed hence the technique was only applicable for one time use. Other reports demonstrated repeatable sensing in elastomers through chemical modification of the polymer chains. Thus to develop multicycle strain sensing in Magpol, which can correlate to the multicycle self healing ability, the shape memory assisted recovery is also used to reorganize BBS chromophore aggregates as well as to recover from plastic deformation. Shape recovery is obtained by the heating of Mn0.8 nanoparticles embedded in EVA. Mn0.8 nanoparticles show more efficient heating (chapter 5) and are therefore used in all the following experiments.

Figure 6-4: Strain sensing in Magpol a] Color change due to plastic deformation observed under UV light @ 377 nm. Deformed regions are deep blue , undeformed material is bluish green b] Photoluminescent spectra of Magpol shows the change in the relative heights of the peaks at 425 and 515 nm, which indicate the original colour and the colour after straining respectively; the peak at 515 nm becoming more pronounced with increasing strain c] Sensitivity of Magpol to a range of strain values measured by the relative change in intensity of 425 and 515 nm peaks as a function of strain.

6.6. Shape memory properties of Magpol

To utilize the shape memory properties of Magpol for multicycle strain sensing, the efficiency of the shape recovery process is first studied. The shape fixity (R_f) and shape recovery (R_r) were calculated for three cycles of strain and AMF induced recovery (N) using equation (38) and (39).

$$R_f = \frac{\varepsilon_{\text{unloaded}}(N)}{\varepsilon_{\text{max}}(N)} \times 100\% \quad (38)$$

$$R_r = \frac{\varepsilon_{\text{unloaded}}(N) - \varepsilon_{\text{permanent}}(N)}{\varepsilon_{\text{unloaded}}(N) - \varepsilon_{\text{permanent}}(N-1)} \times 100\% \quad (39)$$

Where $\varepsilon_{\text{unloaded}}$ is the fixed strain, ε_{max} is the maximum strain and $\varepsilon_{\text{permanent}}$ is the residual strain.

Shape recovery of Magpol was carried out by placing samples in an AMF; the magnetic nanoparticle filler provides sufficient heat *via* relaxation losses to trigger the shape memory effect. Table 6.1 gives the values of the shape fixity and recovery obtained over the three cycles and shows the shape fixity and recovery values of 12 wt%, 16 wt% and 20 wt% Magpol.

According to the Magpol film heating data from chapter 5, increased loading generates more heat, resulting in a more efficient shape recovery process. The initial cycle had lower shape recovery, while subsequent cycles showed better performance without much difference in the values between cycles. This similar behaviour from the second cycle onward is due to alignment of the hard segments in the strain direction during the first cycle. This alignment is retained during subsequent cycles, improving shape recovery. The DMA analysis also supports this result; less stress is required during the second cycle to achieve the same strain. (Chapter 4)

Table 6-1: shape fixity and recovery values of 12 wt%, 16 wt% and 20 wt% Magpol over 3 cycles

Wt. Loading %	Shape Fixity (%)	1 st cycle Shape Recovery (%)	2 nd &3 rd cycle Shape Recovery (%)
20	63	99	100
16	75	90	100
12	72	83	98

6.7. Multicycle strain sensing

In order to test the recoverability of Magpol, samples with different filler loading, were subjected to three cycles of plastic deformation (~200% strain) and recovery in an AMF (additional cycles to test the performance of the BBS chromophore are described later). The I_E/I_M ratio was recorded before and after strain deformation as well as after recovery. The percent change in the I_E/I_M ratio was calculated for each case and recovery was determined (Figure 6-5). It was observed that changes in emission spectra upon damage and recovery increased with filler loading.

Figure 6-5: Change in relative intensities in the photoluminescent spectra of Magpol at 425 and 515 nm plotted as a ratio IM/IE after damage and again after recovery over 3 cycles. Cycling was done for 12, 16 and 20wt % filler samples.

Additionally atomic force microscopy (AFM) images also show that recovery of the initial surface roughness of the film indicating the presence of chromophore aggregates after the shape recovery step. (Figure 6-6)

6.8. Effect of shape recovery on polymer matrix crystallinity

The strain sensing ability of mechanochromic dyes has been linked to the semicrystalline nature of the polymer matrix, as described in the literature review. The crystallinity of the EVA polymer matrix was determined using a DSC at each stage of the damage and recovery process; i.e. the original sample, after plastic deformation and after recovery. All the nanoparticle loading (12, 16 and 20 wt. %) were studied. Based on the DSC curve obtained, the heat of melting is calculated. This is then used to calculate the percentage crystallinity using equation 37. For EVA, the ΔH_m is approximately equal to 293.6 J/g. Table 6.2 shows the percentage crystallinity calculated for different nanoparticle loadings.

Figure 6-6: AFM images showing BBS chromophore aggregates a) before damage, b) after strain and c) after recovery

Table 6-2: Percentage crystallinity in EVA

Weight% of nanoparticles	Polymer Condition	% Crystallinity
0	Original	7.4
12	Original	10
	Strained	9.2
	Recovered	6.9
16	Original	12
	Strained	7.8
	Recovered	6.5
20	Original	8.5
	Strained	8.1
	Recovered	6.1

In each case it is observed that the percentage crystallinity of the original specimen (before strain) is the highest. This is due to the annealing process that the sample is subject to, which is necessary for BBS aggregate formation. According to theoretical predictions, plastic deformation of the polymer causes elongation and drawing of the polymer chains in the direction of the applied force. This will result in an increase in the amorphous content of the sample and alignment of the remaining crystallites. This is also observed experimentally.²³³

On exposure to the AMF, the deformed samples are heated above their transition temperature, resulting in shape recovery. In the case of EVA, the transition temperature is the melting point of the polymer. Immediately after shape recovery, the sample is removed from the coil and cooled in air to room temperature. There is no annealing step required for aggregates to re-form. This fast cooling, results in the amorphous regions being retained, consistent with the results in

Table 6-2. This is an interesting result, as it shows that high crystallinity is not necessary for the functioning of mechanochromic molecules. In the case of Magpol, it is possible that dye molecules aggregate around the magnetic nanoparticles in the matrix, and the shape recovery is sufficient for the aggregates to reform after strain. Further

investigation of the actual nucleation sites of the BBS molecules and its interactions with nanoparticle fillers is required to understand this phenomenon.

6.9. Stability of strain sensing BBS over multiple cycles

The response of the mechanophore (BBS) to strain and its repeatability in a multicycle situation is studied using 16 wt.% sample that was run through 15 cycles of repeated straining and recovery. At the interval of every three cycles (after recovery), the fluorescence spectra of the specimen was measured and a comparison was made at the end of the 15th cycle. Figure 6-7 shows the fluorescence spectrum of the original specimen and five other spectra that were observed at the 3rd, 6th, 9th, 12th and 15th cycle of strain and recovery.

