Advanced Lightweight Multifunctional Materials

11. Magnetic field into multifunctional materials

b. Magnetorheological, magnetostrictive and magnetocaloric

Authors: P. Martins, S. Lanceros-Mendez, email: pmartins@fisica.uminho.pt, senentxu.lanceros@bcmaterials.net

University of Minho and BCMaterials

Society is facing serious challenges towards achieving highly efficient utilization of materials and devices. Magnetoactive lightweight materials, such as magnetorheological, magnetostrictive and magnetocaloric materials are attracting increasing interest once they allow a high number of applications such as energy generation, conversion, storage, sensing and actuation, as well as in the biomedical field. In this chapter, the latest research and development in multifunctional lightweight magnetorheological, magnetostrictive and magnetocaloric materials is summarized and discussed in the scope of different application areas. Furthermore, it will be also illustrated the unique functions of inorganic nanomaterials to improve performance of organic materials, as well as combination of the functions of nanomaterials into a device. Final remarks and future perspectives allow to look into a "magnetoactive crystal ball" aiming to foresee what will/should happen in this fascinating research field.

1. Introduction

Magnetoactive materials are a group of smart materials that can adaptively modify their physical properties as a response to external magnetic fields, allowing wireless activation, response and controllability[1]. They are widely used in electric motors, power generators, memory devices, windmills, biomedical devices, energy conversion and transportation, among others [2, 3].

The characteristic *fingerprint* of magnetism is the existence of an ordered arrangement of magnetic moments over macroscopic length scales, with a spontaneous breaking of symmetry[4]. This is classically driven by the interaction between the neighbouring spins that tend to favour specific relative orientations between them. At T≈0 K, this local order

can extend over macroscopic length scales. With increasing temperature, thermal fluctuations lead to misalignment of magnetic moments in neighbouring regions, so that long-range order disappears above a certain critical temperature (T_c). The possibility of a system to suffer a phase transition at a finite T_c depends, particularly and mostly, on the effectiveness of thermal fluctuations, which are controlled by a small number of general parameters of the system. Specifically, dimensionality issues play a key role on the determination of the impact of thermal fluctuations on the critical behaviour of magnetoactive systems[3, 4].

In a 3D magnetoactive system, the magnetic phase transition can certainly occur at a finite temperature, whereas in a 1D magnetoactive system is possible only at zero temperature[5]. Between 1D and 3D, the situation in 2D systems is far more complex and intriguing once the existence of magnetic long-range order at any finite temperature critically depends on the number n of relevant spin dimensionality (Figure 1), being determined by physical parameters of the system such as the presence and strength of magnetic anisotropy[4].

