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The shape – morphing performance of magnetoactive soft materials performance

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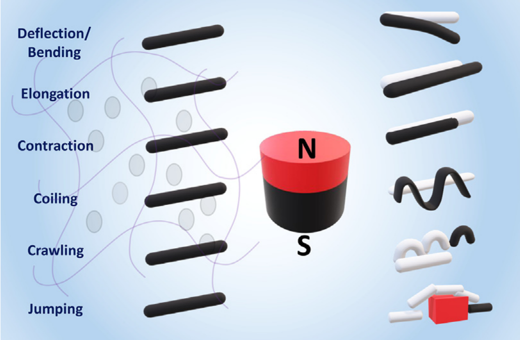
HIGHLIGHTS

- A comprehensive picture of the shape-morphing phenomenon of MSMs is highlighted.
- Materials and advanced 3D printing techniques for MSMs are discussed in detail.
- Programming (re-programming) and actuation of MSMs are delivered in detail.
- Applications of MSMs are classified using a length-scale (macro/milli/micro/nanoscale) for the first time.
- Specific examples and properties of extensively used MSMs and potential direction are presented.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetoactive soft materials (MSMs) are soft polymeric composites filled with magnetic particles that are an emerging class of smart and multifunctional materials with immense potentials to be used in various applications including but not limited to artificial muscles, soft robotics, controlled drug delivery, minimally invasive surgery, and metamaterials. Advantages of MSMs include remote contactless actuation with multiple actuation modes, high actuation strain and strain rate, self-sensing, and fast response etc. Having broad functional behaviours offered by the magnetic fillers embedded within non-magnetic matrices, MSMs are undoubtedly one of the most promising materials in applications where shape-morphing, dynamic locomotion, and reconfigurable structures are highly required. *This review article provides a comprehensive picture of the MSMs focusing on the materials, manufacturing processes, programming and actuation techniques, behaviours, experimental characterisations, and device-related achievements with the current state-of-the-art and discusses future perspectives.* Overall, this article not only provides a comprehensive overview of MSMs' research and development but also functions as a systematic guideline towards the development of multifunctional, shape-morphing, and sophisticated magnetoactive devices.

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1. Introduction

Smart materials are known for changing their one or more properties in a controlled fashion in the presence of external stimuli such as temperature [1,2], humidity [3,4], pH [5], electric field [6-9], magnetic field [10-16], and light [2,17-21]. Such stimuli-responsive materials possess static and dynamic properties that can be controlled to provide various interesting functional behaviours, for example, shape memory effect, reconfigurable structure, sensing, actuation etc. Therefore, soft intelligent materials are attracted in many applications including soft robotics [22,23], biomedical engineering [24,25], shape-morphing structures [26,27], sensors and actuators [12,22-30].

Magnetoactive materials are one of the biggest categories of smart materials [31-42]. These functional and intelligent materials are capable of changing their mechanical properties such as elastic, damping, form and shape in the presence of an external magnetic field. Fundamentally, a magnetoactive material consists of two major constituents: a non-magnetic matrix and magnetic fillers. Depending on the type of matrix materials, various types of magnetoactive materials can be categorized. Magnetoactive materials can broadly be classified into two main categories: magnetoactive fluids and magnetoactive solids. Magnetorheological (MR) fluids and ferrofluids are the two widely-used examples of magnetoactive/magnetic fluids, in which magnetic particles ranging from micro-size to nano-size are suspended in a carrier fluid [31,36,43,44]. On the other hand, magnetic particles are locked within a solid carrier medium in the case of magnetic solids, the common examples of magnetic solids are MR elastomers, MR plastomers, and MR foams [33,34,45–57,267]. In the presence of an externally applied magnetic field, the magnetic fluids are widely known for changing their viscosities and thus the damping properties, whereas the magnetoactive solids are known for changing their elastic properties (e.g., moduli). Both functional materials have their own advantages and have been widely used in various applications in which tunable damping and elastic properties are desired, for example, in vibration isolators and absorbers [31,34,35,58-67].

The applications of magnetoactive soft materials (MSMs) are not limited to the areas in which their damping or elastic properties play a major role. In recent years, we have been observing an exponential growth of MSMs' applications in the areas such as soft-robotics [68,69] biomedical fields [70], sensors and actuators [71-75], and shape-morphing structures [3,26,30,76,77] etc., in which the shape-morphing or shape-shifting phenomena of these soft-bodied responsive composite materials are the main characteristics [6,10,22,78,79]. In addition to magnetoactive soft elastomeric materials, magnetic soft gel-like materials (e.g., hydrogels filled with magnetic particles) have attracted a huge amount of interest in both the research community as well as in the industry due to various appealing advantages over pure magnetic fluids [80,81] or magnetoactive solids [82-88]. Such MSMs can demonstrate intricate shape-morphing phenomena even in the presence of a small amount of externally applied magnetic field [89]. Hereafter, "MSMs" is used throughout the article to refer to such shape-morphing magnetoactive soft materials that include mostly soft deformable elastomers and polymeric gels. The noteworthy aptitudes of MSMs include fast realization, programmable shape, and untethered control via an external magnetic field. Moreover, MSMs demonstrate other interesting capabilities, for example, locomotion [16,90,91], highly programable [92,93], and precise shape transformation [94,95] and even remote heat generation [96,97]. These superior behaviours make MSMs one of the most potential candidate materials in the field of soft robotics, minimum invasive surgery, controlled drug delivery in precision medicine, and other biomedical applications as well as in sensors and actuators [26,30,77]. However, most of the research outputs are still laboratory-based prototypes, and there is yet a big room for improvements to implement such outstanding multifunctional materials in industrial applications. Therefore, it is always noteworthy to explore the latest research and development of MSMs.

Very recently, there are a couple of excellent review papers appearing in the literature that focus on various aspects of multifunctional materials such as three-dimensional (3D) printing, also known as additive manufacturing (AM) techniques, hydrogels and other soft polymers and their smart variants, active filler materials, different actuation mechanisms, and the wide range of potential applications of soft smart materials [27,98-108]. For instance, Li and Pumera [109] give an exhaustive overview of microscale soft robots made of multifunctional soft and active materials including MSMs. Their review is focused on different 3D printing techniques of soft materials followed by an excellent account of microrobots that can potentially be used in biomedical applications. A very similar review is published by Soto et al. [110], in which they mainly discussed different soft materials, actuation, and propulsion/loco motion/navigation mechanisms of microscale soft robots. Furthermore, Tan et al. [104] focused on smart polymers that can be used in manufacturing the so-called soft micro-machines. On the other hand, Kim et al. [98] give an extensive overview of various soft composites used in manufacturing the actuator, a key part is in the soft robots. Likewise, Liu et al. [24] give an excellent account of soft and active hydrogels and their applications in producing soft micro-machines such as actuators, sensors, harvesters, function coatings etc. that authors termed as 'hydrogel machines'. In another review, Li et al. [23] show how biomimicry inspired researchers to design more complex and intricate soft small-scale machines. In this case, their main focus is the design freedom offered by the 3D printing techniques to manufacture soft materials. Hydrogels and their smart variants such as magneto-gels, electro-gels, pH/humidity/light-responsive gels are the key materials in almost all microscale soft machines. For a wide range of works focused on these multifunctional materials, we refer to [29,38,106,107,111-117]. We have seen that the 3D printing is an inseparable part of synthesising soft and active machines with extremely complex geometries. For instance, Wan et al. [106] give an illustrative account of the four-dimensional (4D) printing (3D printing of active materials such as MSMs is typically known as the 4D printing) of soft materials using direct ink writing (DIW), a widely used 3D printing technique for highly viscous paste-like soft materials. Almost all of the aforementioned review works focus on different soft materials, actuation methods, 3D printing techniques, and potential applications in which activating fields include heat, light, electric-field, magnetic-field, humidity, pH are briefly discussed.

There are a few articles available in the literature focusing particularly on an actuation method, i.e., magnetic field activated materials [41,69,116,118-120]. The arrangements of magnetic fillers and external fields play critical roles in obtaining desired shape-morphing features of MSMs. In that regard, Cao et al. [37] extensively studied various manipulation techniques of micro- and nano-objects with magnetic fields. Furthermore, in a comprehensive account, Sanchez et al. [121] theoretically studied the magnetic-field activated microstructural changes experienced by a hybrid MSM consisting of both soft and hard-magnetic fillers. Using molecular dynamics simulations, they predicted that the combined use of both types of filler particles will create more complex deformation phenomena such as elongation and contraction even under a single magnetic field depending on its magnitude. Field-driven 3D printing techniques have been proved to be effective in improving microstructural and mechanical properties with tailored characteristics of additively manufactured composites. These fields include electric-field, magnetic-field and acoustic-field. Very recently, Hu [122] put forward an extensive overview on field-assisted 4D printing including materials, processes and potential applications. Despite few review papers focusing on the materials and mathematical modelling of MSMs, any extensive review highlighting all key aspects of the MSMs such as materials, manufacturing processes, design of actuation mechanisms, and potential applications are still limited in the literature. One of the first attempts in this area is due to Wu et al. (2020) [118]. Therein, they particularly focus on the multifunctional soft magnetoactive composites by giving a brief account of matrix materials and fillers, fabrication techniques, functions and operations, and potential applications. Furthermore, Eshaghi et al. (2021) [123] exhaustively explored various bio-inspired design options that have been used in prototyping flexible robots based on magnetoactive soft materials. Very recently, Lucarini et al [266] reported an extensive review

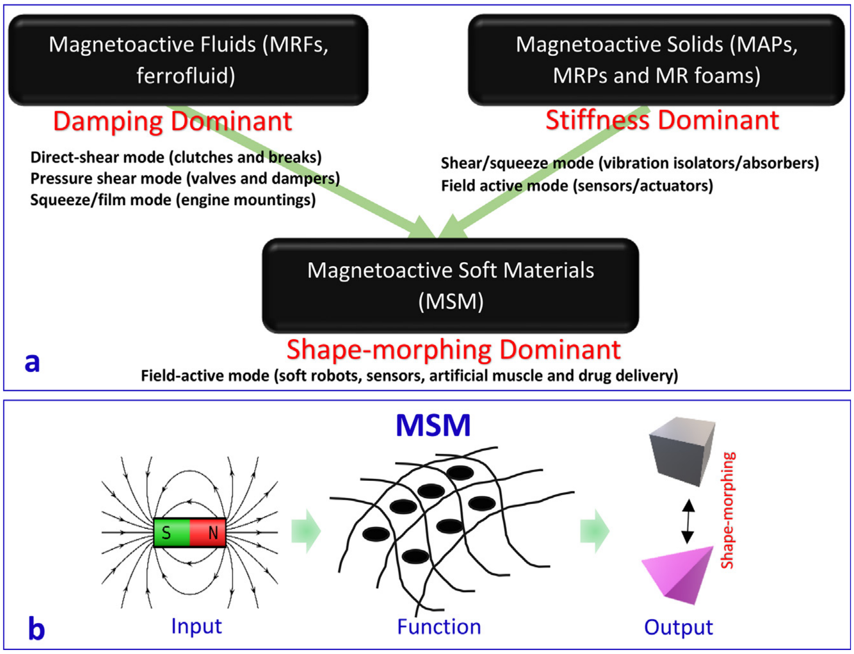

Fig. 1. The overall concept of this review work. (a) Illustration of magnetoactive materials and (b) illustration of the workflow for the shape-morphing magnetoactive soft materials.

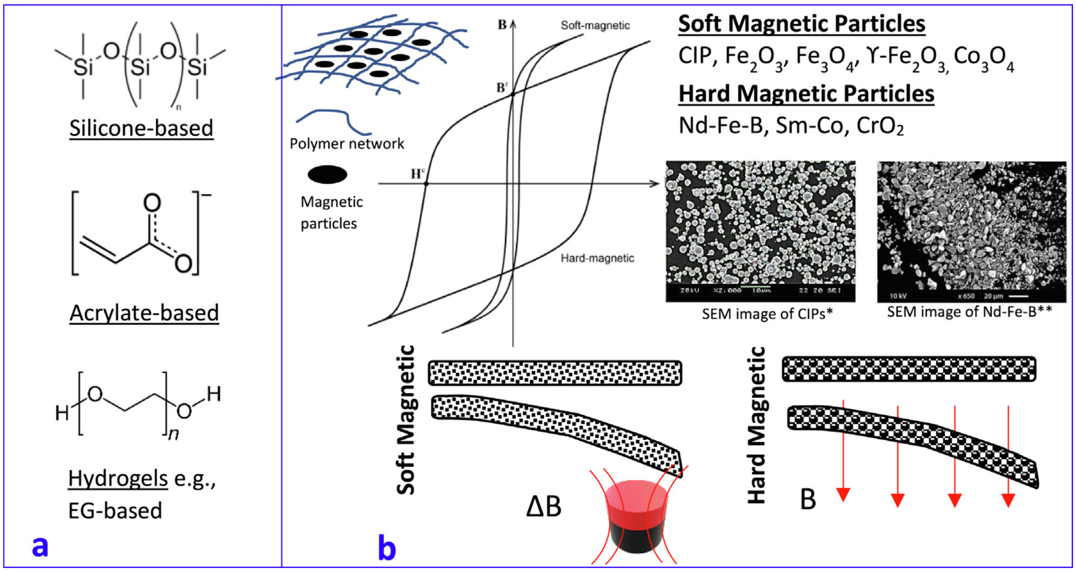

Fig. 2. The key raw materials to manufacture MSMs. (a) Matrix materials and (b) magnetic fillers along with MSMs working mechanisms. *adapted from [144] and **adapted from [11].

only on hard-magnetic soft polymers ranging from material synthesis to computaional modelling. To this end, to the best of our knowledge, a comprehensive review focusing on ***programming and actuation*** techniques, magnetoactive ***material characterisations*** and summarising all potential ***applications across the length scale*** is yet to be delivered, in addition to materials and manufacturing techniques. We aim to fill this gap.

A plethora of remarkable successes in the field of MSM can be seen in recent years via a synergistic utilization of various polymeric matrices, magnetic fillers, and advanced manufacturing techniques (3D printing) [11,12,77,96,118,124]. This review aims to provide a full picture of the advancement of MSMs including the choices of materials to their potential applications. Yet, our specific focus is the shape-morphing/shape-shifting phenomena offered by the MSMs. The overall scope of the review work is also provided in Fig. 1. First, we discuss the selections of suitable materials to manufacture MSMs. Thereafter, fabrication strategies using conventional methods (e.g., moulding) and advanced manufacturing methods (e.g., 3D printing) are discussed. After that, the programming, actuation, and experimental characterization behaviour of MSMs are discussed in detail. We then extensively focus on the potential applications offered by the MSMs. In this case, for the first time, we use the **length-scale** as the yardstick to categorise various shape-morphing/shape-shifting devices made out of MSMs. Finally, we summarize the recent advancements with an outlook towards the development of multifunctional and sophisticated MSMs devices.