Figure 6-7: stability of BBS dye based sensing over 15 cycles of strain and recovery

The peak of higher intensity observed in the fluorescence spectrum indicates the presence of BBS aggregates; its intensity gives an approximate quantification of the aggregates within the polymer matrix. From Figure 6-7, it can be observed that the original and 3rd cycle fluorescence spectrum does not differ significantly. This indicates that the majority of isolated molecules after strain were able to reform into aggregates upon recovery on the 3rd cycle. Whereas from the 6th cycle onwards, peak intensity is comparatively lower. This also indicates that there is lesser re-formation of BBS aggregates upon recovery compared to the original and 3rd cycle. Although there are smaller numbers of BBS aggregates, the intensity peak contribution from these BBS

aggregates is significant for strain sensing functionality. Hence, in the event of repeated deformation and recovery, the BBS molecules will still be able to respond to the mechanical stimuli for strain sensing.

6.10. Proposed mechanism of Multicycle strain sensing in Magpol

As mentioned earlier, EVA has a dual segment structure consisting of a hard elastic segment and an amorphous soft segment that can alter its stiffness on heating above its melting temperature. Thus, EVA shows a dual-component mechanism of shape recovery. The magnetic nanoparticles can act as net points which can store elastic energy, providing the driving force for shape recovery.²⁰⁸ This explains both increase in storage modulus as well as the increasing shape recovery with increasing filler concentration. (chapter 4) The nanoparticle fillers may also act as physical crosslinks to store energy required for efficient shape recovery.

Strain sensing in Magpol depends on BBS aggregate sensitivity to plastic deformation. During plastic deformation the polymer chains undergo reorganization and slippage. This causes the chromophores associated with the chains to disaggregate and mix with the matrix, the magnitude of this effect depends on the degree of crystallinity and mobility of the polymer chains.²³³

The DSC analysis shows that there is a slight decrease in crystallinity of Magpol during plastic deformation. This can provide greater volume for disaggregation of the chromophore molecules into the matrix. The almost linear decrease in I_E/I_M ratio (upto 150%) followed by a more gradual decrease can be explained by the semicrystalline nature of the EVA matrix. The initial deformation of semi-crystalline polymers is through a combination of inter and intra-lamellar shear. Initially, the amorphous domains in the inter lamellar regions undergo (visco-)elastic deformation. At yield, two lamellar deformation mechanisms occur: Fine slip and coarse slip. In fine slip, the polymer chains slip through the lamellae. This is responsible for the linear strain sensing behaviour of Magpol. During coarse slip the lamellae fragment because of intra-crystalline shear. This does not affect the I_E/I_M ratio but decreases crystallinity of Magpol.²³⁴

The decrease in intensity of I_E signal after recovery compared to the original sample could be due to the healing process in which chain rearrangements and entanglements

disrupt chromophore aggregates on a small scale. This can be overcome by annealing the films to regain the aggregate structure.

A correlation was also observed between the shape memory based self healing property of Magpol and the I_E/I_M ratio recovery. The I_E/I_M ratio was measured during the shape memory based self healing described in the previous chapter in section 5.8. The two damaged sections of the Magpol sample were held in contact with each other for 20 min. to regain the original sample.. Shape recovery of the plastically deformed regions (within the first 60 seconds) resulted in recovery of the original I_E/I_M ratio, as seen in section 6.7 as well as almost all of the mechanical strength (figure 5.10 c). No change in the I_E/I_M ratio was seen after the initial shape recovery

Figure 6-8 illustrates our model of the processes occurring during strain and recovery of Magpol. During plastic deformation, BBS chromophore aggregates present in the amorphous part of the EVA break up into single molecules with a corresponding change in the emission spectrum. This is also accompanied by alignment of polymer chains and crystallites along the strain direction. The nanoparticles may also act as crosslinkers in the matrix. On triggering heating by exposure to the magnetic field, Magpol recovers its original shape, though some of the crystallites may still retain their orientation. Also, a small fraction of chromophore molecules may remain their monomeric form. Subsequent cycles of strain and recovery follow the same path as the first cycle.

6.11. Summary

From chapter 5 we see that Magpol can undergo multicycle healing without deterioration of its mechanical properties. Enabling recovery of strain sensing ability along with recovery of the mechanical properties is important for repeated use of the material in practical applications. The mechanochromic response of Magpol is recovered during the first step of shape recovery. This novel finding enables us to reuse Magpol over several damage cycles. Thus, the chromophore based strain sensor can act as an early warning system of plastic deformation before failure of the material.

Figure 6-8: Model of recoverable strain sensing and self healing in Magpol a) Original: Sample shows high crystallinity, BBS molecules aggregated and nanoparticles form links between the polymer chains b) After plastic deformation and failure: a decrease in crystallinity, single BBS molecules formed due to disaggregation (resulting in a colour change). c) Recovery: shape recovery causes recovery of the original dimensions. Polymer chain entanglement at the failure interface results in self healing BBS aggregates also re-form resulting in recovery of the original colour. Further cycles of strain and recovery follow the same pattern described above.

Chapter 7

7. Results and Discussion: Actuation in Magpol

In this chapter, the actuation behaviour of Magpol composites in an externally applied direct magnetic field was studied. The actuation behaviour could be tuned by changing the position of the sample relative to the field. Two modes of actuation were studied: bending and buckling. The relatively higher modulus of the thermoplastic EVA, as compared to the more common silicone used in previous studies, limited the deformation to only these two modes, while elongation and contraction of the sample were not observed. The bending actuation of Magpol containing both Mn0.7 and Mn0.8 fillers was studied, while buckling actuation was studied only with Mn0.8 filler samples, as these nanoparticles showed higher stress and strain compared to the less magnetic Mn0.7 nanoparticles. The work output was calculated for both modes of actuation and compared to other current soft actuator technologies.

7.1. Magnetic field measurement

The magnetic field generated by the electromagnet was measured for different pole gap distances. Smaller pole gap distances generated a higher field at lower current, but eventually saturated. A larger pole gap generated a linear field increase with increasing current. Figure 7-1 shows the measured magnetic field at a given current, for pole gap distances of 5 cm, 2.5 cm and 1.8 cm.