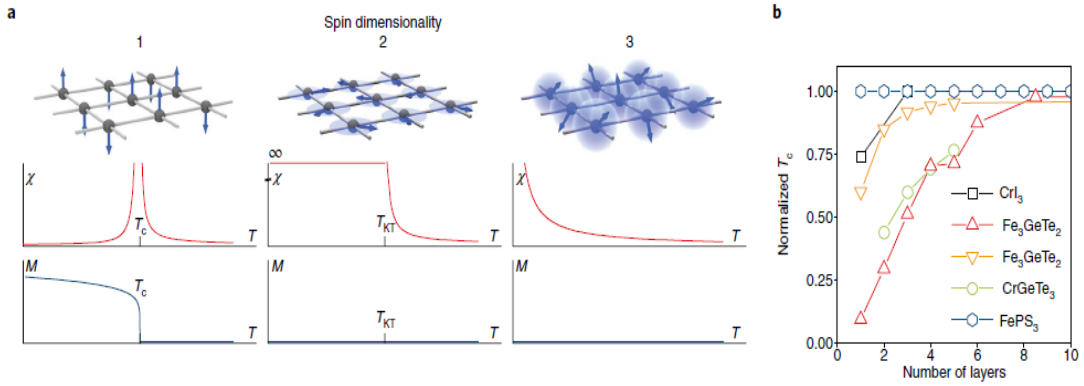

Figure 1. Role of spin dimensionality and evolution of Tc. (a) A spin dimensionality n = 1 means that the system has a strong uniaxial anisotropy and the spins point in either of the two possible orientations (‘up’ or ‘down’) along a given direction. The system behaves effectively as if it has only a single spin component along the easy axis, and the underlying spin Hamiltonian for localized spins is the Ising model. The case n = 2 corresponds to an easy-plane anisotropy that favours the spins to lie in a given plane, although the orientation within the plane is completely unconstrained. The spins can thus be considered to have effectively only two components (associated with the two in-plane directions), which are successfully described within the XY model. Note that in this case magnetic susceptibility (χ) $\rightarrow \infty$ for $T < T_{KT}$ (Kosterlitz–Thouless temperature). Finally, for isotropic systems, n = 3 and there is no constraint on the direction of the spins. The underlying spin Hamiltonian in this case is the isotropic Heisenberg model. (b) Tc (normalized to bulk critical temperature 3D for the particular material) as a function of the number of layers. Taken with permission from[4].

In a challenging 4.0 industry paradigm and contextualized in a dynamic Internet of Things (IoT) environment, a new generation of magnetoactive multifunctional materials, such as magnetorheological, magnetostrictive and magnetocaloric materials (Table 1), capable of changing their physical properties (rheology, strain capabilities and heat generation respectively) under the influence of external magnetic fields, are attracting increasing interest due to the wide range of interesting physical phenomena observed in these materials and the large potential of their practical application in technological devices.

Magnetorheological materials are a class of magnetoactive smart materials whose rheological properties may be varied by application of a magnetic field. These materials traditionally consist of micron-sized ferrous particles dispersed in a fluid or an elastomer[6]. Thus, the mechanism responsible for this bulk effect is the induced magnetic interaction of particles within the matrix.

On the other hand, magnetostrictive materials can be seen as a collection of magnetic domains whose orientations depend on the interplay between magnetic and mechanical energies and whose dimensions may be varied by application of a magnetic field. The magneto-mechanical coupling induces several behaviours that are relevant to structural vibration control: the Joule effect, the Villari effect, material hysteresis, and the Delta-E effect[7]. Ni, Fe, Fe_3O_4, $CoFe_2O_4$, Terfenol-D, $Tb_{0.5}Zn_{0.5}$, $Tb_{0.5}Dy_xZn$ are the most studied magnetostrictive materials[8]. It is also important to notice that magnetostrictive materials combined with piezoelectric ones allow the development of magnetoelectric composites already discussed in a previous chapter.

Analogously, the magnetocaloric effect is referred as the isothermal change of entropy (ΔS) and adiabatic change of temperature (ΔT) upon the variation of the magnetic field. The value of ΔT is directly measured using a thermometer or indirectly from specific heat data while ΔS is calculated from magnetization or specific heat[9]. Perovskites (usually structures with the general formula of ABO_3), glass composites/alloys and spinel ferrites are the most studied magnetocaloric materials.

Table 1. Figures of merit (FOM) of some of the most reported magnetorheological, magentostrictive and magnetocaloric materials (χ_r magnetorheological coefficient - expressing the variation of the shear stress as a function of the variation of the magnetic field, S_m is the maximum strain in ppm, and RCP is the relative cooling power in $J.kg^{-1}$).

Material	*Type*	*FOM*	*Ref.*
$ZnFe_2O_4$	Magnetorheological	χ_r= 11 kPa/T	[10]
Fe_3O_4		χ_r= 3 kPa/T	[11]
Carbonyl iron/γ-Fe_2O_3		χ_r= 34 kPa/T	[12]