2. MSMs: Materials and syntheses

2.1. Materials

MSMs are a multi-material system. They consist of two main materials of distinct characteristics; the first one is a non-magnetic matrix and the second one is the magnetic filler. For an overview of the materials of MSMs see Fig. 2. The behaviour of the MSMs highly depends on the properties of the bulk matrix materials and the embedded magnetic fillers. A proper selection of the materials and the right structural design is necessary to realize the shape-morphing properties with programable deformation as well as large strains under the application of external stimuli.

2.1.1. Matrices

The shape-morphing structures can be achieved with flexible matrix materials that are mechanically soft (possess modulus from 10^4 to 10^9 Pa [125]). The commonly used soft materials to develop MSMs are elastomeric polymers which can largely be classified into silicones, acrylate-based polymers, and polyurethanes. Another most widely-used soft materials are hydrogels; both synthetic and natural hydrogels and even the use of shape memory polymers as MSMs' matrix is gaining popularity [26,30,77]. One of the key requirements of the matrix materials for MSMs is their high elastic nature. In other words, the matrix materials must possess a reversible deformation under the application of an external load.

In order to achieve large deformations in MSMs, soft elastomers are the best choice. The very common choice of the soft elastomer is the commercially available silicone-based matrices (e.g., Ecoflex, Elastosil, Sylgard, and polydimethylsiloxane (PDMS)) due to their facile synthesis process, mechanical and thermal stability, low cyclic dissipations, insensitive to environmental degradation, biocompatibility, and non-toxic nature [11,45,126-130]. In a uniform magnetic field, a combination of hard-magnetic particles and soft elastomers provide an intricate shape-morphing phenomenon such as twisting, bending, jumping, crawling, and coiling etc [131]. On the other hand, the combination of soft-magnetic particles and soft elastomers provide an excellent enhancement of the elastic and damping properties, which are typically known as magnetorheological (MR) elastomers [33,45]. See Section 2.1.2 for the definition of soft-magnetic and hard-magnetic particles.

Other types of elastomeric matrices are acrylic-based polymers which can be soft at different degrees by tuning the crosslinking amount. One of the salient features of acrylic-based polymers is that at the same time they facilitate 3D printing via photopolymerization (e.g., micro-stereolithography [132]) due to the low viscosity of the resin. Such 3D printable soft materials can also be mixed with magnetic nanoparticles (MNPs) to develop magnetoactive materials [133-135]. Hydrogels are another category of matrix materials that have attracted tremendous attention to the development of MSMs thanks to their extreme to medium softness, biocompatibility etc [24,80,84,86,87,136-138]. Hydrogels are polymers that can contain water up to 90 wt% in polymeric networks. A common example of hydrogels is ethylene glycol (EG)-

based polymers. Recently, the gelatin-based hydrogel has also been used as a matrix material to develop untethered magnetic hydrogel milli grippers [139] and even the use of highly flexible double network hydrogels has been reported [140]. Other hydrogels such as alginate-based [141,142], alginate-methylcellulose based [137], and collagen-based [143] MSMs have also been demonstrated. Compared to elastomers (e.g., silicone-based), magnetic hydrogels have shown significant advantages for in vivo applications, because of their superior biocompatibility, as well as their soft and wet nature [140]. Furthermore, shape memory polymers (SMPs) such as polycaprolactone (PCL) are also used as the matrix materials in MSMs [94]. In SMPs, magnetic particles are used as the media for remote heating mechanisms. The magnetic particles vibrate within the polymer network in the presence of an alternating magnetic field and generate the heat required for the shape-morphing phenomena of SMPs, for example, shape locking [94,96].

2.1.2. Magnetic fillers

The typical magnetic fillers are ferromagnetic particles and are accountable for the responsive behaviour of the MSMs unless otherwise a shape memory polymer is used as the matrix material. The magnetic fillers are of two types: the first type is soft-magnetic particles, and the second type is hard-magnetic particles.

Fig. 2b provides an overview of the magnetic particles used in the development of MSMs. The soft-magnetic particles have a narrow loading–unloading hysteresis loop, while the hard-magnetic particles have a wider hysteresis loop and retain high magnetic remanence and large coercivity in the magnetization process. The most widely used soft-magnetic particle is carbonyl iron powder (CIP), while Neodymium iron boron (Nd-Fe-B) is a common example of hard-magnetic particles. On the other hand, it should be noted that there are other kinds of soft-magnetic particles, that are typically nanoparticles of oxides of pure ferromagnetic materials such as Iron (II, III) oxide (Fe_2O_3, Fe_3O_4), and Cobalt (III) oxide Co_3O_4 [145]. Similarly, other hard-magnetic particles include Samarium-Cobalt (Sm-Co), Chromium (IV) oxide (CrO_2), hard ferrite, and alnico alloys [118,145,146].

The soft-magnetic fillers loaded MSMs demonstrate shape-morphing phenomena when there is a gradient in the magnetic field (Fig. 2). This is a result of simple deflection due to the attraction of magnetic fillers towards the magnetic field [89,137]. On the other hand, the hard-magnetic fillers loaded MSMs demonstrate the shape-morphing phenomena even in the presence of a uniform magnetic field. In the hard-magnetic fillers-filled MSMs, when the magnetic particles are magnetized (see hysteresis loop, Fig. 2b), they retain magnetic remanence and orientate the magnetic domains in a specific direction. When such MSMs are exposed to an external magnetic field, the aligned domains of the magnetic fillers either repel or attract (depending on the pole of the magnet) in the direction of the applied magnetic field resulting in an overall change in the shape of the MSMs and, therefore, a shape-morphing phenomenon is achieved [147,148]. Such phenomenon has also been realized by the computational modelling of hard-magnetic fillers based on soft materials [69,148,149]. These theoretical studies on the mechanics of hard-magnetic fillers not only help to get insight into materials behaviour but also provide a useful guideline for shape-changing structural designs and optimisations.

It is noteworthy to mention here that the hard-magnetic fillers have attracted a greater amount of interest within the MSMs research community in contrast to the soft-magnetic fillers because of the re-programmability and large deformations that can be achieved just by a change in the magnetic pole of the externally applied magnetic field.

2.2. MSMs fabrication

The selection of matrix materials and fillers type play a decisive role in determining desired properties of MSMs. Moreover, suitable structural/geometrical designs and fabrication methods are also instrumental to achieve the desired shape-morphing phenomena of MSMs. Note that the shape-shifting phenomena of MSM systems largely depend on the articulation of intricate designs. The complex but fascinating designs are mainly inspired by nature (i.e., biomimicry), geometric manipulations such as origami, kirigami etc. [85,120,150,151]. In this case, the 3D printing techniques illustrated below not only open new horizons for further design complexity and implementation but also offer a wide range of customised design freedom for MSMs. In this section, general fabrication methods for soft magnetoactive polymeric composites are discussed which are categorized into two groups as the conventional methods and advanced manufacturing methods such as the 3D/4D printing. Furthermore, some fabrication methods can be termed as hybrid methods in which a traditional method and an additive manufacturing technique are utilized, see Section 2.2.3 for details.

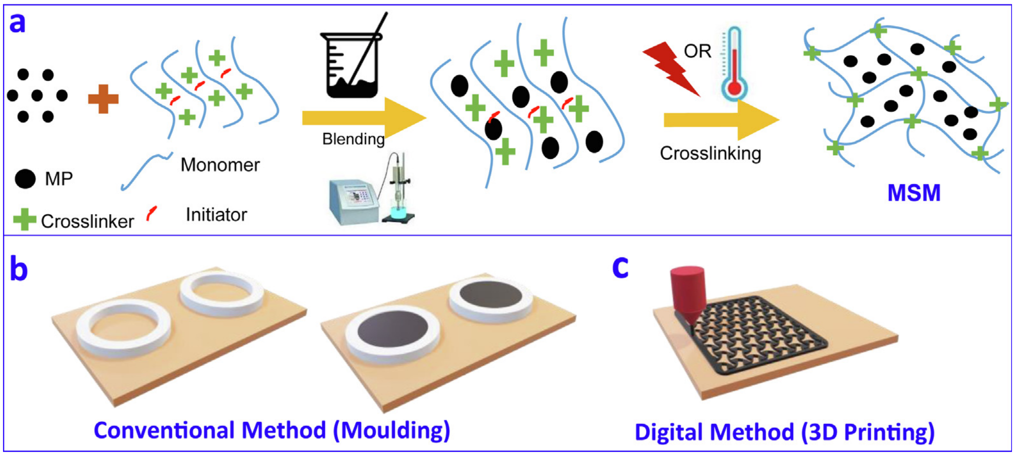

Fig. 3. The key manufacturing processes for developing MSMs. (a) Schematic illustration of a synthesis process. (b) Conventional method (reproduced from [154]) (c) Additive manufacturing or 3D printing method (reproduced from [155]) to develop MSMs.

2.2.1. Conventional techniques

Moulding is the most widely used primitive and conventional fabrication method for MSMs. In this case, the fabrication of MSMs is similar to those of common polymer-based materials. The MSMs synthesis procedures are illustrated in Fig. 3a. Raw materials of MSMs usually consist of monomers, crosslinkers, initiators, and magnetic particles, either hard or soft. Monomers provide the overall properties of the soft materials by forming polymer networks whereas crosslinkers usually tune the mechanical stiffness/elasticity of the polymeric networks. An initiator (it initiates the chemical crosslinking, that's why it is called initiator) is to trigger the polymerization process (also known as the solidification process) and it will be usually a thermal or a photoinitiator. Magnetic particles are filler materials that are the main responsive parts of the MSM composites. Firstly, all the raw materials are properly mixed in which a homogenous mixture can be achieved first via mechanical mixing followed by sonication. Thereafter, the mixture is allowed to polymerize in the mould system. The polymerization can be completed using a heat-assisted medium or under ultraviolet (UV) light depending on the type of the initiator. Depending on the intended use of MSMs, the solidification process can be performed with or without the application of a magnetic field. In the absence of a magnetic field during the polymerization process, more or less a homogeneous (i.e., isotopic) MSM will be produced. Whereas, the curing process performed under an applied magnetic field will align or program the magnetic fillers to develop directional-dependent (i.e., anisotropic) MSMs [33,152,153]. However, it should be noted that, for the hard-magnetic fillers, the magnetic domains can be oriented and magnetized in a specific direction even after being fully cured by exposing the MSM to an external magnetic field [12,124,154]. Although the moulding technique is a simple and robust process, however, it only has the capability to manufacture two dimensional (2D) and simple three-dimension (3D) geometries. Nevertheless, such regular shapes or 2D structures later can be engraved to acquire the desired shapes, for instance, see [124].

2.2.2. 3D/4D printing techniques

Three-dimensional (3D) printing, also known as additive manufacturing (AM) is an advanced fabrication process whereby objects are created directly from 3D model data of the computer-aided design (CAD) in a layer-by-layer approach. 3D printing has been employed in a number of different fields with various materials including metal, polymers, composites, cement, and ceramics [156-160]. The additive manufacturing of smart and multifunctional materials is now referred as the 4D printing [27,106,161-167]. The stimuli-responsive behaviour of 3D printed MSMs can be considered as the 4th dimension and hence the term '4D printing', likewise used for other smart materials. The 4D printing offers several unique advantages for the development of smart materials and structures over traditional manufacturing processes. The most important advantage is the reduction of the need for external power or electromechanical systems to program the smart materials' microstructures [168]. Some of the other key advantages of AM are limitless design freedom, capability to produce near-net shape and end use parts, reduced post-processing requirements, high material utilisation rate and less wastage [169]. Therefore, the

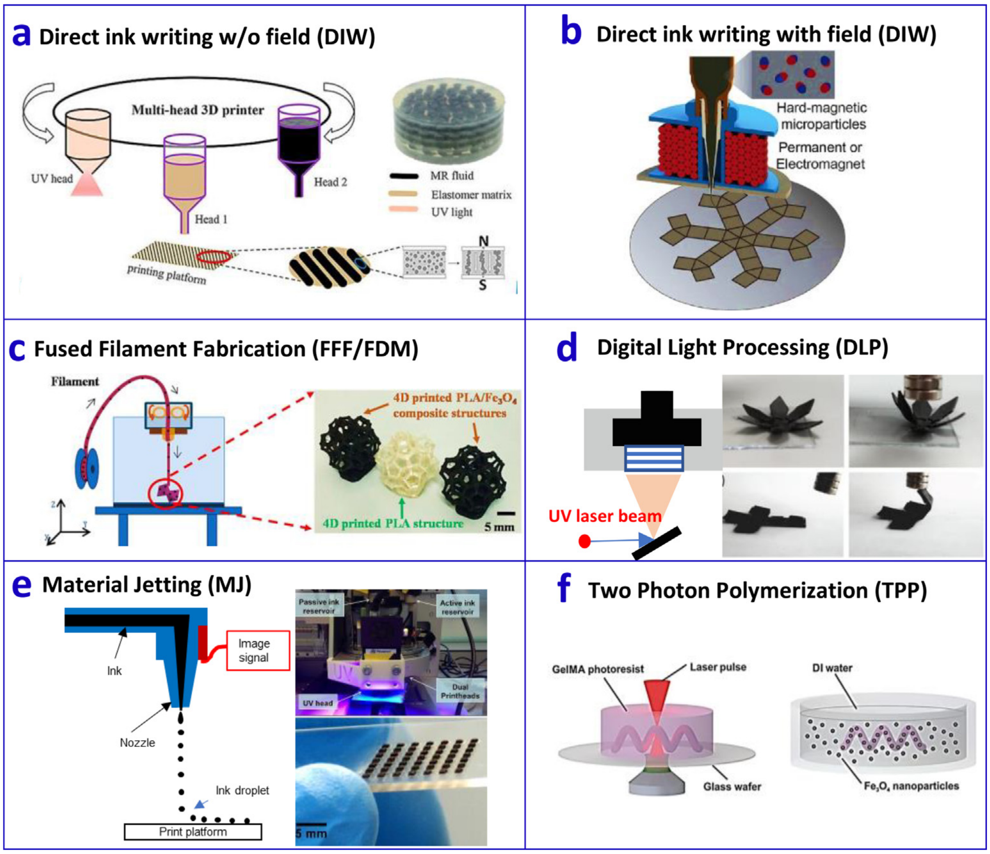

Fig. 4. 4D printing methods for developing MSMs. (a) Multi-material Direct Ink Writing (DIW) method without applying a magnetic field (reproduced from [155]), (b) DIW method with the application of a magnetic field (reproduced from [11,148]), (c) FDM method using a magnetic filament (reproduced from [79,176]) and (d)) An example of Digital Light Processing/Projection (DLP) technique (reproduced from [133]). (e) Multi-materials jetting of active and passive inks (reproduced from [177]) (f) TPP method to develop MSMs (reproduced from [178]).