Figure 7-1: Magnetic field generated vs. current applied for a given pole gap distance

The 5 cm air gap has the closest fit to a linear relationship ($R^2 = 0.98$) and was therefore the most suitable parameter for subsequent measurements. Once the maximum magnetic field ($B_{\max}$) at a given current was measured experimentally, it was possible to obtain the magnitude of the magnetic field at various distances from the poles. (Equations 19-21) For a δ value of 40 and pole radius of 1.5 cm, the magnetic field for different $B_{\max}$ values is shown in Figure 7-2

Figure 7-2 shows that the highest magnetic field gradient exists from 1.5 cm to 5 cm away from the pole center. Therefore this region will show the highest strain rate behaviour, and samples placed within this distance showed the best response.

7.2. Bending Actuation

Bending is measured as the maximum deflection of Magpol when the external magnetic force is applied perpendicular to the longitudinal axis of the sample. To study the bending mode of actuation, samples were clamped in an aluminum holder and placed 5 cm away from the poles. The current through the electromagnet was gradually increased

and the sample displacement measured. Bending was studied in samples containing both Mn0.7 and Mn0.8 fillers. Figure 7-3 shows the strain obtained with increasing filler loading in varying magnetic fields. The trends observed for both Mn0.7 and Mn0.8 nanocomposite films were similar; the displacement was lower for nanocomposite films containing lower filler loading levels and increased with filler loading. However the higher M_s of Mn0.8 ensures that Mn0.8 enables the samples to achieve higher strain at low magnetic fields as explained in the model below.

Figure 7-2: Electromagnetic field distribution from the center of the poles outwards for different B_{max} values

Saturation magnetization (M_s) influenced the displacement behaviour of Magpol. Threshold strain was observed in samples in samples with nanoparticle loading below 10 wt%. The gradient of the electromagnet's magnetic field is responsible for threshold deflection behaviour.

From Figure 7-2 it is clear that above a critical distance, magnetic field gradient is negligible. Below this critical distance, there is an exponential increase in both the field, and the gradient. The gradient changes more rapidly as compared to the field strength. The rapid increase in the gradient is responsible for threshold deflection behavior. This threshold behaviour can be exploited for novel switching applications.

Figure 7-3: Strain vs. applied magnetic field for increasing filler loadings in (a) Mn0.7 and (b) Mn0.8 samples

7.2.1. Model of bending actuation

The strain can be calculated depending on the force (F) that acts on Magpol. The total force acts on the volume (V) of the sample and is influenced by the magnetic potential (U). The field gradient produced by the electromagnet and magnetic moment (M) of the sample also contribute to the total force. The magnetic moment can be calculated from the applied magnetic field (H_0) and the sample susceptibility (χ).¹⁸¹

$$\frac{d\vec{M}}{d\vec{H}} = \chi \quad (40)$$

$$\vec{U} = \int_0^H \vec{M} d\vec{H} \quad (41)$$

$$\vec{U} = \frac{1}{2} \chi H_0 \quad (42)$$

$$\vec{F} = -\nabla \vec{U} \quad (43)$$

$$F_y = M_y \int_0^V \frac{dH_y}{dy} dV \quad (44)$$

To achieve actuation in Magpol, the applied force must be greater than the weight of the sample. The force acting on the sample can be increased by increasing the magnetic field. According to the equations above, increasing the nanoparticle loading of the sample increased its susceptibility and therefore sample deflection occurred at lower magnetic fields. Due to the difference in the magnetic properties of Mn0.7 and Mn0.8 nanoparticles, the Mn0.7 and Mn0.8 composites also showed different susceptibilities. The higher susceptibility of the Mn0.8 composite resulted in greater displacement at low fields with higher strain rate as compared to Mn0.7. However the maximum

achievable strain was similar for Mn0.7 and Mn0.8 films. This was due to the force generated in the samples for loadings greater than 20 wt% exceeding the maximum deflection force. (Figure 7-4)

Figure 7-4: Maximum strain obtained for increasing wt% loaded samples for Mn0.7 and Mn0.8 films

7.2.2. Work loop measurements

The bending actuation mode was also used to calculate the work capacity of Magpol. The method used was similar to that used for biological muscles and is useful in designing Magpol actuators.⁷⁰ Figure 7-5 shows the force obtained for Mn0.8 60 wt% Magpol during a work loop cycle. The area under the curve was used to calculate the work capacity of Magpol.

Figure 7-5: General structure of a work loop obtained for Magpol with 60 wt% loading

The maximum work density obtained for different wt% loading is shown in Table 7.1. Higher wt% loading generated a higher force and a greater work density. No saturation was observed in the total work output at higher loadings. This was in contrast to the strain behaviour observed previously. The increasing force can be explained by increasing M_s values at higher wt% loading.

Table 7-1: Work density calculated for different wt% filler loadings of Magpol

Concentration (wt%)	$Mn_{0.7}Zn_{0.3}Fe_2O_4$		$Mn_{0.8}Zn_{0.2}Fe_2O_4$	
	Work (mJ)	Work Density (J/kg)	Work (mJ)	Work Density (J/kg)
20	.32	0.5	.67	1.4
40	.58	1.1	1.14	1.8
60	1.13	1.5	1.91	2.3

Both $Mn_{0.7}$ and $Mn_{0.8}$ nanocomposite films exhibit similar trends in the graphs. With increasing levels of particle loading, the area under the curves becomes larger and more work is done; e.g. for 60 wt % $Mn_{0.7}$ samples was 1.1 mJ whereas 60 wt % $Mn_{0.8}$ films showed close to 2 mJ. As expected, $Mn_{0.8}$ films have better magnetic properties which accounts for higher work density produced for all strain levels.

Furthermore, 60 wt % $Mn_{0.8}$ nanocomposite film was subjected to the maximum field of 1.5T to obtain the highest amount work output possible in the experimental set-up. Increasing field resulted in increase in the force generated from 53.7mN to 61.7mN and a maximum work density of 2.8J/kg.

7.2.3. Comparison of bending actuation with available actuator technologies

The efficiency of the bending mode for actuation was compared to other actuator technologies (Figure 7-6). The yellow star indicates Magpol, while the white square in the upper left corner indicates the optimum actuator technologies.

From the figure, it is clear that the bending mode of actuation does not possess sufficient work output to be a truly viable soft actuator.²³⁵ Thus, the geometrical or material parameters of Magpol must be adjusted to obtain a better stress-strain response. Hence, in the next section, we will study a new buckling mode that can be used for actuation.