$CoFe_2O_4$		χ_r= 1 kPa/T	[13]
$MnFe_2O_4$/ graphene oxide		χ_r= 10 kPa/T	[14]
Ni	Magnetostrictive	S_m=-50 ppm	[8]
Fe		S_m=-14 ppm	[8]
Fe_3O_4		S_m=-60 ppm	[8]
$CoFe_2O_4$		S_m=208 ppm	[15]
Terfenol D		S_m=2000 ppm	[8]
$Tb_{0.5}Zn_{0.5}$		S_m=5500 ppm	[8]
$Tb_{0.5}Dy_xZn$		S_m=5000 ppm	[8]
EuTiO3	Magnetocaloric	RCP=328 J.kg^{-1}	[16]
$HoMnO_3$		RCP=540 J.kg^{-1}	[17]
Gd (bulk)		RCP=690 J.kg^{-1}	[18]
$Zn_{0.6}Cu_{0.4}Fe_2O_4$		RCP=289 J.kg^{-1}	[19]
$Ni_{0.5}Zn_{0.5}Fe_2O_4$		RCP=161 J.kg^{-1}	[20]

In this chapter, a brief history, classification and state-of-the-art of magnetoactive multifunctional materials will be presented. Next, it will be discussed the need of the transition from *highweight* to lightweight and from ideas to applications. Finally, the conclusions and future trends of this dynamical research field will be presented.

2. From *highweight* to *lightweight*

With a unique freedom regarding material selection, magnetoactive composites allow novel designs able to drive operation conditions to new limits, unlocking the potential for novel applications[21].

Although the first idea to apply soft magnetic composites based on iron powders in electrical machinery was produced as early as the 19th century, it did not attracted much attention until the 1980s, where Kordecki and Weglinski[22] described several soft magnetic powder composites and the problems associated with their potential application as magnetic cores in electrical devices[23]. Since then, and boosted by both the aeronautics and aerospace industries[24], research on the development of lightweight magnetorheological, magnetostrictive and magnetocaloric materials and their technological applications has been intensified and strong progress has been achieved.

After those first magnetoactive materials being reported (namely soft ferrites) revealing good magnetic properties, some shapes and sizes problems emerged, making them unsuitable for effective technological device applications[25]. To solve those problems, polymer-iron-based composites have emerged as a solution, overpassing the problems found in silicon steels and ferrites. The production of these materials usually consists on magnetic powders such as pure Fe or Fe-based alloys with Ni, Co, P, Nd, B, Mn, Zn and

Ba within a polymeric matrix[25, 26]. Some studies reported/discussed effects such as compaction pressure[27], sintering temperature[28], annealing treatments[29], polymer content[30] and grain size[31] , in order to determine the possibilities and limitation of the developed materials to perform specific functions on device applications[25].

In order to produce highly efficient polymer-based magnetoactive and multifunctional materials, the addition of magnetic nanoparticles made of inorganic matter (traditionally Fe_3O_4, γ-Fe_2O_3, "soft" magnetic Fe and also "hard" magnetic such as Co, Ni, FeN, FePt, FeP) into polymeric materials has been consolidated as the more appealing and efficient solution[32]. Indeed, this approach allows to produce nano/micro-scaled magnets with magnetic moments higher than those of molecular magnets, allows them to respond to weak magnetic stimulation (static or alternating magnetic field) with a significant effect (change in the rheology, strain or temperature), making them suitable for example for drug delivery or separation applications (Figure 2).