AM is undoubtedly the suitable technique to realize the highly bespoke geometrical designs required in MSM applications.

American society for testing and materials (ASTM) international F42 on additive manufacturing (2009) ascertained seven main processes for the 3D printing of polymeric materials [170]. These are Material Extrusion, Material Jetting, Binder Jetting, Sheet Lamination, Vat Photopolymerisation, Powder Bed Fusion, and Directed Energy Deposition. Not all these printing methods are suitable for MSMs yet. For instance, Fused Deposition Modelling (FDM/FFM) and Direct Ink Writing (DIW) from the Material Extrusion, inkjet 3D printing from the Material Jetting, Digital Light Processing/Synthesis (DLP/DLS), Stereolithography (SLA) and Two-Photon Polymerisation (TPP) from Vat Photopolymerisation, Selective Laser Sintering (SLS) from Powder Bed Fusion have been considered in the 3D printing of magnetoactive composites, irrespective of hard- or soft-magnetic fillers [156,158]. Note that DIW, DLP, and SLA are ink-based 3D printing techniques in which the inks (viscous fluids/low viscosity resins) are polymerized either using heat or UV power or both at a time during the printing process. In the following sections, the most widely used 3D printing methods used to develop MSMs are described. More details on the 3D/4D printing of polymers, some excellent reviews can be consulted [29,100,103,106,171,265].

The key steps of frequently used 4D printing techniques to develop MSMs are delineated in Fig. 4. Normally, a homogenous mixture of the magnetic fillers laden print materials (i.e., customized ink/filament/resin) is loaded into the 3D printer instead of the commercially available materials to develop MSMs. As described in Fig. 3a, a homogenous mixture of magnetic ink can be generated by blending the key raw materials of MSMs.

2.2.2.1. DIW. The Direct Ink Writing (DIW) 3D printing method is based on the extrusion of a viscous ink through a nozzle under pressure using a computer-controlled dispenser [106]. The DIW is one of the most common 3D printing techniques for the development of MSMs via AM due to its simplicity and extreme ability to dispense highly viscous inks. As illustrated in Fig. 4a and b, the DIW printing technique can be performed either with or without the application of an external magnetic field during the printing and curing (solidification/polymerization) process. Various patterns or alignments of the magnetic fillers within a polymeric material can be achieved even without applying a magnetic field. Whereas the application of a magnetic field during the printing process allows to orient the magnetic domains of hard-magnetic fillers within the printed patterns. The biggest advantage of applying a magnetic field during printing is that the magnetic domains can be aligned in a highly customized and desired fashioned by synchronizing the magnetic pole of the pooling magnet with the printing patterns (by a computer-controlled dispenser). In order to successfully print MSMs using a DIW printing method, the rheological properties of the printing inks play a vital role in which the so-called shear-thinning and thixotropic properties of inks are required. That means the printing inks must demonstrate a decrease in viscosity while passing through the nozzles and prompt recovery of the viscosity when a shear force is applied and removed, respectively. The details of the rheological study and parameters influencing the printing process for the DIW can be found in articles [155,172].

2.2.2.2. FDM. The Fused Deposition Modelling (FDM) printing method is mainly suitable for thermoplastic polymers, in which a filament of such polymers is used. During the printing process, the filament is melted to print on a bed (i.e., a print platform) and solidified after being printed. For the development of MSMs, the printing filaments need to be loaded with magnetic fillers (sometimes other additives such as carbon nanotubes (CNTs) are also added) before printing in order to provide the magnetic field-dependent properties. For instance, Fe_3O_4 is blended with PLA to develop composite filaments for the FDM printing [11,148] (Fig. 4c). Also, composite filaments of PCL (Polycaprolactone)/TPU (Thermoplastic polyurethane) loaded with MNPs are used to develop magnetoactive smart structures via the FDM 3D printing [173-175].

2.2.2.3. DLP/DLS. Another ink-based 3D printing technique that has attracted significant interest for MSMs fabrication is the DLP/DLS (Digital Light Processing/Synthesis) technique [179]. The DLP 3D printing takes the light-mediated conversion of a liquid resin comprising of monomer or oligomer into a solid object. As only photocurable resins can be used in the DLP techniques, to date, only MNPs are utilized as magnetic fillers to develop MSMs via DLP 3D printing [180,181]. The use of micron-sized particles leads to non-homogenous ink due to the sedimentation of the heavier particles. Hence, this is one of the basic reasons for not using micron-sized fillers in DLP printing [181]. For a successful DLP printing, the relation between UV (ultraviolet) light dose and the curing depth of the resin has to be understood in detail. Other important parameters to be studied in the DLP printing process are exposer time per projection, magnetic filler loading percentage, layer thickness, and wait time before exposure. A number of different articles [133,181,182] have investigated the optimization process of the DLP printing for MSMs fabrication. Note that DLP/DLS is fundamentally different from other traditional SLA printing techniques. The former uses a UV light source in the projection form and focuses a layer (x-y plane) at a time while the latter uses the light source in the laser form and focuses point by point in a single layer (x-y plane) before moving to the next layer (z-axis), see Li and Pumera [109] or Ligon et al. [170].

2.2.2.4. MJ. Material Jetting (MJ), also conventionally known as the inkjet printing, is one of the powerful printing methods particularly for low dimensional (2D) printing, where low viscosity inks are deposited through micron-sized nozzles directly onto the substrates (e.g., papers) [177,183,184]. Inkjet printing can be utilized to create microscale to milliscale devices made of MSMs. One of the biggest possibilities of MJ is that multi-inks can be deposited at the same and cured in-situ to develop MSM devices. For instance, Saleh et al. [177] demonstrated the development of co-printing of active (magnetoactive) and passive inks and UV cured to create a 3D structure via MJ (Fig. 4e). Nonetheless, one of the main concerns associated with the MJ is the droplet formation, which is governed by the physical parameters of the inks such as viscosity and surface tension, which are therefore required to fall within the specific requirements to successfully develop MSM devices via MJ [183,184].

2.2.2.5. TPP. One of the most favoured vat-based 3D printing techniques for micron-scale fabrications is the so-called multi-photon polymerisation (also known as the two-photon polymerisation or direct laser writing). In Two-Photon (i.e., TPP) process, for instance, laser pulses at 800 nm wavelength is focused on photo-polymerisable resins containing in a vat to initiate the curing process [109,114,170]. Once the laser beam focuses a small volume of photo-resin in which a suitable photoinitiator will absorb the two photons of 800 nm wavelength and act as one photon of 400 nm wavelength which is the range of UV light region. Such a photoinitiator will help in initiating cross-linking reactions among initiators, monomers, and cross-linkers. In TPP, the laser only focuses on a tiny volume of the photo-sensitive resin for creating a 3D printed object without affecting areas outside the focal point (Fig. 4f). With such excellent characteristics of creating micron to nanoscale fabrications, TPP becomes one of the most used 3D

Table 1
Summary of 4D printing method for MSMs and general guidelines to select a suitable technique based on the information such as material requirements, print process requirement as well as strengths and weaknesses of print methods.

Printing method	Print material requirement	Key materials parameters	Key print process parameters	Strengths & weaknesses of printing method	
				Strengths	weaknesses
DIW	– Low to high viscous inks – Heat/photo-curable – Non-Newtonian fluid	– Shear-thinning Thixotropy – Viscosity recovery Rheology	– Dimensionless print speed – Dimensionless print height	– Facile customization (apply magnetic field during printing) – High viscosity ink – Micro to nano-size active particles	– Low printing resolution – Poor layer bonding – Anisotropy
FDM	– Thermoplastic polymers filaments	– Modification of filaments – Thermal behaviour of modified filament – Morphology	– Extrusion temperature – Extrusion diameter – Filament swelling	– Simple printing process – Low cost	– Re-extrusion of modified filament is needed – Better with nanofillers
MJ	– Low viscosity inks – Heat/photo-curable – -Newtonian fluid	– Viscosity – Surface tension – Density	– Droplet formulation & deposition	– High print resolution – Low viscosity ink	– Mostly nanosize fillers – Nozzle clogging
DLP	– Low viscosity inks – Photo-curable only	– Filler loading percentage – Effect of additives – Rheology	– Exposer time – Layer thickness – Wait before the next exposer	– High resolution – Fast printing process – High surface finish	– Only photo-curable resin – Micron-sized particles are difficult to use
TPP	– Photo polymers only – Laser beam only	– Thermoset resins – Highly cross-liked resins	– Smaller print height – Narrow focal volume of the laser	– Very high resolution – Isotropic property – Not layer-by-layer printing	– Costly instrument – Slow printing process – Limited materials

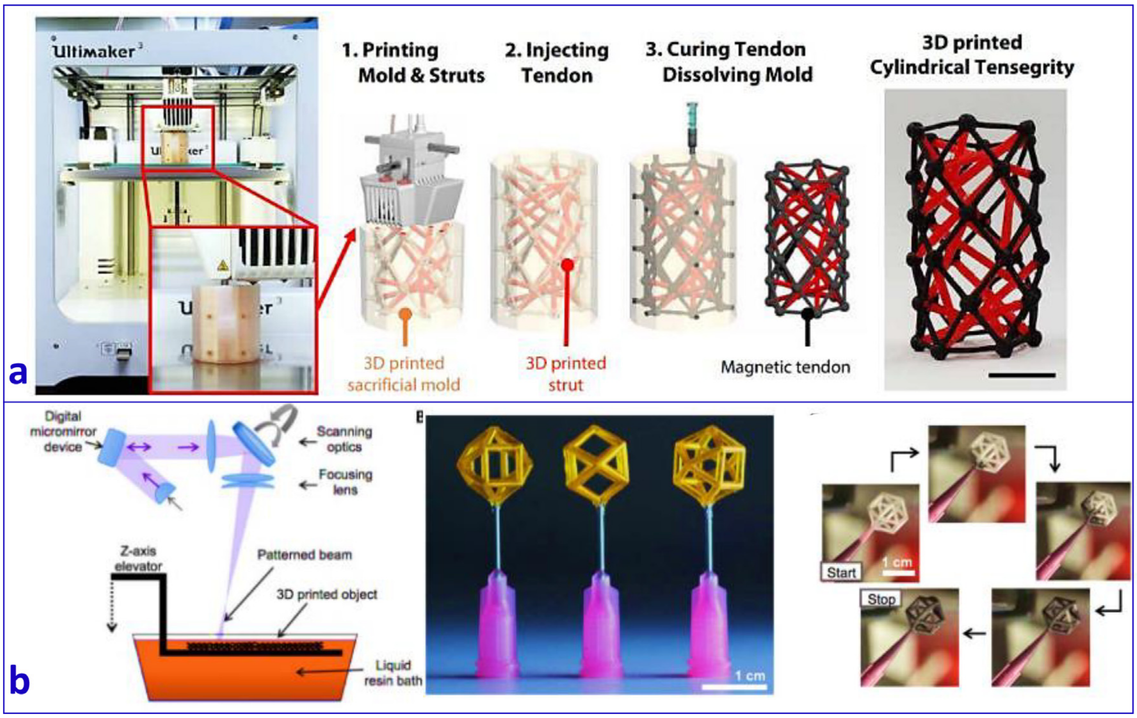

Fig. 5. Hybrid techniques for developing MSMs by combining conventional and digital methods. (a) The fabrication process of the tensegrity structure through the FDM 3D printing technique and sacrificial mould technique (adapted from [187]) and (b) DLP-based 3D printing and MR fluid infilling of 3D printed metamaterial unit cells (reproduced from [132]).

printing techniques in manufacturing micro-and nanoscale MSM devices using soft and hard-magnetic polymeric composites [109]. For instance, using the TPP technique, Medina-Sanchez et al. [185] created a micro-scale robot that can carry immotile sperm cells having motion deficiencies towards successful fertilisation.

Not only resin or ink-based materials are considered for the MSMs 4D printing, but 3D printing of magnetic parts by laser powder bed fusion (PBF) of iron oxide nanoparticle functionalized PA (polyamide) powders have also been reported [186]. The current filament or powder-based 3D printing techniques have not yet provided the large deformations usually required for shape-morphing phenomena. However, such 3D printing techniques provide added research pathway for magnetoactive materials. Table 1 is created to provide general guidelines to select a suitable 3D/4D printing technique to manufacture MSMs.

2.2.3. Hybrid techniques

Successful designs of the shape-morphing constructs rely on a clever structural design, however, the exclusive utilization of the

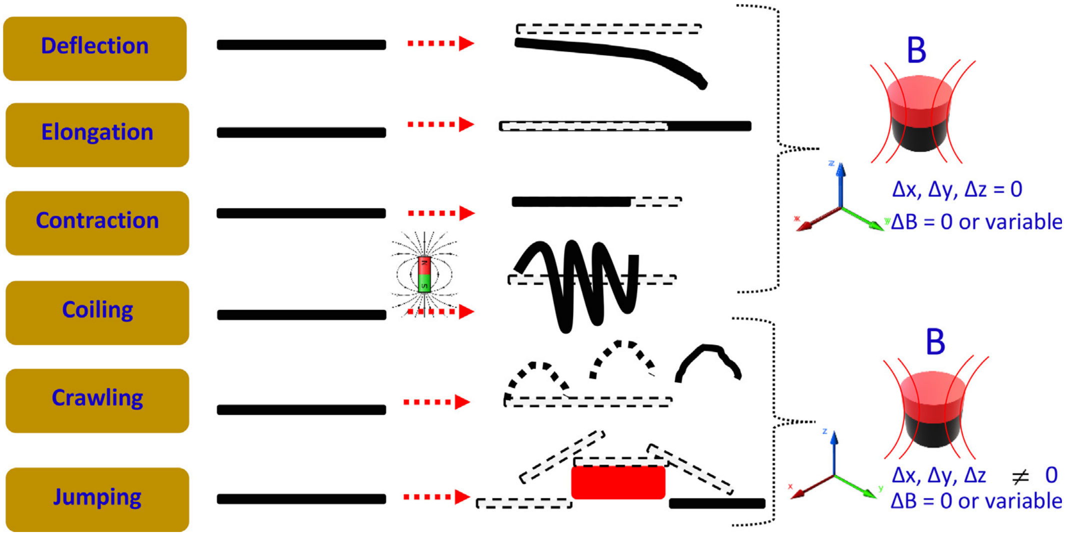

Fig. 6. Various functional behaviours exhibited by MSMs in the presence of an external and remotely controlled magnetic field.

traditional method or 4D printing technique might not always be the best option. Therefore, taking the advantage of a particular 3D printing and combining it with another conventional method(s) is noteworthy to implement to realize unique MSMs' systems. Lee et al. [187] reported magnetoactive structurally complex tensegrity systems using FDM 3D printing and combining with a conventional method (Fig. 5a). In their work, the tensegrity structures consisting of monolithic tendon networks based on magnetic smart materials was realized without an additional post-assembly. Similarly, acrylic polymer-based smart metamaterials were developed combining DLP 3D printing and the conventional method by Jackson et al. [132], see Fig. 5b. In their study, an MR fluid was injected into 3D printed structures to develop magnetoactive metamaterials with unique properties. Such works might not offer fully shape-morphing structures; however, these works provide the possibilities that we can effectively combine AM and traditional methods to develop sophisticated magnetoactive structures with multifunctional characteristics. Recent examples for the successful use of hybrid techniques to develop magnetoactive materials that show shape-morphing behaviour are biomimetic structures, e.g., inchworm, manta ray, and soft grippers [188].