Figure 7-6: Comparison of the bending mode work capacity of Magpol (yellow star) with other actuator technologies ²³⁵

7.3. Buckling actuation

Buckling is characterized by a sudden sideways failure of Magpol subjected to compressive axial stress, supplied by the external magnetic field. During buckling, the compressive stress at the point of failure is less than the ultimate compressive stress that the material is capable of withstanding. Buckling mode of actuation can be observed when the sample is placed in between the two electromagnetic poles, with a section of the sample protruding beyond the pole boundary. Thus, the magnetic field will exert a contractile force on the Magpol sample. Depending on the material properties, the force will act on the sample in different ways. If the modulus of the Magpol matrix is low, contraction will occur under certain boundary conditions. In materials with high modulus or placed in a constraining tube, buckling will occur.²³⁶

In previous studies, it was observed that silicone based Magpol underwent buckling actuation when placed under certain sample constraints.⁴⁵ Buckling was characterized by a helical “coiled” structure and was determined by the diameter of a constraining cylinder surrounding the sample. Smaller diameter constraining cylinders only resulted in sample contraction with large hysteresis. The coiling mode was capable of generating higher stress and strain, compared to contraction.

To develop an actuator based on buckling mode, it would be beneficial to eliminate or reduce hysteresis. This can be achieved by using a higher modulus polymer like EVA as the matrix in Magpol. The higher modulus (14 MPa) of Magpol opposed the contraction mode of actuation and channels the magnetic force towards buckling. This ensured maximum strain, even at lower nanoparticle loadings and or low M_s samples.

Strain was calculated by measuring the displacement of the free end of the sample and dividing it by the original length. Figure 7-7 shows the strain obtained for increasing filler loading.²³⁶⁻²³⁷ The load v/s strain plot follows a similar pattern for all samples and is similar to the theoretical load v/s displacement curve obtained for a beam undergoing constrained Euler buckling (Figure 7-7a). Figure 7-7(b) shows the shape of the Magpol sample obtained during buckling. The contact points observed during buckling matched the theoretical predictions. At low magnetic field, the sample tended to align with the field lines and showed a minimal strain. Further increase in the magnetic field showed a sharp increase in strain; indicating the critical field for buckling was reached. Subsequent increase in the field again showed only limited displacement until the field for the second buckling mode was reached. This again caused a large increase in strain. This continued until the entire sample length entered between the electromagnet poles. Significant buckling displacement was only observed in Magpol films with 20 wt% or higher loading. Therefore the actuation behaviour of 20, 40 and 60 wt% samples was studied. Initially, the maximum sample length of 9 cm, calculated according to electromagnetic field gradient distribution, was used to study the displacement. Figure 7-8 shows the strain v/s applied magnetic field for 20 to 60 wt. % Magpol.

It was observed that, while all samples underwent buckling, the maximum displacement was obtained for the 40 wt% sample. The field at which buckling occurred increased with a decrease in the loading. This behaviour is explained by the classical Euler buckling theory, which states that a certain critical force is necessary for buckling to occur. Increasing the loading increases the saturation magnetization of Magpol. This causes more force to act on the sample at lower field, resulting in sample buckling at lower applied magnetic field.

Figure 7-7: (a) Predicted load vs. displacement obtained during Euler buckling in a constrained system. Hysteresis is also observed. (i-iv) Predicted sample deformation at different regions of the load vs. displacement graph (b) Experimental results of buckling observed in Mn_{0.8} 40 wt% sample²³⁶⁻²³⁷

Figure 7-8: Strain vs. applied magnetic field for different nanoparticle loadings

The displacement of Magpol depends on both the force acting on the sample as well as the weight of the sample, as discussed in the bending mode. To optimize the displacement, shorter sample lengths were also studied, to reduce the weight. 7 cm and 8 cm samples were compared to those of the 9 cm sample (Figure 7-9).

Figure 7-9: Maximum strain vs. nanoparticle loading for 20 wt%, 40 wt% and 60 wt% samples with increasing sample length. Highest strain was obtained in the 40 wt% samples.

In each case, the highest displacement was observed in the 40 wt.% samples. Interestingly, for the 20 wt% samples, the shorter sample lengths resulted in a higher displacement, while the opposite occurred for the 40 wt.% and 60 wt.% samples. This behaviour is again explained by the force-weight balance acting on the Magpol, as is explained in section 7.3.2.

7.3.1. Hysteresis behaviour during actuation

As mentioned above, to develop an ideal actuator, the hysteresis behaviour must be minimized. Therefore, the hysteresis behaviour of 7cm, 8 cm and 9cm Magpol samples was also studied by increasing the applied field to the maximum value and then decreasing it to zero and measuring strain during both loading and unloading (Figure 7-10).

The Magpol samples exhibited hysteresis (higher strain during unloading as compared to loading values) for all sample lengths. The samples did not retrace the strain path when the force was decreased, instead relaxing only once regaining the original

geometry. Interestingly, the critical buckling field decreased with increasing sample length. Longer samples showed buckling at lower magnetic field as well as reduced hysteresis.(Figure 7-10) This has been analytically modelled in the next section

Figure 7-10: Strain obtained for 40wt% sample during loading (increasing field) and unloading (decreasing field) for (a) 7cm, (b) 8 cm and (c) 9 cm samples.

7.3.2. Model for buckling in Magpol

Buckling can be modelled based on a relationship between applied force and sample load. The total load acting on the sample is composed of two forces: magnetic force (F_{magnetic}) resulting from application of the magnetic field and a counter force due to the sample weight (W_{weight}), (discussed in chapter 2 section 2.4)

Buckling will occur on the application of a critical load (P_{cr}) which is dependent on the applied magnetic field; referred to as the critical magnetic field (B_{cr}). P_{cr} is calculated from equation 22 in chapter 2. Using Euler's theory, a linear buckling analysis was

carried out using the magnetostatics and structural mechanics modules of the finite element simulation COMSOL software. The first two buckling modes are shown in Figure 7-11. The first mode corresponds to a bending type deformation, while the second mode shows sample curvature.

Figure 7-11: (a) COMSOL model of mode 1 linear buckling in Magpol. (b) Difference in Mode 1 & 2 is can be observed by the difference in the sample edge displacement.

The magnetic field at which buckling occurred could be calculated analytically from the equations 15-22 in chapter 2. Figure 7-12 shows the calculated v/s experimental critical magnetic field values required for buckling to occur at increasing nanoparticle loadings.

The decrease in critical field required for buckling follows similar trends in both cases. The large difference between the 20 wt% experimental and calculated values may be due to the sample adhering slightly to the constraining cylinder.

The critical magnetic field was calculated for both mode one and mode two ($n=2$) using equation 22. It was observed that while the 40 wt% Magpol could generate enough force to undergo the second buckling mode, 20 wt% sample could not; (Figure 7-13) this is also which is consistent with experimental observations.