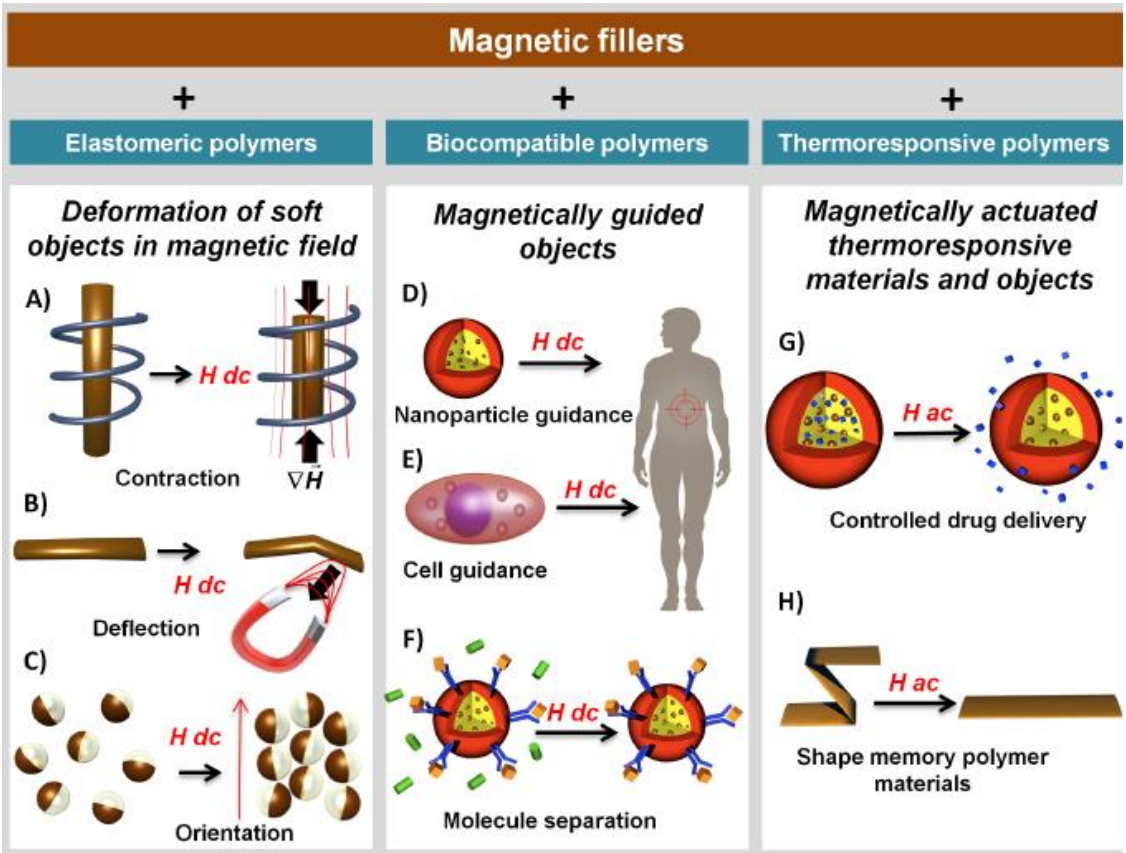

Figure 2. Schematic representation of different types of magnetic responsive materials obtained from the doping of various polymers with magnetic particles and illustration of their response when exposed to a static magnetic field (H_{DC}) or to an alternating magnetic field (H_{AC}). From left to right: composites made from elastomeric polymers can be deformed in homogeneous fields or gradients in a controlled fashion; magnetoresponsive polymer composite (MRPC) particles made of polymers designed

for biomedical applications can be used for magnetic guidance for drug delivery or separation purposes; MRPC from thermoresponsive polymers can be activated by magnetic induction using alternating fields. Reproduced with permission of[32].

The combination of the magnetic properties of those fillers with the elastic properties of the polymers leads to prominent new phenomena that are exhibited as a response to external magnetic fields[33]. Other interesting effects such as the giant deformational effects, the high elasticity effect, the anisotropic elastic effect and the swelling effects linked to a fast response to external magnetic fields and their real-time controllable elastic properties open new opportunities/challenges for using such magnetoactive/multifunctional materials for numerous applications as smart materials in engineering devices[33].

More recently, increasing and focused interest has been devoted to development and use of multiresponsive magnetic polymer-based composites, which exhibit sensitivity to several external stimuli, namely, magnetic field, temperature variations, and pH changing.

3. From idea to applications

Magnetorheological lightweight materials

Magnetorheological lightweight multifunctional materials have been used in many applications in recent years. Wilson *et al.*[34] developed polyurethane and silicone polymer gels whose rheology was qualitatively controlled for each system by proper selection of reactants and diluents concentrations. The resulting polymer-based materials exhibited solid, gel, or liquid states, depending on the crosslinking and dilution, with potential applications on vibration control, damping and energy-absorption.