3. Behavioural characterisations of MSMs

MSMs demonstrate a number of exciting shape-morphing phenomena in the presence of a static external magnetic field (constant or variable) such as deflection or bending, elongation, contraction, and coiling or twisting. With such interesting behaviours, MSMs further demonstrate more stimulating features such as crawling, swimming, and even jumping in the presence of a dynamic magnetic field (constant or variable). Here, static and dynamic fields refer to the spatial position of the magnet in x, y, and z coordinates, while the constant and variable refer fields to the strength of the magnetic field (B in Tesla), see Fig. 6. Every so often, the constant magnetic field is referred as a homogenous field and a variable magnetic field is referred as a non-homogenous field [89,189,190]. MSMs undergo various deformations (macroscopic/microscopic or even nano level) to demonstrate such interesting behaviours. These deformations could be the combination of different types of working modes such as compressive, tensile, shear, and biaxial. Therefore, characterizations and understanding of mechanical/rheological properties of MSMs in both the absence and presence of an externally applied magnetic field is unavoidable to successfully attain the targeted shape-shifting phenomena. There are several testing methods available in the literature in order to characterize the magneto-mechanical properties of magnetoactive materials. The rheological and magneto-mechanical properties are major features of MSMs that need to be investigated and, therefore, are discussed in this review. Our recent work [45] can be referred to for the detailed and comprehensive overview of the magneto-mechanical characterizations of the magnetoactive polymers including MSMs.

3.1. Magneto-rheological experiments

Linear visco-elastic behaviour of MSMs can be investigated by means of the rheological testing methods in both the absence and presence of an externally applied magnetic field. Frequently used commercially available rheometer instruments (e.g., Anton Paar (Austria) & TA instruments (USA)) can be used to characterize magneto-rheological properties of the MSMs. These systems do not require any major modifications as such sophisticated instruments already offer good control of a magnetic field in the experimental tests (Fig. 7a-i). Generally, the responses of the storage modulus (G') and the loss modulus (G'') within a linear visco-elastic region are investigated using rheological analyses. The storage and loss moduli represent the ability of MSMs to store and dissipate the energy of distortion, respectively. The trend of G' and G'' with respect to strain amplitude, frequency, temperature, and magnetic field are studied in rheology [191-194], an example of amplitude sweep is given in Fig. 7a-ii. With such standard and commercially available magneto-rheometers, the data obtained via magneto-rheological tests are more reliable for the computational modelling of the behaviours of MSM within linear and small strain regions [195]. Moreover, time-dependent properties such as stress-relaxation behaviour can also be studied using rheology.

3.2. Magneto-mechanical experiments

Understanding the elastic modulus, elongation at failure, elastic zone, plastic zone, toughness, heat dissipation under a cyclic loading, fatigue failure and other several mechanical properties of the MSMs, in both absence and presence of a magnetic field, allow the smart and successful design and development of the multi-functional MSMs without a failure. Unlike rheology, a bespoke lab-

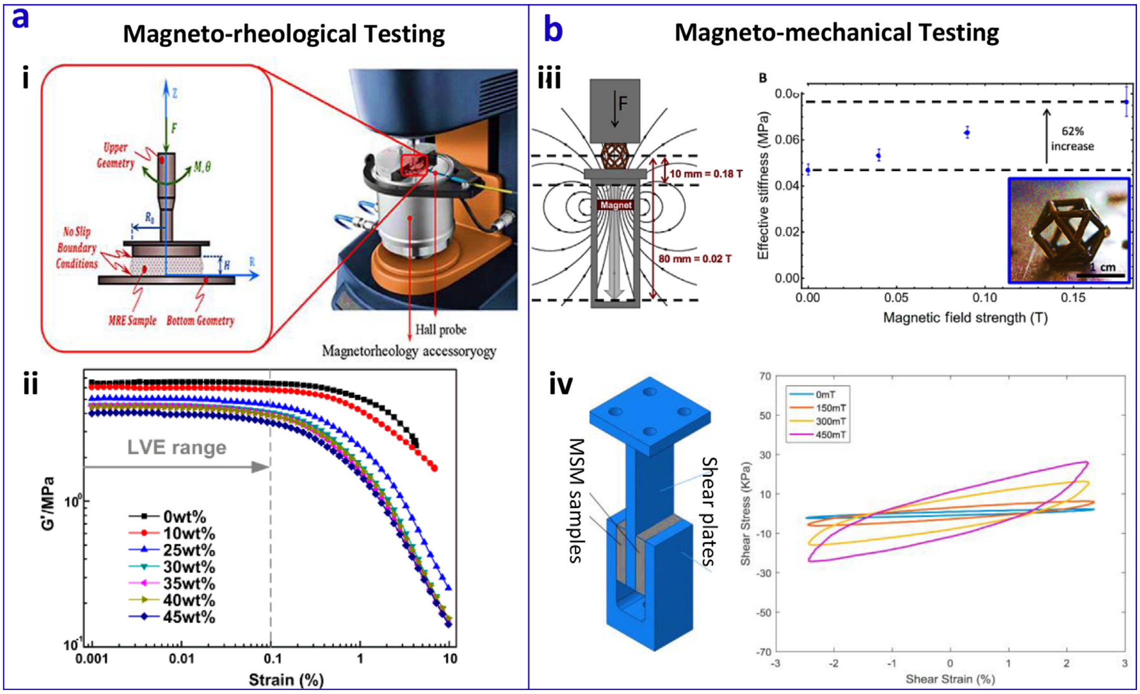

Fig. 7. Mechanical behavioural characterization methods for MSMs: (a) magneto-rheological and (b) magneto-mechanical tests. (i) A widely-used rheometer apparatus with a magnetic field (adapted from [196]) and (ii) the response of MSM using an amplitude sweep test in the rheometer (adapted from [197], (iii) schematic illustration of a bespoke test setup for compressive properties of MSMs in compression/tensile loading and its response (adapted from [132]) and (iv) illustration of the shear test setup and dynamic response of MSMs at different magnetic flux densities (adapted from [198]).

oratory setup is required for magneto-mechanical characterizations of MSMs (Fig. 7b). However, note that such a customized setup is mostly for the studies involving the magnetic fields, otherwise existing standard instruments can be used. In order to investigate and understand the magneto-mechanical properties of MSMs, exhaustive characterizations can be performed by implementing various techniques such as compression tests, tensile tests, shear tests, biaxial tests and fatigue tests with customized test setups, they are well summarized in [45].

The magneto-mechanical testing can be both static and dynamic, which can be decided depending on the nature of the force/deformation to be experienced by the MSMs in the targeted applications. A force versus displacement can be used to characterize the mechanical properties of MSMs where the structures of MSMs are not regular in shape (not defined cross-section), as the conversion of the corresponding force and displacement data to the stress and strain data are non-trivial. Otherwise, for a regular-shaped MSM specimen, the stress versus strain at various magnetic fields with respect to strain rate and strain amplitude at different testing modes can be investigated. Some very crucial properties to be investigated for MSMs are elastic modulus/stiffness, elongation at break, and the ultimate tensile strength. Note that similar to the experimental study of MSMs, constitutive modelling and numerical simulations of these fast-growing active materials is an active area of current intense research [148,199-212].

4. Programming and actuation

In shape memory polymers (SMPs), programming generally refers to a method to teach the polymer a temporary shape. The programming can usually be well-maintained unless it is activated by an external stimulus such as heat, light, electric/magnetic field, pH, etc. For MSMs, programming basically refers to the alignment of the magnetic domains (especially for hard-magnetic fillers) or magnetic particles (for soft magnetic fillers) in a specific or desired fashion within the polymer networks. As demonstrated in Fig. 2, the soft-magnetic fillers display shape-morphing behaviours due to the gradient magnetic field, while the hard magnetic fillers can demonstrate shape-shifting behaviours due to the attraction or repulsion of the magnetic domains even in the presence of a uniform magnetic field. Therefore, the programming is much reasonable for the hard-magnetic fillers, and thus hard-magnetic particle-filled MSMs are more attractive in the case of producing shape-morphing structures. On the other hand, soft-magnetic fillers can be aligned to obtain anisotropic properties (e.g., modulus) of the MSMs. Here, we, therefore, mainly focus on the programming for the hard-magnetic fillers-based MSMs. At this point, the programming essentially means magnetization of the hard-magnetic fillers within the MSMs.

It must be noted that, for soft-magnetic fillers, the alignment or patterning of the magnetic particles can only be performed during the synthesis process. However, the programming of the hard-magnetic fillers can be achieved even after the polymerization of the matrix materials. This is one of the most striking features and advantages of the hard-magnetic fillers over the soft-magnetic fillers and thus allows the re-programmability.

4.1. One-way programming

One-way programming is the process of magnetizing the magnetic domains of the hard-magnetic fillers in a specific direction. The techniques for one-way programming for MSMs are well described in an article by Lum et al. [154]. There are two ways of programming the magnetic domains; the first way is to magnetize the hard-magnetic fillers' domains only after the matrix material is fully cured (solidified) [124] and the second way is to magnetize the domains before or during the polymerization process of the matrix materials [11]. However, it should be noted that the first way of patterning/programming is not applicable to soft-

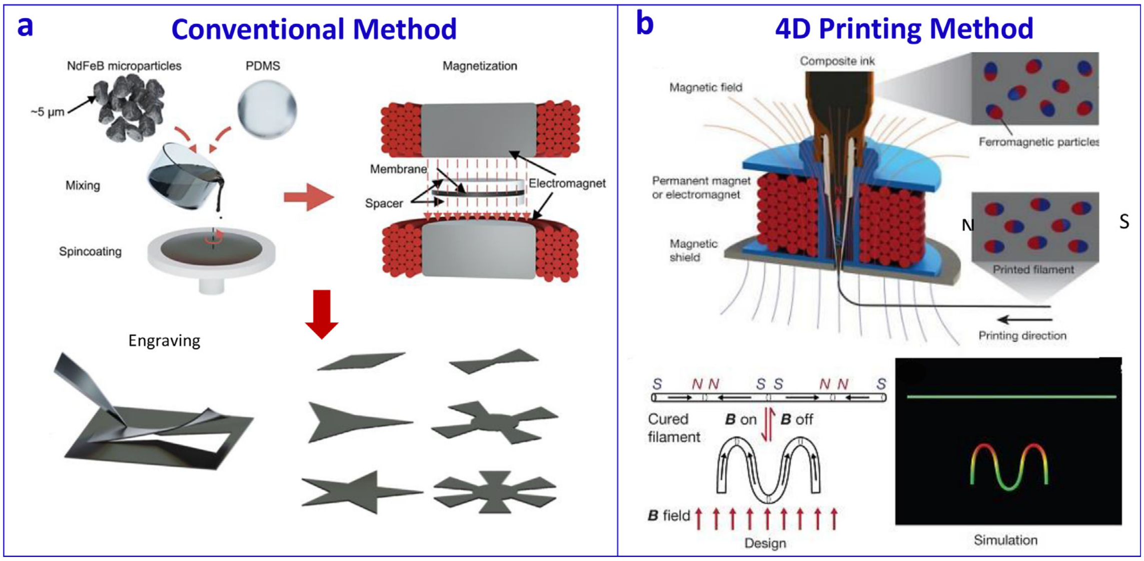

Fig. 8. One-way programming methods for MSMs. (a) A conventional method, in which elastomeric membranes are magnetized by an out-of-plane magnetic field induced by an electromagnet after the elastomer is being fully cured and later engraved into the desired shapes (adapted from [124]). (b) A 4D printing method, in which magnetic particles are magnetized at the printing nozzle tip before the structures are printed and the elastomer is cured afterwards (adapted from [11]).

magnetic fillers. Such magnetization process can be achieved by means of a conventional method or 4D printing method. The conventional method is that magnetization is performed by exposing the MSM composites to a large magnetic field (Fig. 8a). In the 4D printing method, magnetization can be achieved before printing the MSM composite inks (Fig. 8b). The first way of magnetization does not provide greater flexibility as the magnetic domains can only be aligned or oriented into a single specific direction depending on the magnetic pole of the pooling magnet. However, 4D printing can be used to generate highly tailored patterns and alignment of the magnetic domains within the same structural design. The pole of the pooling magnet can be synchronized with printing patterns in the 4D printing process to achieve the desired orientation of the magnetic domains. Therefore, 4D printing is a much more advanced technique and is highly emerging in the field of MSMs.

Another notable work on one-way programming is the development of magnetic anisotropy within the polymer networks by means of the self-assembly of MNPs [213]. The study has demonstrated that heterogeneous magnetic anisotropy can be achieved for microactuators. The advantage of their technique is that the programming was achieved before fabricating a static microstructure by applying a magnetic field during the crosslinking of the matrix material. The actuation was achieved by a rotational torque of the programmed chains of the MNPs for microactuators when the magnetic field was applied. The technique can be applied to both soft-magnetic and hard-magnetic fillers.

In addition to the programming of the magnetic fillers, the 4D printing technique can be used for the programming of magnetic shape memory composite structures [176]. For instance, using FDM 3D printing, PLA/Fe_3O_4 composite shape memory polymer structures were programmed in the printing process. The 3D printing of such magnetic SMP provides the advantage that the programming for SMPs is not necessarily to be performed after the fabrication because the programmed SMP shape can directly be 3D printed.