Constrained buckling has been explained theoretically by Holmes et al., and Manning et al.²³⁶⁻²³⁷ in an elastic rod system under an applied field. According to their theory buckling occurs in several stages. Initially, the rod buckles at a single point. This point contacts the constraining wall. On further increasing the load, the sample increases contact with the constraining wall, until the applied force equals the critical force for

the second buckling mode or bifurcation point. The sample then buckles into a three turning point configuration (Figure 7-7). The hysteresis behaviour observed during unloading was also considered in this model.²³⁶ When the applied force is decreased, the sample follows the path beyond the second loading transition (Figure 7-7a:iii). Below a certain field, the sample separates from the contacting wall and the displacement will again overlap with the loading curve. This is similar to the theoretical plot in Figure 7-7. where the loading curve shows several step-wise increases in strain while the unloading curve only shows a single jump resulting in hysteresis.

Figure 7-12: Experimental and calculated critical buckling fields for different wt% loading of Magpol

This theory can also be used to tune the displacement of the sample by changing the distance between the constraining walls (h) and the critical buckling field. The wall distance has a maximum length beyond which the sample cannot contact the wall irrespective of the sample length. If the wall distance is less than the critical length, the magnetic field required for the buckling point to contact the wall can be changed by changing the wall distance.

Figure 7-13: Model of force generated by 20 wt% and 40 wt% Magpol with increasing magnetic field. Buckling occurs when the force intersects the mode 1 and mode 2 critical field lines.

7.3.3. Work output measurement

The buckling actuation mode was also used to calculate the work capacity of Magpol. In this case, the work loop method was not used due to geometrical constraints. To measure the work capacity of Magpol in buckling mode, loads of 0.55g, 0.48g and 0.35g were attached to 20wt %, 40wt % and 60wt% Magpol samples of 9cm length. The total work was calculated based on the displacement of each load under an applied magnetic field of 1T. Figure 7-14 shows the total work performed by each Magpol sample.

60 wt% sample generated the largest work output of 15.8 Nm using a load of .48g. This experiment showed that the actuation of Magpol can be obtained at relatively low fields and still produce high work output enabling the sample to lift >4 times its own weight.

7.3.4. Comparison with other buckling based actuators

In order for Magpol to be a competitive soft actuator, it must achieve stress and strain values similar to other buckling based actuators. This is compared in Figure 7-15. The competing technologies include thin shell Shape Memory Alloys,²³⁸ piezoelectric stacks,²³⁹ ionic polymer metal actuators (IPMC), electrostatic comb drives etc.²⁴⁰ SMAs and dielectric elastomer actuators (DEA) generate large stress but have very low strain and strain rates. IPMC electrodes are prone to cracking low and generate low stress¹⁵⁴

While electroactive polymers (EAPs) and Magpol can both generate sufficient stress and strain, Magpol is also capable of wireless, remote actuation in ambient conditions; which is a problem faced by current EAP technologies.

Figure 7-14: Total work obtained for 20 wt%, 40 wt% and 60 wt% Magpol. Highest work was obtained for 60 wt% Magpol

Figure 7-15: Stress vs. strain Ashby chart of Magnet-Polymer composite and other buckling actuators^{154, 239-241}

The work capacity of Magpol during buckling was also compared to other actuation technologies in Figure 7-16. An improvement is observed in the work capability in the buckling mode as compared to the bending mode. In the buckling mode, the work

capacity is comparable to electroactive polymers which are the main competing technology of Magnet-polymer actuators.

Figure 7-16: Comparison of the work capacity of buckling mode of Magpol (yellow star) with other actuator technologies²³⁵

7.4. Summary

In this chapter we studied two actuation modes of Magpol: bending and buckling. The strain and work capacity of both these methods was studied and compared to other available technologies. The mechanisms behind the actuation was discussed and modeled. This data was also compared to experimental results. While the bending mode does not produce sufficient work output, buckling actuation is a promising method for the construction of new soft actuators. Thermoplastic Magpol produces less stress and strain as compared to elastomer based Magpol, but the self healing and damage sensing properties provide additional advantages for a multifunctional material.⁶

Chapter 8

8. Results and Discussion: Magpol Guidewires

The multifunctionality of Magpol enables it to be used for multiple applications that have requirements of remote actuation, high flexibility, low weight etc. The possibility of damage over time, either due to repeated actuation of the composite, or due to impact and other kinds of externally induced damage requires self healing nature of the composite. The potential uses of the self healing Magpol transducers extend to several fields. For example, polymer composite skins in morphing aircraft wings and biomedical coatings used in catheters and guidewires during minimally invasive surgery can benefit from the ability to actuate, damage sensing and healing. This chapter describes the development of a proof-of-concept Magpol guidewire coating capable of guided actuation, damage sensing and self healing.

8.1 Introduction

Endovascular intervention is a minimally invasive technique that uses X-ray guidance to treat various vascular diseases. This minimally invasive method has several advantages over conventional surgery, including faster recovery and less pain for the patient. This method however, requires advanced devices and greater training to be successful.²⁶

Interventional surgery requires the manipulation of long, flexible sheaths, guidewires, and catheters that need to be guided through the vascular system.²⁴² Guidewires are defined as wire or spring inserted into a confined or tortuous space in the vascular system, to act as a guide for subsequent insertion of a stiffer or bulkier instrument. Currently used devices have a standard configuration with limited flexibility, which hampers their maneuverability. This maneuverability decreases further as the device passes through lesions etc., which may result in complete deviation of the guidewire into unwanted side branches of the blood vessels.²⁴³ Due to this drawback, the technique is not applicable to certain locations of the body which cannot be reached due to the limited flexibility of the guidewires. Moreover, each procedure requires multiple insertions and instrument exchanges through a guiding sheath. During a routine procedure, a guidewire may be inserted and extracted upto 20 times. This repeated extraction and insertion causes wear damage, resulting in flaking of the guidewire coating. This in turn can increase the chance of infection and embolization.

In order to visualize the passage of the guidewire through the vasculature intermittent projection fluoroscopy image guidance is used. This is highly disadvantageous as the operator has to rely on intermittent 2D images to manipulate the guidewire in a continuous 3D environment. Additionally, fluoroscopy also requires the presence of a nephrotoxic, iodine-containing contrast media which could cause unwanted reactions in the patient.²⁴⁴

Magnetic resonance imaging (MRI) can provide an alternative to overcome the problems of fluoroscopy based interventions as MRI does not utilize ionizing radiation or toxic contrast agents. In addition, vascular structures are easily imaged using MRI with image quality on par with fluoroscopy techniques.^{25, 245} However, there is a lack of MR compatible medical devices in the market, which has prevented the development of MRI based intervention therapies.

8.2 Gap in current guidewire technology

8.2.1 Coating Adhesion and Wear

The large number of extractions and insertions of guidewires and sheaths required in each procedure have shown to result in wearing of the PTFE coating. The debris resulting in this wearing could result in embolization as well as increased chance of infection. Figure 8-1 shows some of the types of damage that has been observed in the guidewire during use. Additionally, for biomedical catheter and guide wire coatings the U.S. Environmental Protection Agency requires that manufacturers eliminate the suspected carcinogen perfluorooctanoic acid (PFOA) from their PTFE formulations by 2015. PFOA is a synthetic perfluorinated carboxylic acid and fluorosurfactant. It is used as a surfactant in the emulsion polymerization of fluoropolymers like PTFE. In PTFE processing, PFOA is in aqueous solution and forms micelles that contain tetrafluoroethylene and the growing polymer. The carboxylate "head" of PFOA is hydrophilic while the fluorocarbon tail is hydrophobic and lipophobic. The "tail" is hydrophobic due to being non-polar and lipophobic because fluorocarbons are less susceptible to the London dispersion force than hydrocarbons. PFOA is an ideal surfactant because it can lower the surface tension of water more than hydrocarbon surfactants while having exceptional stability due to the presence of multiple carbon–fluorine bonds. It was thought that these properties enhanced interfacial adhesion, particularly on smooth wire products like guidewires. The removal of PFOA from the PTFE coating process led to flaking and delamination of the PTFE coatings, which has resulted in FDA recalls of several types of guidewires produced by various companies. Thus, there is significant demand for a new reusable coating capable of damage detection and healing before each use.²⁴⁶

Figure 8-1: Flaking damage observed in the PTFE coating of currently available guidewires²⁴⁶

8.2.2 Heating

In addition to flaking damage observed in conventional guidewires, these products are not suitable for interventional MRI procedures due to the presence of metal cores in the wires. Metal-based guidewires are electrically conducting and can generate heat or sparks during an MRI procedure causing blood vessel perforation. The conventional guidewires used in percutaneous angiographic procedures have a stainless steel core and therefore cannot be used in a MR environment. However nonferrous materials such as NiTiNOL also present problems in the form of heating caused by the RF radiation through the mechanism of eddy currents, induction loops and resonating RF transverse electromagnetic waves along long continuous wires.²⁴⁷⁻²⁴⁸

8.2.3 Positioning and guidance

Positioning and navigation of guidewires is usually achieved through visual methods using 2D data obtained from fluoroscopy imaging. Such stereotactic procedures depend on an external mechanical frame or landmarks to establish reference points for their operation. Magnetic based navigation could be used to overcome the need for such external reference points. This is achieved by the use of external magnetic fields to navigate magnetically responsive instruments.²⁴⁹⁻²⁵⁰ Currently, the only magnetic targeting system available is the Niobe system, developed by Stereotaxis Inc., Saint

Louis, Missouri. This system consists of permanent magnets placed on each side of the patient and capable of generating a focused magnetic field of 1T which is used to direct the guidewire. Currently only two companies have developed guidewires that are capable of utilizing the Niobe system: Cronus and Titan. These guidewires have a permanent magnet inserted into the tip of the guidewire (Figure 8-2), allowing it to be deflected in any direction by manipulating the external magnetic field.²³

Figure 8-2: Diagram of a standard guide wire. A NiTiNOL core is surrounded with platinum coil at the tip and stainless steel coil around the shaft. The entire wire is covered with an outer protective polymer coat that can be either hydrophobic or hydrophilic. For magnetically steerable guidewires, a permanent magnet is included in the distal tip.²³

For the ultimate goal of merging MRI interventional therapy and magnetic based guidance and navigation, the design of such a guide wire tip configuration is not advisable due to the previously mentioned heating problems. Hence the material design requirements must be changed to allow for combined magnetic actuation and MRI guided interventions.

8.3 Material design requirements

Magpol coating that is used for combined magnetic actuation and MRI guided interventions must have the following properties:

- i. Biocompatible (EVA is already used as guidewire coatings)
- ii. Provide MRI contrast (superparamagnetic ferrites are used as contrast agents in MRI e.g. MagnaFy MRI markers: Fe_3O_4 nanoparticle solution)

- iii. Non-conducting to reduce chances of heating via eddy currents. (ferrites are non conducting)
- iv. Damage sensing and self healing for repeated use

8.4 Magpol guidewire coating

Boston Scientifics' NiTiNOL stone retrieval basket (ZeroTip: sheath outer diameter 3F (1mm)) was obtained from Singapore General Hospital as a representative guidewire. The sheath material is a multilayer polyimide/PTFE design. To obtain a Magpol coating over the NiTinol core, the outer polyimide/PTFE coating was first stripped off and replaced by 20 wt% Magpol through a process of dip coating over the exposed core. Multiple dip coating process were carried out till the thickness of the coating matched that of the original PTFE sheath. A hollow PTFE sheath coated with Magpol having the same outer diameter as the ZeroTip guidewire was also made to study the actuation behaviour of the guidewire. Figure 8-3 shows the ZeroTip NiTinol basket coated with Magpol.

Figure 8-3: (a) Magpol coated NiTiNOL basket guidewire (b) inserted into a model vascular system

8.5 Tip deflection in Magpol Guidewires

The ability of the Magpol coating to cause deflection of the guidewire tip was studied by placing a permanent magnet at decreasing distances from the guidewire tip, while deflection of the tip is measured. A permanent NdFeB magnet with a magnetic field of $\sim 0.5\text{T}$ at the surface was used for the measurement. The magnetic field at a given distance from the magnet is plotted in Figure 8-5.

Figure 8-4: Magnetic field vs. distance from NdFeB magnet pole

A steep magnetic field gradient was observed from ~3 cm away till the magnet surface. As the magnetic force mainly depends on the magnetic field gradient, the largest actuation response was observed in this region.

Figure 8-5 shows the deflection observed in the guidewire tip at different distances from the magnet. At a distance of 5 cm away from the magnet, no discernable tip movement was observed. The magnetic field experienced by the tip at this distance is ~.15T. A 5 cm displacement is observed when the magnetic field is increased to 0.18T (4 cm). This displacement is sufficient for navigation through blood vessels. A sharp increase in the tip displacement is seen on decreasing the distance between the magnet and the guidewire (3 cm or less) as the magnetic field gradient is much higher in this region, ultimately resulting in the tip contacting the magnet.

Figure 8-5: Tip displacement of Magpol coated guidewire in an external increasing magnetic field

8.6 Self healing Guidewire coating

Damage occurs in guidewire coating due to the multiple extractions and insertions that a guidewire undergoes during each procedure. These extractions were simulated by

pulling the guidewire repeatedly through a 1.2 mm diameter ring which is similar to the diameter of a working channel sheath used in such types of procedures. The process was continued until visible damage was observed. After damage, the guidewire was held within an AMF for 10 minutes to heal the wear damage. Figure 8-6 shows the damaged and recovered coating observed under an optical microscope at 5X magnification.