Having said that the above-mentioned techniques are the most common ways for one-way programming, there are few other methods used for the re-programming of MSMs that can also be used for one-way programming. These will be discussed in Section 4.2.

4.2. Re-programming

Re-programming refers to aligning magnetic domains or states of magnetic fillers to a new direction from the prefabricated designs and thus to realize another shape-morphing phenomenon with the same structurally designed MSMs. Note that the re-programming of MSMs should not change the intrinsic magnetic properties of embedded magnetic fillers or the molecular properties of the matrix materials. In addition, the shape-morphing phenomenon aims to achieve a customized actuation in a designed fashion, therefore, re-programming should only be performed in the desired spatial positions of the MSM system. Research studies have adopted two different ways to re-program the magnetic domains. The first way is to locally heat the magnetic fillers above the Curie temperature of the hard-magnetic fillers and re-orient the domains by exposing them to a pooling magnet [78], see Fig. 9a. Usually, a laser heating technique is used for the localized heating. Soft matrix materials should not change their molecular properties by heating above the Curie temperature of the ferromagnetic particles. For instance, the re-programming has been reported using CrO_2 particles which have the Curie temperature of about 118 °C that well falls within the operating temperature of most elastomers [78,214]. The second way of re-programming is to heat the components of matrix materials to their melting point and thus to allow the free movement of the magnetic fillers and the ferromagnetic state. Heating can be achieved by means of localized heating, for example, direct laser writing (DLW) in a highly controlled fashion [215] or bulk heating [216]. In bulk heating, a hierarchical structure comprising magnetic microspheres are incorporated within an elastomeric matrix with static and rotatable ferromagnetic states. In these cases, the microspheres of phase change polymers (e.g., PEG (Polyethylene glycol) or PCL (polycaprolactone) microspheres loaded with magnetic particles) are used and are additional components of matrix materials (Fig. 9b & 9c). In the rotatable ferromagnetic state, above the melting temperature of the PEG/PCL microspores, the magnetic particle chains can freely rotate. However, in the static ferromagnetic state below the melting temperature of the PEG/PCL, the magnetic particle chains are locked in the solidified PEG/PCL, maintaining the programmed ferromagnetic domain patterns [215,216]. In such programming and re-programming conditions, the reported

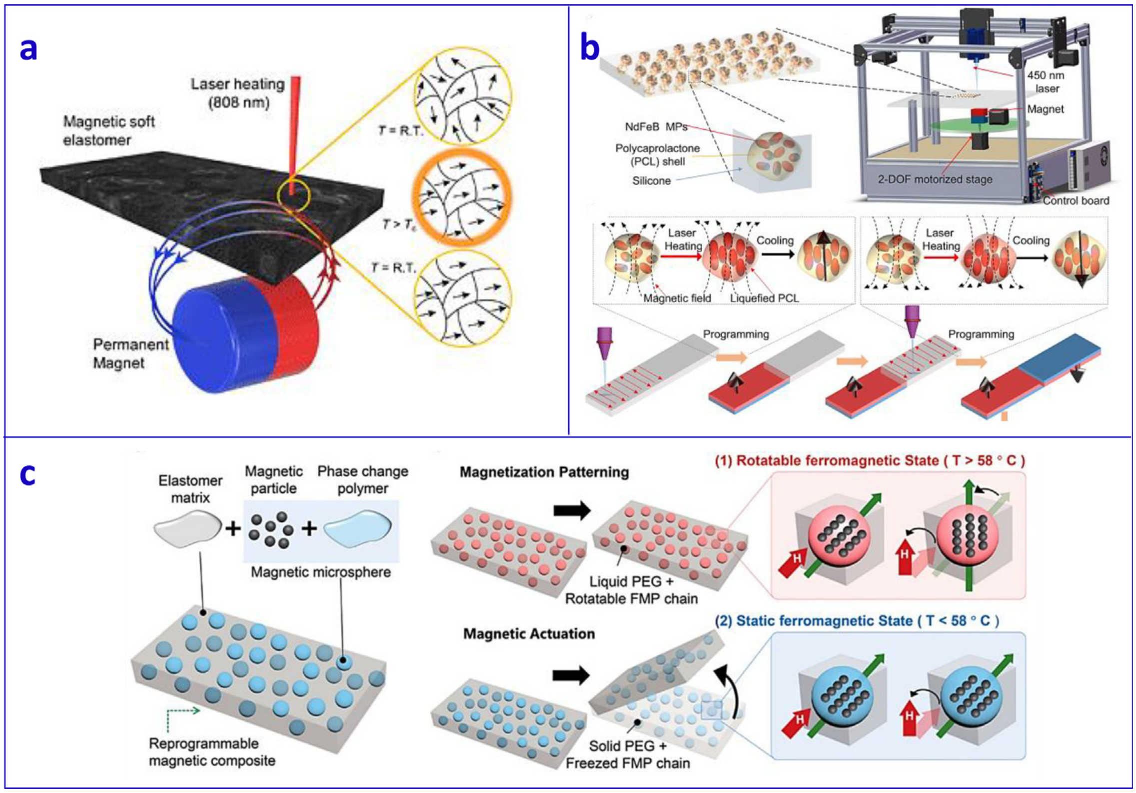

Fig. 9. Techniques to re-program the magnetic fillers or the ferromagnetic state of MSMs. (a) Localized heating of the magnetic fillers using a laser heating technique to orient the magnetic domains in the desired direction [78] and (b) illustration of the programming and re-programming processes using a DLW technique in the ferromagnetic states of the magnetic fillers embedded within microspheres of polycaprolactone (PCL) [215]. (c) Rotatable and static ferromagnetic states of magnetic microspheres of Polyethylene glycol (PEG) oligomers [216].

temperature is about 60 °C to melt the microspheres, which is much lower than the Curie temperature of magnetic fillers.

Very recently (2021), on-demand and highly re-programmable MSM devices have been reported [119,217]. These advanced materials can alter the mechanical behaviour in the presence of a magnetic field using a design framework for a tileable mechanical metamaterial with a stable memory at the unit-cell level. Encoding the binary instructions of such novel metamaterials can provide on-demand re-programmable mechanical properties in addition to the stable memory effect.

4.3. Magnetic field-driven actuation

In MSMs, the actuation means attaining the shape-changing phenomena of the designed structure by the application of an external stimulus. The actuation can be categorized into two types, i.e., (i) pure magnetic field-driven actuation and (ii) multi-stimuli actuation [218,219]. In addition to a magnetic field, the other stimuli can be pH, heat, light, humidity, and electric field.

Magnetic field-driven actuation focuses only on the magnetic field as the external stimulus. Such an actuating field can be generated either using permanent magnets or electromagnets. Permanent magnets only offer a static pole of a magnet at a fixed position. In contrast, an electromagnet provides the flexibility to change the pole of the magnet without changing the spatial position but by changing the pole of the supplied current. For an electromagnet, the amount of current in the electromagnet controls the strength of the magnetic field. In contrast, for the permanent magnet, the device itself can be rotated to switch the pole of the magnet and similarly magnet itself can be moved toward or away from the MSM specimen to change the strength of the magnetic field.

A number of different cases of magnetic actuation are sketched in Fig. 10. For example, a magnetic field produced by a permanent magnet can complexly change the shape of 3D printed tensegrity for a soft robotics structure [187] (Fig. 10a). The use of an electromagnet to actuate the magnetic components is given in Fig. 10b, in which soft intelligent structures are programmed to reshape and reconfigure under the magnetic field required for soft robotics in biomedical applications [220]. Similarly, the magnetic shape-memory elastomers can be actuated using a magnetic field to change shape as given in Fig. 10c [221]. Static and dynamic actuation of 3D printed magneto-responsive soft robots can also be achieved by using a permanent magnet in a static or dynamic way, which was greatly demonstrated by a breakthrough study in the field of magnetoactive soft materials [11], an example of such actuation is given in Fig. 10d. In order to achieve the shape-morphing phenomena such as bending, elongation, contraction, and twisting, a static magnetic field can be applied, but an alternating magnetic field is the better way to achieve the shape-shifting phenomena [84]. On the other hand, to achieve dynamic shape-morphing phenomena such as crawling, swimming, and jumping, a time-varying dynamic magnetic field has to be applied by changing the strength and spatial position of an external magnetic field. MSM structures are untethered and show dynamic movement but in a controlled fashion regulated by the external magnetic field, therefore, possess high potential to be used in medical applications. More detailed applications will be discussed in Section 5.

4.4. Multi-stimuli actuation (magnetic field + other stimuli)

Magnetic field-based actuation in the MSMs is the only way until recently. These single field-dependent characteristics of MSMs limits their applications in areas where complex and multi-

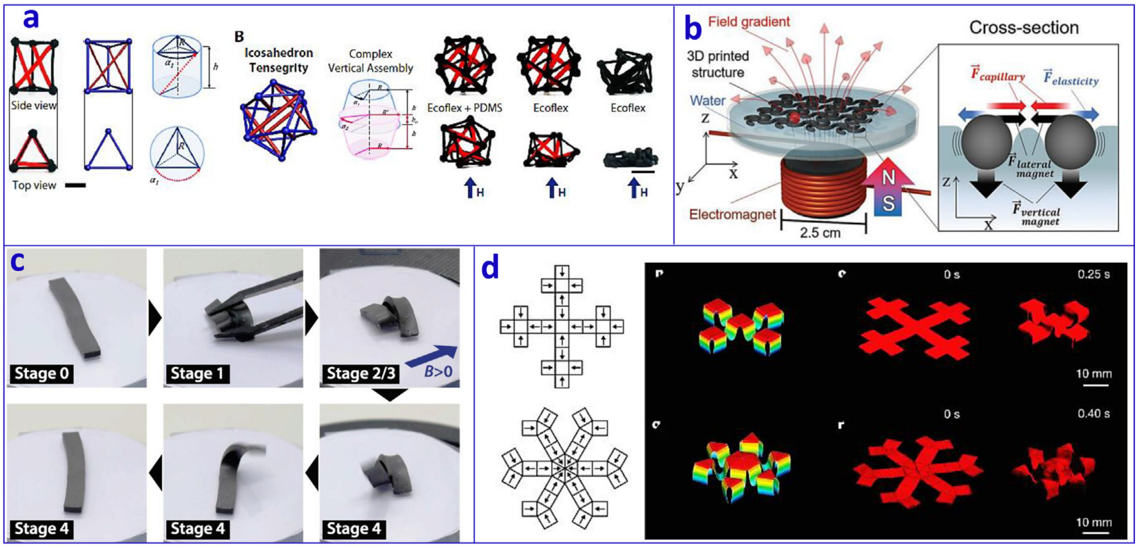

Fig. 10. Examples of magnetic actuation of MSM-based structures. (a) A tensegrity structure composed of magnetic and non-magnetic components and their actuation [187]. (b) Magnetic actuation and forces exerted on a magnified part of the 3D-printed filament by an external magnetic field [220]. (c) Demonstration of magnetic shape-memory effects in an unconstrained strip deformed in three dimensions via a magnetic field generated by a permanent magnet [221]. (d) Magnetic actuation of MSM specimen developed via 3D printing and actuated by a permanent magnet [11].

dimensional mobility required for various applications such as in soft robotics [115,222]. Therefore, multi-stimuli actuation is much needed for MSMs to widen their large and versatile applications. Other stimuli such as humidity, light, sound, and heat can also be coupled to actuate MSMs. In order for MSMs to be actuated by other stimuli, some factors such as choice of matrix materials, for example, the use of shape memory polymers and the choice of other fillers like carbon-based materials (graphene oxide or carbon nanotubes) have to be considered in the developmental phase.

Some interesting examples of multi-stimuli actuation are given in Fig. 11. A multifunction MSM robot was made from multi-responsive materials, which were fabricated through a magnetic-field-assisted gradient assembly of soft magnetic particles (Fe_3O_4) and graphene oxide as filler materials. Such MSMs demonstrate shape morphing phenomena (capture, hold, carry, rotate and release) when actuated by a combination of various stimuli such as humidity, light, and magnetic field [222] (Fig. 11a). Here, it should be noted that the light or sound is used to generate heat within the MSMs. At the same time, MSMs and magnetic shape memory polymers have attracted significant interest in the field of multi-stimuli responsive smart structures in recent years. An exciting example of MSMs and magnetic shape memory polymer developed via 3D printing is illustrated in Fig. 11b, in which two external stimuli, i.e., magnetic field and heat, are used simultaneously [77] to realize the fascinating shape-morphing phenomenon such as bending. Another example includes a similar type of magnetic shape memory polymer which is actuated by means of a magnetic field and heat generated by a photothermal process [223] (Fig. 11c).

5. Applications of MSMs

Wang and Gao [224] helped us in recalling a six and a half decades old Hollywood science fiction movie *Fantastic Voyage* (1966). In the science movie, a small-scale submarine is shown which can meticulously navigate through the complex human fluidic blood stream aiming to treat life-threatening diseases. Luckily, today science is there to turn the human imagination into a reality. Now, we may create a soft-bodied multifunctional, multi-material tiny robot that can navigate through the human arteries to pick up any tissues for biopsy to identify possible illness, can deposit a drug to a precise location for the cancer therapy, can clean clogged arteries, can delivery human sperm to a targeted place for the fertilisation, can contain a camera for image collections inside the human body, can even interact with an individual cell, etc. to mention a few. However, in designing these *fuel-free* bioinspired machines, several key features must be met, e.g., they must be soft and compliant to human tissues, flexible, biocompatible, biodegradable, non-toxic, etc. Moreover, these machines must be controlled and navigated without any direct wire connection to their surfaces (e.g., they must be tetherless, cable-less or tubeless). In the last decade, as a result of intense research efforts due to the pressing demand mainly from biomedical engineering, a plethora of bioinspired untethered soft-bodied robots ranging from nanoscale to millimetre-scale have been proposed (and tested in vivo conditions, to some extents) that can meet almost all of the aforementioned criteria. In this case, soft- or hard-magnetic particle-filled elastomers and hydrogels are the main candidates that can be actuated remotely for propulsion and locomotion using a static or dynamic magnetic field. In the following sections, such *fuel-free* machines made of MSMs that are designed and are demonstrated over the last few years [225-232] are discussed. For the first time, here we attempt to present the applications of MSMs taking length-scale as a gauge to categorize them. **Macro-/milli-/micro-/nanoscale** is as sketched in Fig. 12. Please note that if one or more dimensions (thickness/diameter/length/height) of the MSM device fall within the stated range then such a device is included in the corresponding classification. Additionally, a pie-chart is created to provide an overview of the distribution of the length scale-wise applications of MSMs — microscale devices are the most prominent. See supplementary information for the detail of papers collected to produce the pie chart.