Figure 8-6: (a) Wear damaged and (b) healed Magpol guidewire coating. Shape memory based self healing was observed on exposure of the guidewire to AMF

Shape memory based recovery was observed in the coating. On exposure to the AMF, Magpol initially returned to its initial shape and subsequently there was a smoothening of the surface, resulting in decreased probability of wear occurring in the same regions

8.7 Damage sensing Magpol Guidewire coating

The ability of the Magpol coating to sense damage through colour change was studied in concurrently with self healing. The damaged sheath was observed under both visible and UV light in Figure 8-7

There was visible colour change to dark blue in the areas that had undergone both wear and kink damage. While the wear damage was also prominent under visible light, it is interesting to note that kink damage was more easily visible under UV light due to the contrast in colour in the damaged region while it was not easily observed in visible light. This feature could be extremely useful in detection of damaged guidewires before use. Thus the damage sensing ability of the Magpol coating can be extremely useful in improving the safety and reliability of guidewires.

Figure 8-7: Damaged area highlighted within the red circles show a change in colour showing both (a) wear damage in UV and (b) visible light and (c) kink damage in UV and (d) visible light

8.8 Comparison of Magpol guidewires with competing technologies

Through the previous experiments it was seen that Magpol is a suitable candidate for the development of next generation biomedical guidewires that can be used for both MRI interventional therapies as well as for magnetic field based positioning. The ability of such Magpol guidewire to self heal from damage will also increase its service life and reduce overall costs. Figure 3-2 compares the properties of Magpol based guidewires to currently available and in-development guidewires over several categories required for the development of next generation guidewires.

Figure 8-8: properties of Magpol based guidewires and currently available and in-development guidewires over several categories required for the development of next generation guidewires

While ZeroTip and the Cronus/Titan guidewires are already marketed commercially, the MaRVis and EPflex are a new technology still under development for interventional MRI. From the figure it is clear that of the currently available or under development guidewires, the MaRVis provides the most features for developing a next-generation guidewire, but without the damage sensing or self healing properties provided by Magpol. Magpol provides the greatest flexibility for the development of a bioinspired multifunctional guidewire coating that can provide functionalities not present in other available products, thus enhancing its value.

Chapter 9

9. Conclusions

In this work, the next generation of multifunctional magnet-polymer composites has been developed. Taking inspiration from biological systems, Magpol has been adapted to exhibit the biological properties of multicycle damage sensing, self healing and actuation through a process of material selection and optimization of both the magnetic filler and the polymer matrix. Magpol was adapted to fulfill the required property metrics for advanced biomedical guidewire coatings. The sensing, healing and actuation behaviour of Magpol is studied in relation to the properties of its magnetic filler and polymer matrix. The main findings and future implications of this work are described.

Curie temperature tuned $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles were synthesized *via* wet chemical methods. Tc tuning was achieved by varying the Mn to Zn content in the nanoparticles. The hydrothermal method produced nanoparticles with a narrower size distribution and better heating ability as compared to co-precipitation. The particle composition, size, morphology and magnetic properties were characterized by XRD, TEM and VSM. It was observed that increasing Mn content caused an increase in particle size, saturation magnetization and Tc.

In order to obtain a homogenous distribution of nanoparticles in Magpol, solution casting proved more efficient as compared to haake mixing and compression molding. To obtain even distribution in solution, the nanoparticles we first converted into a colloidal suspension. The nanoparticles were colloiddally stabilized using PEAA in an organic solvent. ~11 wt% PEAA coating could be achieved on the nanoparticles which remained stable in suspension for over 24 hours.

$\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ and $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles synthesized *via* hydrothermal method were subsequently used as fillers in Magpol. Samples with 2wt% to 60 wt% filler loading were synthesized by solution casting using EVA as the matrix. The mechanical properties, elastic modulus, saturation magnetization, glass transition temperature, shape fixity and shape recovery increased with increasing magnetic nanoparticle filler loading.

Sample heating was measured by exposing Magpol to an AMF. Mn0.8 samples showed higher maximum temperature and heating rate as compared to Mn0.7 samples due to their higher Ms. This heating rate was also be predicted by Rosensweig's model which showed good agreement with experimental results.

Heat generated on exposure to AMF, due to the magnetic filler in Magpol, was used to heal damage caused by different mechanisms. The "failsafe" Tc tuned nanoparticle heating prevented pyrolysis of the matrix by limiting the maximum heat generated by the magnetic nanoparticles. Healing efficiency increased with increasing temperature and AMF exposure time. Multicycle healing was observed in Mn0.8 samples which also showed higher healing efficiency compared to Mn0.7 samples.

A novel shape memory assisted self healing process was developed wherein, the heat produced by the particles in the AMF was used to trigger a shape memory process followed by polymer chain entanglement. These two processes resulted in healing of the polymer matrix. By tuning the properties of the filler, it was possible to achieve greater healing efficiency at lower filler loading content and shorter healing time.

The shape memory properties of EVA were exploited to trigger both recoverable strain sensing as well as self healing. Visible damage sensing was achieved by the incorporation of stilbene dyes (BBS chromophores) into Magpol; which showed a linear change in fluorescence intensity with increasing strain of upto ~150%. Through this shape memory assisted recovery process, BBS aggregates could re-form due to the shape recovery of the surrounding matrix enabling BBS to be used as a multicycle strain sensor for the first time.

The magnetic filler content influenced the extent of shape recovery as well as healing efficiency. Interestingly, multiple cycles of failure and recovery did not adversely affect the sensing properties of the BBS chromophore. Healing, along with restoration of the mechanical properties of Magpol was achieved within 10 mins of exposure to the AMF.

Actuation behaviour of Magpol under varying magnetic fields and filler loadings was studied. Two deformation modes were observed: Bending and buckling. The maximum stress and strain were calculated for each mode. In the bending mode, the maximum strain saturated above 20 wt% loading while stress continuously increased with loading. This behaviour was dependent on the saturation magnetization of the nanoparticle filler.

The work density in bending actuation was calculated using the work loop technique used to measure the efficiency of artificial muscles. Similar to stress, the work output increased with increasing filler loading. Higher magnetic fields resulted in greater work output.

Buckling actuation was obtained by constraining Magpol films between the electromagnet poles. The deformation behaviour was similar to the constrained Euler buckling model. Higher order buckling modes could be obtained by increasing the filler loading beyond 20 wt%. Buckling was also modelled through finite element analysis

and the compared to experimental results. Work output was also calculated for buckling mode and 16.8 J/kg work density was obtained, comparable to electroactive polymers (EAP). The buckling actuation mode could generate significantly higher work output as compared to the bending mode, due to the placement of Magpol between the electromagnet poles.