5.1. Macroscale applications

In this section, shape-shifting actuators and soft robots made up of MSMs where their sizes vary from *several centimetres to metres* are covered. One of the earliest shape-morphing applications of MSMs at the macroscale is due to Bose et al. [233]. They prepared a ring-shaped MSM body that is placed in a valve-type device. It

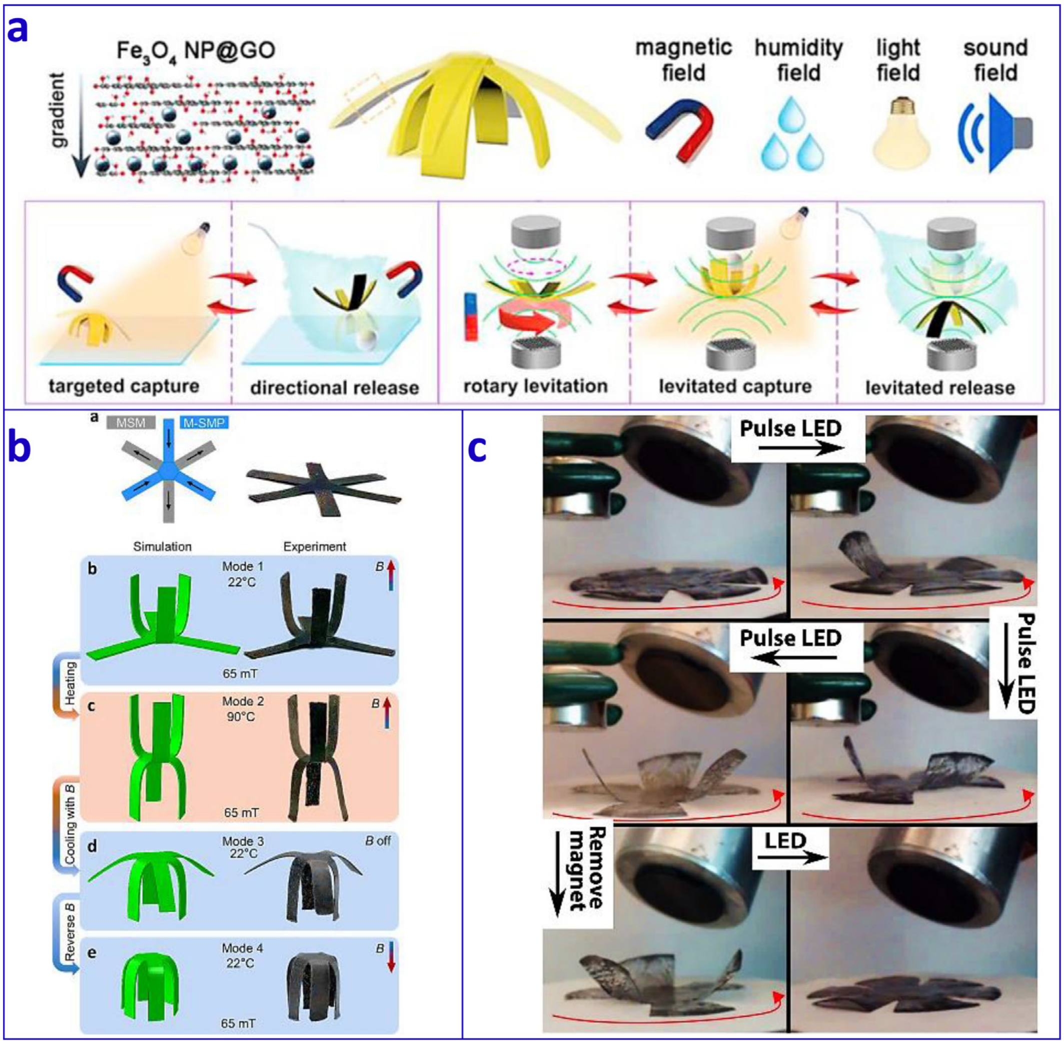

Fig. 11. Multi-stimuli actuation of MSMs. (a) A simple claw with distinct actions is controlled under specific stimuli; complex, and cooperative motilities were realized by various cooperative conversions using different external stimuli [222]. Different deformation modes achieved by cooperatively controlling the temperature and magnetic field for a 3D printed MSM, (a-e) asterisk design with alternating material distribution and magnetization directions [77]. (c) Shape-memory magnetic polymer actuated by the application of a magnetic field and photothermally generated heat, a rotation of a shape-memory flower while pulsing the light-emitting diode [223].

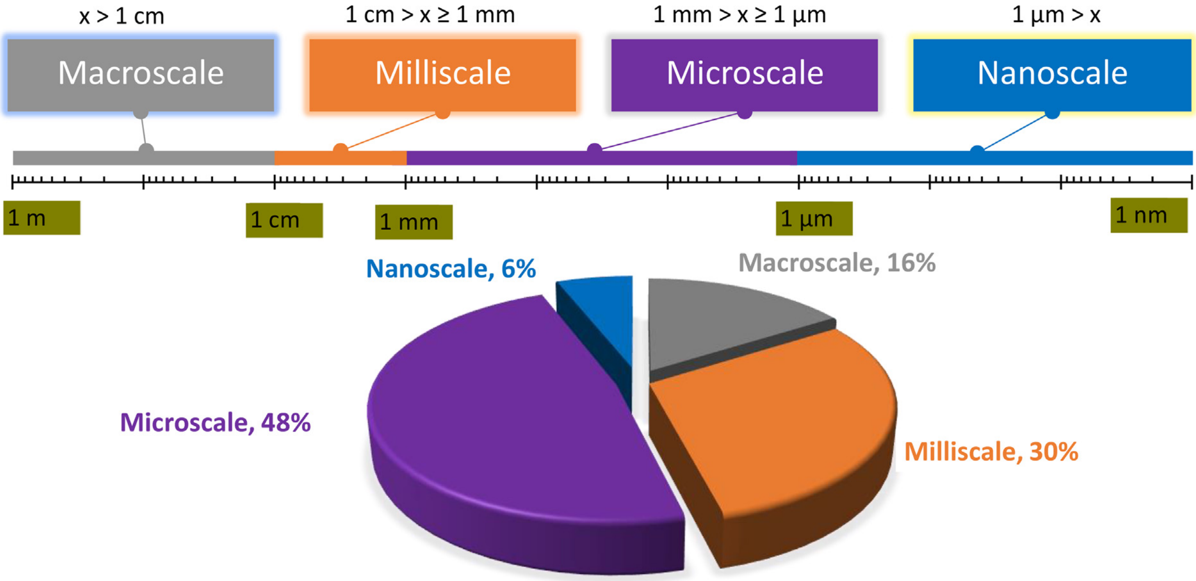

Fig. 12. The length scale-wise classification and pie-chart showing the distribution of scale-wise MSM applications considered in this review.

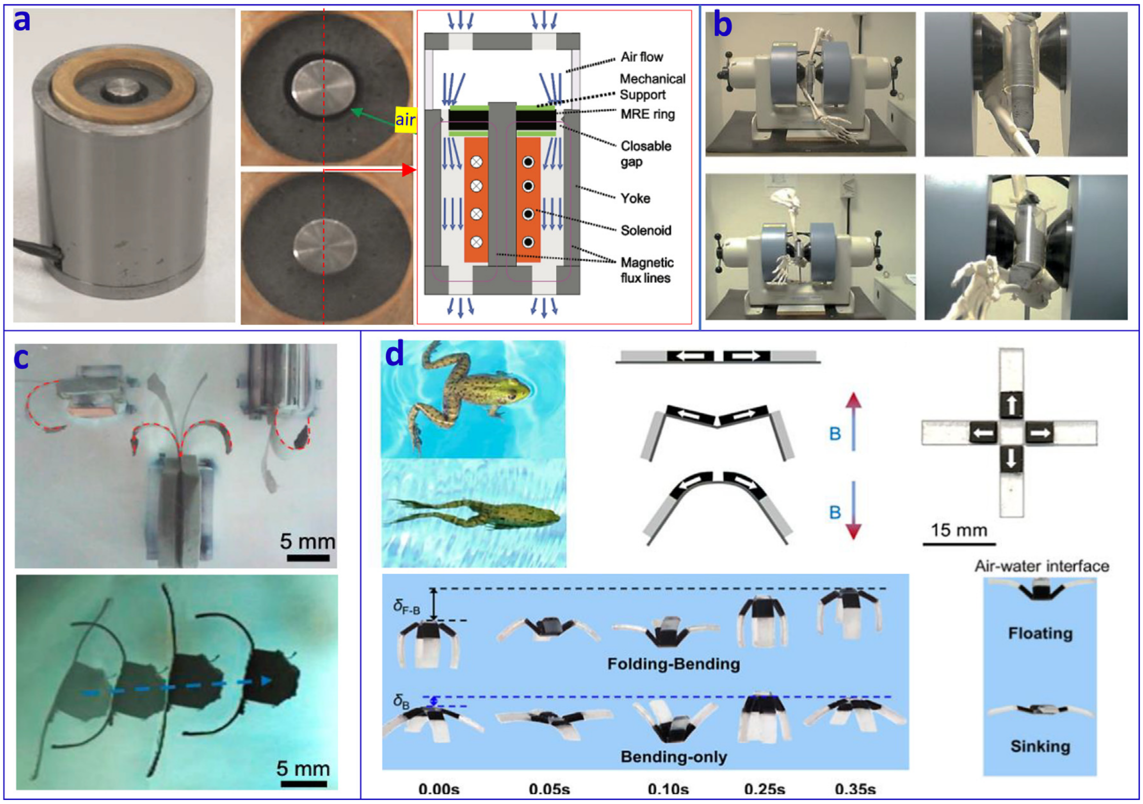

Fig. 13. (a) One of the earliest MSM-based prototypes used in a valve for controlling air flow (adapted from [233]), (b) prototype of an artificial muscle biceps based on the MSMs that mimics human hands (reproduced from [89]), (c) A jellyfish-like robot having two soft tentacles made of the programmable MSM. The robot could propel itself on an oil–water interface by bending its tentacles back and forth when a magnetic excitation coil is used resulting in a smooth movement of the artificial arm (adapted from [154]), (d) A swimming robot that mimics the propulsion mechanisms of a swimming frog (taken from [147]).

can control air or fluid flow in a nozzle, see Fig. 13a. The inside diameter of the circular ring is approximately 4 mm while the outside ring is about 1.5 cm. When the ring expands radially and closes the gap between the steel bar and the MSM ring, the air stops flowing. For the actuation purpose, a spatially varying magnetic field is created in the closable gap. The matrix is a silicone elastomer of various Shore hardnesses filled with micrometre-size iron particles (i.e., soft-magnetic particles).

Lu et al. [234] proposed a generalised strategy for inculcating shape-programming in magnetically activated soft materials. Using the method, a continuous spatial and temporal magnetisation can be created within a magneto-responsive soft composite polymer that can be actuated further by an external magnetic field. The authors further demonstrated the efficiency of their method by designing millimetre-scale bio-inspired soft machines such as jellyfish-like soft robots, synthetic cilia etc. (Fig. 13c).

Although a wide range of artificial muscles made of electro-active polymers on the macroscale has been proposed in the literature over the last two decades [235-237], only very few efforts are made to create similar synthetic muscles using MSMs. For instance, Nguyen et al. [89] made a model of biceps muscles using soft-magnetic polymeric composites. Under an external magnetic field, the artificial muscles can show several modes of deformations including extension, contraction, and bending. Their results demonstrated that the artificial biceps could mimic human hands by operating under multiple cycles of contraction, elongation, and bending (Fig. 13b).

Inspired by the flexibility, resilience, and promptness of motions of biological worms, a worm-like robot of several centimetres long is proposed by Niu et al. [238]. In contrast to most other bio-inspired machines where active hard-or soft magneto-particles are embedded into the robot body, this body is made of a pure polymeric material in which a set of permanent magnets are decorated over its surface resulting in easy manufacturability of the macroscale machine. Moreover, due to its relatively larger size over other micro-or millirobots, this magnetically actuated untethered robot can be more suitable for carrying larger loads and for regular inspection tasks such as the identifications of defects/leakages in gas/water pipelines. Magnetoactive metamaterials have a plethora of applications ranging from materials with tunable properties to soft robotics. However, under the activation of a switching magnetic field, a functional component of metamaterial demonstrates mirror symmetry resulting in a single mode of actuation that limits their wide range of applications. In that regard, Wu et al. [147] devised a new set of programmable magnetoactive composites in which various parts are joined together to create symmetry-breaking multimodal actuation. This novel strategy of asymmetric multimodal actuation opens new horizons in which shape-shifting metamaterials can be used for bio-inspired soft-bodied robots that can give crawling, jumping, bending locomotions. Moreover, this method can be highly scaled up, as an example, they devised four-leg soft robots mimicking a frog (several centimetres) locomotion (Fig. 13d).

5.2. Milliscale applications

In contrast to the limited numbers of macroscale structures consisting of MSMs, there are a sizeable amount of prototypes out of magnetoactive polymers at the millimetre scale available in the literature, see [239-242]. In this section, some selected shape-morphing designs and applications, that have been proposed over the last decade, are discussed.

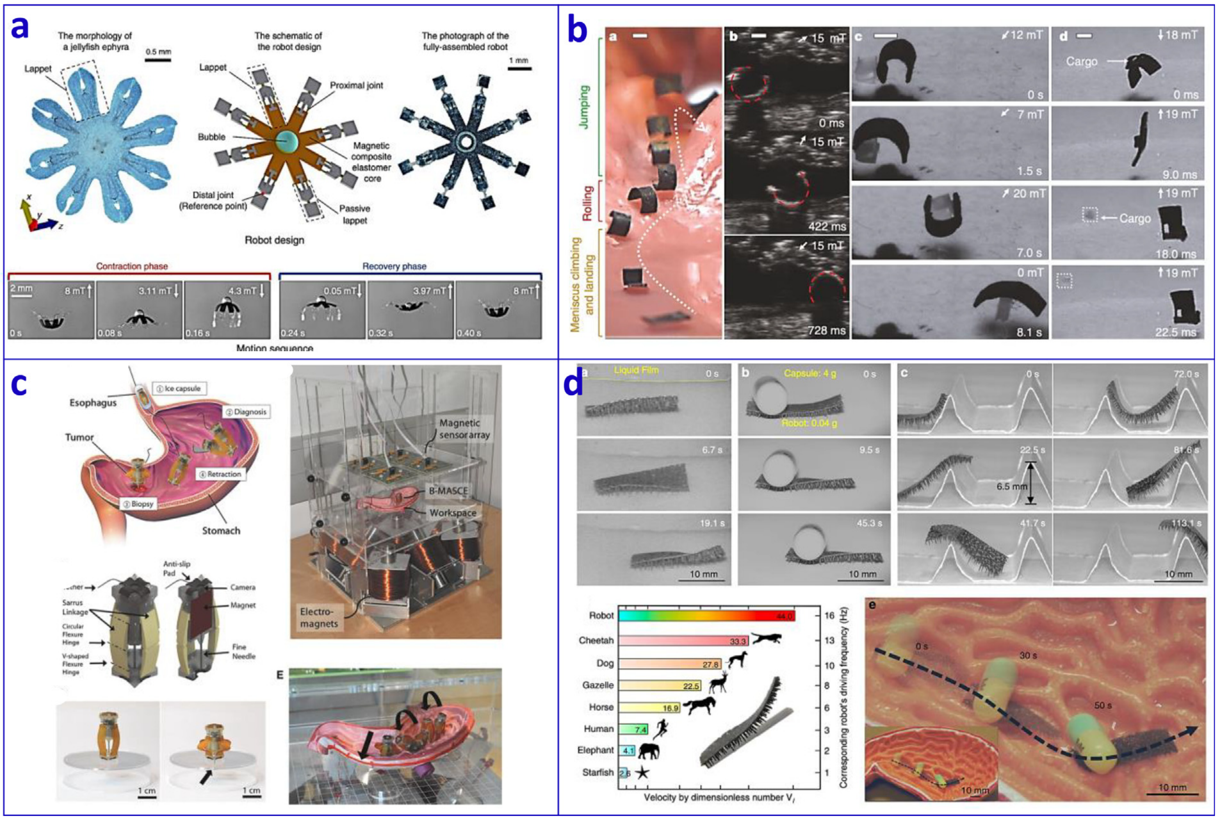

Fig. 14. (a) An untethered jellyfish-inspired soft millirobot that could realize multiple functionalities in moderate Reynolds number (adapted from [234]), (b) A milliscale robot with multiple locomotion modes is navigating through an artificially-made stomach, ultra-sound photography of the robotic motion, the micromachine can walk, grab an object by curling in a C-shape configuration and release it at a new position by uncurling (reproduced from [244]), (c) Magnetically actuated soft capsule endoscope for fine-needle capillary biopsy, various parts of the robot, the working mechanism of the robot with a needle, external magnetic setup (adapted from [12]), (d) A bioinspired multilegged soft machine that can jump, crawl carrying ten times more load than its body weight both in dry and wet conditions (taken from [92]).

Ren et al. [234] devised a millimetre scale jellyfish-inspired swimming soft robot that can navigate fluid flows at a moderate Reynolds number (Re). The main body of the robot consists of a magnetoactive polymeric composite in which Nd-Fe-B is used as the hard-magnetic particle embedded in a soft silicone elastomer. In designing the soft-bodied millirobot, biomimicry of jellyfishes, i.e., scyphomedusae ephyra has been demonstrated. The lappets of the fish-turn-robot are actuated by a remote-controlled magnetic field that can generate fluid flows around its body. Such diverse flows may create multiple functionalities, e.g., propulsion, predation, mixing etc., see Fig. 14a. Lu et al. [243] proposed a leg/foot-based millirobot that imitates the foot structures of many living organisms, in contrast to the wing-based bioinspired soft-bodied robots. One of the most striking features of such a multi-legged soft micro-machine is that it can operate and walk both in dry and wet conditions (Fig. 14d). In designing the miniature robot, they explore the weight/foot height, leg spacing per step etc from hundreds of foot-based living organisms and obtain a leg height/foot space ratio resulting in a soft-bodied robot that can carry weight more than hundred times of its own weight. Moreover, it can climb up obstacles that are aligned even ninety degrees of its main walking trajectory and can jump over a height that is even ten times taller than its own height.

In recent years, untethered capsule-based endoscopes have transformed the landscape of biomedical diagnostic methods inside the human body, particularly in the gastrointestinal (GI) tract in which various diseases can occur. To date, in order to identify any illness in the areas, capsule robots have been utilised to collect specific tissues and surface photographs using different imaging techniques. However, such wireless capsules cannot collect tissues from layers of the GI tract at a greater depth. To circumvent these drawbacks, very recently, Son et al. [244] devised a soft-bodied capsule endoscope containing fine-needle which can collect tissue samples for biopsies at a greater depth in the gastrointestinal tract such as from mucosa/submucosa layers (Fig. 14c). For actuation and locomotion in the capsule robot, an externally applied magnetic field is used. As described in the previous Section 5.2, most of the existing bioinspired miniaturised soft robots have limited modes of locomotion. In contrast, Hu et al. [12] devised a millimetre-scale magnetoactive soft robot with multimodal locomotion (Fig. 14b). Using hard-magnetic micro-size particles and with the help of wireless magneto-actuation, the robot can swim in a fluid flow, can jump over obstacles larger than its body height, can crawl in a narrow and confined channel, in addition to the usual walk-and-roll locomotion. Such a multimodal locomotion capability of a bio-inspired shape-shifting biocompatible micromachine adds a new dimension to the biomedical engineering, cell delivery, and drug release by pick-and-place action, minimally invasive surgery, to mention a few.

5.3. Microscale applications

MSM based shape-morphing and locomotive devices have demonstrated a huge potential to utilise in biomedical areas such as in controlled and precision drug deliveries. Therefore, in contrast to macroscale or milliscale machines, micro/nanoscale devices get more attention. The underlying reason for this is relatively easy navigation and locomotion of such micro/nanoscale MSM devices inside the human body [245-256]. Every so often such devices are frequently called as MedBots [109]. They are

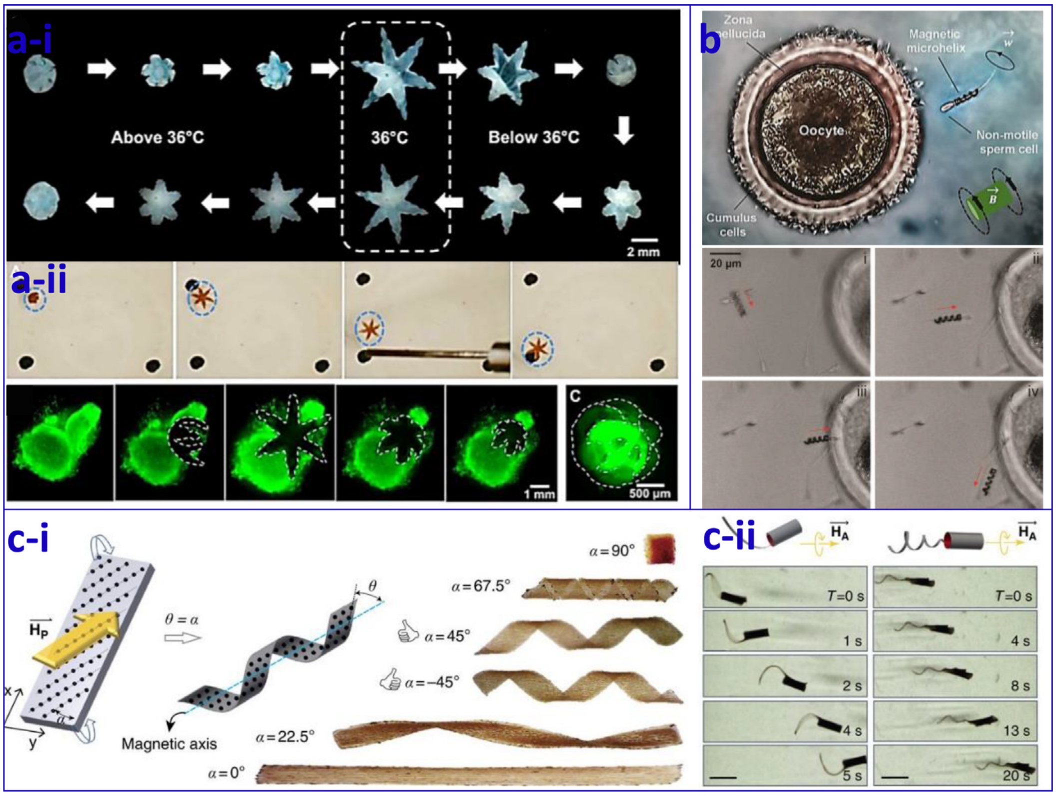

Fig. 15. (a) Experimental and simulation results of a thermal responsive microgripper and magnetic particle doped microdevice grapes and transports an object under a magnetic probe (a-i), while the microgripper captures and excision of cells from a live cell fibroblast clump (a-ii) (adapted from [218]). (b) An untethered magnetic micro helix captures a paralysed sperm cell and delivers it to the oocyte for fertilisation (adapted from [185]). (c) Programming the microstructure of the soft machine parts (tails, heads) using magnetic nanoparticles, single and double layers and a uniform rotating magnetic creates locomotion of the flagellated soft micromachines (c-i) and images present various time lapses of two different machines (c-ii) (adapted from [257]).

designed and navigate in such a way so that they can be operated in confined and complex terrains, difficult-to-reach places inside the human body in which complex physiological environmental conditions do exist.

In the process of drug and cell deliveries, cargo transportation and manipulations, the gripping capacity of bioinspired soft robots is a crucial issue. However, most of the cargo transporting micromachines, especially those that are made of soft hydrogels, have very limited mechanical stiffness to grip an object securely. Therefore, Greger et al. [218] proposed a bi-layered microgripper in which a soft layer is made of photo-cured hydrogels and a relatively non-swellable stiff layer is fabricated using an MSM. Swelling and deswelling of the hydrogel layer under appropriate pH and thermal conditions create large mechanical deformations resulting in gripping and un-gripping capabilities of the microgripper, see Fig. 15a. Furthermore, the incorporation of soft-magnetic particles in one of the layers gives enough flexibility to remotely controlled the micromachine. Unicellular living organisms such as bacteria are great sources of designing soft, flexible micromachines that can navigate through complex and confined terrains. In this case, Huang et al. [257] devised a soft microswimmer made of magneto-hydrogels that has programmable propulsion capability with shape-morphing features. In manufacturing the microrobot, the main body is synthesised using a multi-layered magneto-gel in which MNPs are anisotropically deposited during the curing process to create programmable folding behaviour (Fig. 15c). While the long flagella structure creates enough locomotion for the microswimmer, swelling and de-swelling characteristics of its main body generate flexible morphology that can be used to accommodate the soft-bodied robot in a closed and confined space.

Soft-bodied microrobots can not only transport drugs, cargos, or can take images using an embedded camera from a delicate location inside the human body, but also, they can be used for carrying living cells for a specific purpose. For instance, Medina-Sanchez et al. [185] created a soft spermbot, a microscale robot, that can carry immotile sperm cells having motion deficiencies towards successful fertilisation (Fig. 15b). To create an artificially motile sperm cell, metal-coated polymer micro helices are designed along with the immotile but otherwise functional sperm in which the magnetoactive polymer used in the microtubes can be activated for a remotely controlled locomotion. Note that the tail of the functional sperm helps the propulsion, hence, this micromachine is called a hybrid microscale spermbot. Such a cellular cargo deliverable robot opens up new hopes for robot-assisted fertilisation. It is noteworthy to mention here that most of the microscale prototypes controlled by magnetic actuation, that are available in the literature [258]. However, they are also being used in preventing environmental populations, e.g., removing water pollutants. Bernasconi et al. [258] devised a 3D printed multi-material and multifunctional micromotor that can be used for cleaning pollutants from contaminated waters. For that, they deposited different metallic nanolayers having pollutant killing capabilities within a polymeric matrix. For untethered navigation and control of the micromachine, they used an externally applied magnetic field. Note that this type of wireless microdevice is greatly advantageous over other cleaning machines as the micro-robotic machine can easily be deployed to a place of 'difficult-to-access' for pollution controls and the monitoring of various chemical and physical contaminations.

5.4. Nanoscale applications

Despite significant advances in designing small-scale devices, there are still pressing needs for these flexible soft-bodied devices down to a smaller scale. For instance, when the need for interactions of the devices with cell levels inside the human body, their size must be at the nanoscale that will render localised diagnosis and treatment methods with greater precision and efficacy [259]. In an effort to produce tetherless soft and flexible nanorobots, Chen et al. [260] synthesised electromagnetic hybrid nanowires that can perform controlled drug delivery to a specific cell. In contrast to other large scale soft devices that are solely made of magnetoactive polymers or magneto-hydrogels, this machine is based on a core–shell manufacturing strategy in which an MSM is used as the core (inside) and a piezoelectric polymer is used as the shell (outside), see Fig. 16b (bottom). The key advantage of this hybrid nanorobot is that when an external magnetic field is used for its movement (e.g., propulsion and controlled navigation), the same field may change the polarisation on the robotic surfaces. These changes will trigger on-demand magnetoelectrically assisted drug release to specific cells.

Navigation of nanoscale MSM devices in biological fluids is complicated due to the very low Reynolds number [225-228,231]. This drawback can only be overcome if the tiny system can break the symmetry of motion to achieve net displacement. Overcoming this constraint, Jang et al. [261] devised magnetic multilink nano swimmers in which the planner undulation can be created thanks to an external oscillating magnetic field, see Fig. 16a. The nano swimmers have three parts; one polymeric tail, two magneto-responsive metallic nanowires that are connected by tube-type polymeric hinges. For the synthesis of such a tiny system, they used three different micro/nanofabrication techniques: electrodeposition, layer-by-layer deposition, and selective etching.

6. Concluding remarks and outlook

The past few years have seen exponential growth in the field of magnetoactive soft materials. This is due to the fact that the MSMs offer a highly adjustable and wide range of properties that can be controlled not only by an external magnetic field but also by using other stimuli. The shape-morphing behaviour of the MSMs shows potentials to use in a number of applications not only in academic research but also in the industry. The emergence of sophisticated fabrication techniques such as 4D printing takes the possibility of using MSMs to the next generation by introducing on-demand programming/re-programming and highly customized structures with complex geometries.