The stress and strain obtained during actuation could be tuned by changing the sample geometry. An Ashby chart was used to compare Magpol with other actuation technologies. It was seen that Magpol buckling could lead to attractive combinations of stress and strain comparable to other competing artificial muscle materials.

A Magpol coated guidewire was developed as a proof-of-concept application that requires a multifunctional damage sensing, healing and actuable material. The coating was able to show tip flexibility similar to other commercial guidewires while also showing sensing and self healing ability. The Magpol guidewire is also capable of being used in interventional MRI therapies and was able to be magnetically positioned using low magnetic fields. This proof of concept coating has significant advantages over other products currently in the market or under development due to its multifunctionality.

Future Work

The damage sensing, self healing and actuation properties of Magpol are all comparable to other competing technologies, but Magpol provides the additional advantage of having all three functionalities present in the same material. Due to the flexibility in the choice of polymer matrix and magnetic filler, more efficient Magpol with additional functionalities can be developed.

Magnetic fillers made from FeNiB or FeNiMn alloy nanoparticles have shown T_c tuning ability while simultaneously showing high M_s values. The lack of surface functionalization sites has hindered the use of such particles as fillers due to the difficulty in synthesizing homogenous dispersion. The ability to form stable colloidal suspensions of such nanoparticles will enable their use in next generation Magpol materials.

The polymer matrix can also be extended to include crosslinked elastomers or

supramolecular polymers. Self healing and damage sensing are already well established properties of such polymers and addition of magnetic nanoparticles will enhance the overall functionality of such materials. The ability to achieve self healing and damage sensing through chemical bonds (crosslinked polymer) or through hydrogen bonding (supramolecular polymers) will bring an added value to Magpol.

Additionally, use of such polymers will increase the number of damage and recovery cycles that Magpol can undergo. The ability to break and re-form chemical bonds during self healing will contribute to the preservation of the molecular integrity of the matrix. The higher number of sensing and self healing cycles will dramatically increase the service life of components employing Magpol, either as a surface coating or as a load bearing element.

A great advantage in the use of silicone elastomers can be in actuation, where elongation and contraction of the polymer matrix is possible. The ability of Magpol to show such elongation or contraction gives higher stress and strain as compared to a thermoplastic matrix as seen in earlier work. Future work can include modifying silicone to possess both self healing and damage sensing ability. This would greatly increase the efficiency of Magpol.

In addition to the functionalities of damage sensing, self healing and actuation, for the development of a truly biomimetic artificial skin, additional functions must be added to Magpol. For example, biological skin also acts as both a temperature and pressure sensor. Electronic signals generated on exposure to these elements travels to the brains, which in turn can distinguish between the different levels of exposure and also send a feedback signal to the attached muscle. Therefore future work can focus on developing an autonomous, energy efficient system, where real time data monitoring is possible and a feedback system is available to take immediate action in response to a given stimulus.

Magpol shows great promise as a first step towards the development of bioinspired, truly multifunctional composite materials, though further work is necessary to demonstrate the efficacy of Magpol coated guidewires in in-vivo conditions and

improve its performance.

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Publications and Conferences

Journal Publications

- 1 **Ahmed, A. S.**; Ramanujan, R. V. "Curie Temperature Controlled Self Healing Magnet-Polymer Composites." *J. Mater. Res.* 2015, 30, 946-958
- 2 **Ahmed, A. S.**; Ramanujan, R. V. "Hysteretic buckling for actuation of magnet polymer composites." *Macromolecular Chem. Phys.*, 2015, In Press, available online
- 3 **Ahmed, A. S.**; Ramanujan, R. V. "Magnetic Field Triggered Multicycle Damage Sensing and Self Healing." *Scientific Reports*, 2015, In Press
- 4 Ghadban, A.; **Ahmed, A. S.**; Ping, Y.; Ramos, R.; Cantaert, B.; Ramanujan, R. V.; Miserez, A. "Bioinspired pH- and Magnetic-Responsive Catechol-Functionalized Chitosan Hydrogels with Tunable Elastic Properties", *ChemComm*, 2015, In Press
- 5 **Ahmed, A. S.**; Ramanujan, R. V. "Bio inspired Magnet-polymer (Magpol) actuators" *Proc. SPIE , Bioinspiration, Biomimetics, and Bioreplication*, San Diego, USA, Lakhtakia, A.,ed., 2014, 9044.
- 6 Liu, X. L.; Choo, E. S. G.; **Ahmed, A. S.**; Zhao, L. Y.; Yang, Y.; Ramanujan, R. V.; Xue, J. M.; Fan, D. D.; Fan, H. M.; Ding, J. "Magnetic nanoparticle-loaded polymer nanospheres as magnetic hyperthermia agents." *Journal of Materials Chemistry B* 2014, 2, 120-128
- 7 Nguyen, V. Q.; **Ahmed, A. S.**; Ramanujan, R. V. "Morphing Soft Magnetic Composites." *Adv. Mater.* 2012, 24, 4041-4054.

Conferences

- 1 A. S. Ahmed, R. V. Ramanujan. "Self Healing and Damage Sensing Magnet-Polymer Composites (Magpol)", ICMAT & IUMRS-ICA, Singapore (2015) (**Best Poster**)
- 2 A. S. Ahmed, R. V. Ramanujan. "Magnet-polymer artificial skin actuators ", E-MRS spring meeting, Lille, France (2015) (**Keynote presentation**)
- 3 A. S. Ahmed, R. V. Ramanujan," Multifunctional Smart Magnet-Polymer Composites (Magpol) ", MRS-S, Singapore, (2014) (**Best poster**)
- 4 A. S. Ahmed, R. V. Ramanujan, "Multifunctional Smart Magnet-Polymer Composites (Magpol), IEEE magnetics symposium, Singapore (2014) (**Best oral presentation**)

- 5 A. S. Ahmed, R. V. Ramanujan. “Magnet-polymer composites as artificial skins”, 1st International Conference in Sports Science & Technology, Singapore (2014)
- 6 A. S. Ahmed, R. V. Ramanujan, “ Bio inspired Magnet-polymer (Magpol) actuators” Smart materials and structures, San Diego, USA (2014) **(Best student paper)**
- 7 A. S. Ahmed, V. Nguyen, R. V. Ramanujan. “Multifunctional Smart Magnet-Polymer Composites (Magpol).” International Symposium for Research Scholars on Metallurgy, Materials Science and Engineering, IIT Madras, India (2012)