Having said that the development of MSMs is rapidly growing, it should be noted that the research and development is still not well-established considering the fact that the use of shape-morphing behaviours of MSMs in real engineering applications (e.g., soft robotics or medical devices). However, the tremendous progress in various aspects of MSMs provides a promising direction towards the successful implementation of them in different fields. Table 2 provides a comprehensive summary to understand different aspects of MSMs retrieved from some of the great achievements in recent years. As reviewed in this work, the material section is comparatively matured than other aspects and consideration of common types of materials (for both matrix as well as the fillers) can be remarked. The common matrix material is silicone-based soft elastomers, yet the use of other matrices such as shape memory polymers (e.g., PCL) can also be found. The iron oxide NPs is a classical soft-magnetic filler whereas the NdFeB is the extensively used hard-magnetic filler.

It can be observed that the use of digital manufacturing (3D/4D printing) is widely adopted in fabricating the MSM specimens due to the versatility and design freedom offered by the techniques to uniquely configure the magnetic domains or magnetic fillers. Note that the 4D printing not only offers the manufacturing of unique and tailored structures but also saves time and provides a higher degree of flexibility by offering the programming of magnetic

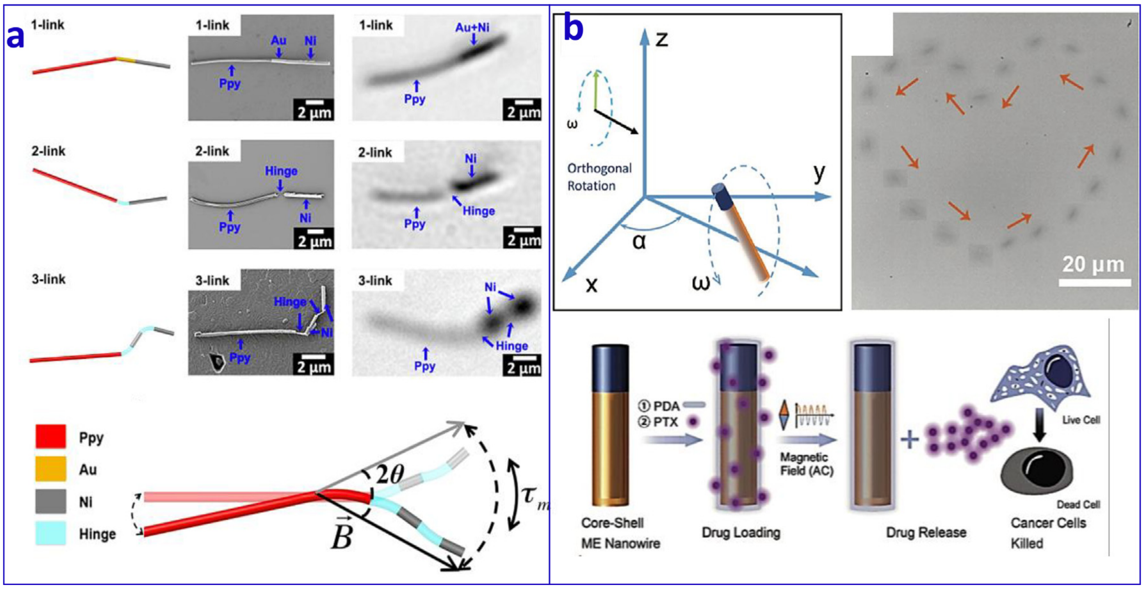

Fig. 16. (a) Various components of 3-link nano swimmer that are activated by an oscillating magnetic field. Schematic and microscopic images of the nanorobot with 1-/2-/3-links (adapted from [261]), (b) Schematic representation of an anti-cancer drug delivery core–shell nanowire device in which the drug is loaded onto the wire (bottom) and is released by applying an external time-varying magnetic field. (b, top) Rotational movement of the wire in the x-y plane while it is following a heart-shaped path (reproduced from [260]).

Table 2
Summary of a few highly notable works on MSMs.

Matrix	Filler	Fabrication	Testing	Programming	Actuation	Behaviour/ characteristic	Ref.
Silicone	NdFeB + silica NP	4D printing (DIW)	Ink rheology Shear properties (shear modulus 330 kPa)	4D printing (field:50 mT)	Magnetic field (field up to 200 mT)	Unthread, fast responsive soft robotics	[11]
Silicone (Ecoflex)	NdFeB	Conventional, moulding	Biocompatibility, Young's modulus	Magnetized by 1.65 T magnetic field	Magnetic field (up to 20 mT)	Small scale multimodal locomotion, medical applications	[12]
Acrylate-based	Fe_3O_4 NPs	4D printing (DLP)	Ink rheology, photo rheology, DMTA	None	Magnetic field	Stretching, shapeshifting, folding	[133]
PLA	Fe_3O_4 NPs	4D printing (FDM)	DSC, TGA	4D printing (no field)	Magnetic field and heat	Coiling, shapeshifting	[176]
PLA + PDMS/Ecoflex	Fe_3O_4 NPs	Hybrid (3DP + conventional)	Magneto-mechanical	None	Magnetic field (250 mT)	Tensegrity, torsion, Auxetic walking	[187]
PDMS	NdFeB	Conventional (spin-coating)	Elastic modulus (2–5 MPa)	Magnetized by 2.3 T magnetic field	Very low magnetic field (<2 mT)	Self-attach, transport cargo, and swim Soft robot, fast response	[124]
PDMS	CrO_2	Conventional moulding	Elastic modulus	Heat assisted magnetic (re) programming (1.5 T field)	Magnetic field (60 mT)	Reprogrammable Soft machines	[78]
Ecoflex	NdFeB@PCL	Conventional	Mechanical testing	Laser writing heat-assisted (re) programming (about 1.1 T)	Magnetic field (150 mT)	Reconfigurable magnetic soft microrobots	[215]
Vinyl polysiloxane	NdFeB	3D printing + conventional	Mechanical testing	Magnetic field (41.4 mT)	Magnetic field (41.4 mT)	Mechanical metamaterials	[217]
Acrylate-based	NdFeB + silica NP	Multi-material 3D printing (DIW)	DMA	4D printing	Heat + magnetic field (65 mT)	Expansion, contraction, shear, and bending	[77]
Polyurethane	Fe	Conventional (moulding)	–	None	Photothermal + magnetic	Bistable, grabbing, soft robotics	[223]

domains on-set of the printing process. One of the biggest advantages of using the 4D printing process is a reduced amount of the externally applied magnetic field for programming. For instance, it has been reported that the use of just 50 mT (magnetic field) is sufficient to orient the magnetic domains at the nozzle tip in the 4D printing process [11], whereas the need of a strong external pooling magnet is required to program magnetic domains after moulding (magnetic field as high as 2300 mT has been reported so far in the literature [124]). Nevertheless, there are some important materials and process concerns related to high-throughput manufacturing via 4D printing. For example, several physical properties of materials such as viscosity, shear-thinning, thixotropic, processability, and printability of composite customized inks/filaments play a critical role in the successful 3D/4D printing of the MSMs. Moreover, the conventional and digital manufacturing processes can effectively be combined to obtain exciting shape-morphing behaviours of MSMs as reported in recent studies [187,188].

It is interesting to see that the use of a very low magnetic field as low as 2 mT [124] has been reported to successfully demonstrate the actuation of MSMs. Such a low field actuation of MSMs can also demonstrate exciting phenomena such as self-attach, transport cargo, swim, soft and fast response robots. In comparison to the programming, the magnetic field needed for the actuation of MSMs remains much uniform among the various studies in terms of the strength of an external magnet. The frequent magnetic field reported for the actuation of an MSM specimen demonstrating key behaviours typically remains below 200 mT. Few common characteristics of MSMs include the untethered soft robot, shapeshifting, and a re-programmable soft machine that has been demonstrated ranging from the nanoscale to the macroscale. Such interesting characteristics are highly desirable in the biomedical field, for example, controlled and precision drug delivery, localized and minimally invasive surgery.

One of the key applications of small-scale soft robots is in biomedical engineering, e.g., controlled and precision drug delivery and cell transportation, where the reduction of fuel-free machine sizes will greatly enhance their potentials. Despite significant advances in designing and in vivo testing of milli-and microscale devices for performing specific tasks that are not possible using conventional rigid machines, there are still pressing needs for these flexible soft-bodied devices down to a smaller scale. For instance, when the need for interactions of the devices with cell levels inside the human body, their size must be at the nanoscale that will render localised diagnosis and treatment methods with greater precision and efficacy [259].

Fig. 17 provides an impression of the future perspectives of MSMs research and development with potential areas to be focused on. These areas of MSMs can be classified into three major categories: material-related, process-related, and device-related. In materials, one of the biggest prospects is expanding the horizons of multi-stimuli responsive materials. For matrix materials, as reported by several studies, the use of shape memory polymers is one of the common trends [77,96]. For fillers, the consideration of carbon-based materials (e.g., CNTs & graphene oxide), in addition to magnetic fillers, has been reported and is unquestionably one of the potential directions. Having said that the consideration of the multi-stimuli responsive materials is needed, it should be

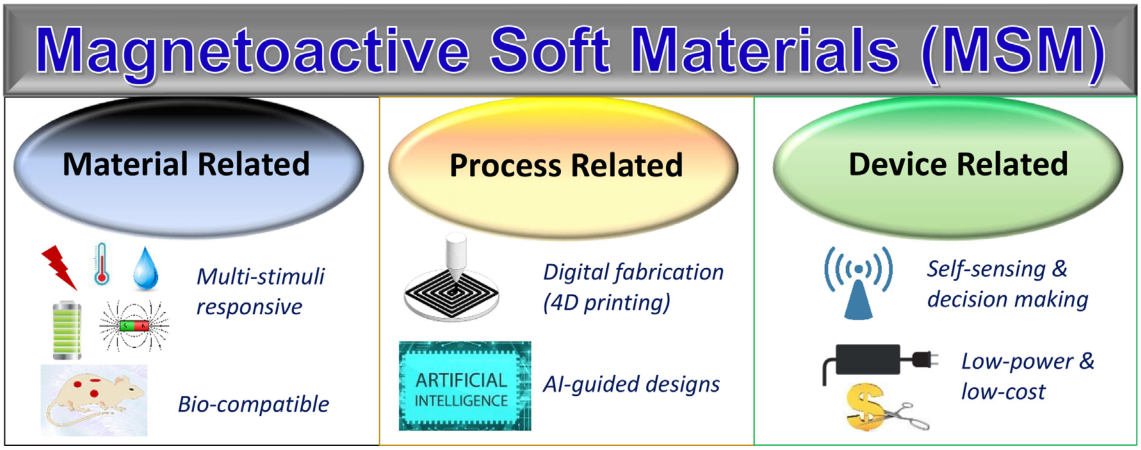

Fig. 17. Outlook of the potential directions of research and development in the field of MSMs.

kept in mind that one of the biggest applications of MSMs lies in the biomedical field. Hence, the biocompatibility of the MSM materials remains one of the core concerns. Therefore, the catalogue of soft polymers and hydrogels and their fillers with biocompatible behaviours must be extended [10]. Furthermore, the integration of both soft-magnetic and hard-magnetic fillers into a single MSM device is highly interesting and provides a complex phenomenon as reported in recent studies [94,121], and it is therefore arguably one of the potential dedicated areas in the near future. In the fabrication process, the use of digital manufacturing techniques (3D/4D printing) is the future of MSM developments, yet the process must not affect the intrinsic properties of MSM materials such as biocompatibility and magnetization. Fig. 18 illustrates the additive manufacturing process-related guidelines for selecting a suitable AM method to develop MSM devices [114]. Note that TPP, having the smallest printing area and resolution among all additive manufacturing techniques, is one of the main 3D printing methods for nanoscale MSMs devices. Furthermore, more innovative and faster approaches are required to speed up the printing process in synthesising both macroscale and nanoscale smart products. Artificial intelligence (AI) such as machine learning and data-driven modelling is extensively developed to optimise compositions of composite materials [262-264]. Such newly emerging techniques need to be considered in future to integrate into the process for providing an in-situ optimization and tailored processing for MSMs. Not only materials and process techniques are essential and play a vital role in the field of MSMs but the devices that are going to be used in real applications should be more intelligent. The intelligent MSM devices are expected to be self-sensing to make their own decision to adjust to the changes in the environment and should be operated by low power resulting in a reasonably low-cost system [222].

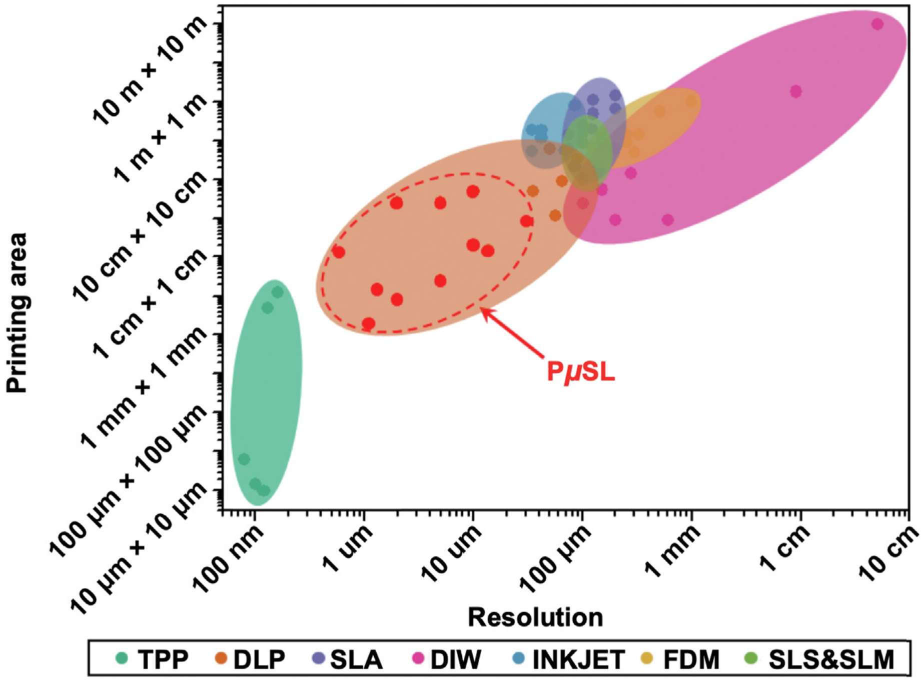

Fig. 18. Scale-wise AM process-related guidelines for selecting a suitable manufacturing process for MSM devices, where the print area is plotted against the print resolution for various 3D printing techniques (adapted from [114]).

CRediT authorship contribution statement

Anil K. Bastola: Conceptualization, Investigation, Methodology, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Mokarram Hossain:** Conceptualization, Investigation, Methodology, Data curation, Formal analysis, Writing – original draft, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matdes.2021.110172.

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