The control of vibrations or switching/control of torque/force in dampers, shock absorbers, isolators and brakes are some engineering applications that can take advantage of core–shell structured magnetic carbonyl iron (CI)-poly(methyl methacrylate) (PMMA) particles fabricated via CI-seeded dispersion polymerization method, in order to enhance dispersion stability of the magnetorheological (MR) fluid when dispersed in mineral oil[35].

A series of magnetorheological lightweight gels, consisting of plastic polyurethane matrix swollen by non-volatile solvent in different weight fractions and carbonyl iron particles were prepared [36]. It was discovered that by introducing a gravity yield parameter, the

mismatch of density between the carrier medium and the iron particles, (essential for particle settling) was improved. Additionally, if the solvent content is lower than 25 wt.% or the gravity yield parameter is higher than 0.865, the polyurethane based magnetorheological gels will be stable and with no particle settling will occur. More important, on the magnetorheological gels with 30 wt.% solvent content, the apparent viscosity can increased by ≈3 orders of magnitude when the magnetic field increases from 0 to 930 mT, showing the strong potential in applications related with smart control.

The synthesis and characterization of magnetorheological elastomers with good wettability, good dispersibility, high thermo-oxidative stability, high chemical stability, and sufficient durability was presented by Cvek *et al.*[37]. This was achieved by adding carbonyl iron particles into a poly(trimethylsilyloxyethyl methacrylate) matrix, using a surface-initiated atom transfer radical polymerization technique. It was detected an increased particle mobility that has as a consequence an enhanced relative magnetorheological effect (23% higher). Such fabricated magnetoresistive lightweight material containing CI-g- poly(trimethylsilyloxyethyl methacrylate) exhibiting multifunctionality (wettability, magnetorheology and magnetostriction) can find applications both in damping systems (high thermo-oxidation stability and antiacid/corrosion properties), and also in magnetostriction based sensors (Figure 3).

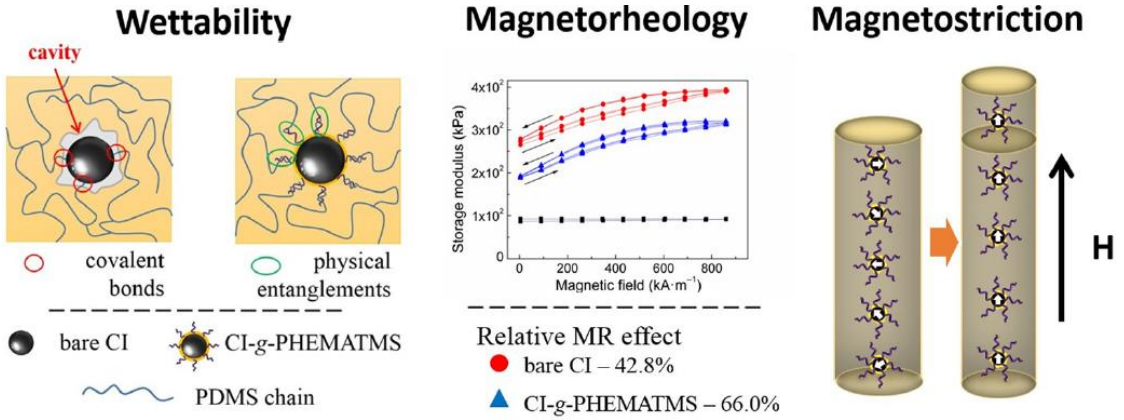

Figure 3. Schematic representation of the CI-g- poly(trimethylsilyloxyethyl methacrylate) (PHEMATMS) magnetoactive multifunctional matesrials: wettability, magnetorheology and magnetostriction. Taken with permission of[37].

Magnetorheological lightweight materials were also recently used as a new tool for controlling the performance of oil reservoirs and reducing hazardous water production. This was achieved by using polyacrylamide-coated magnetite nanoparticles synthesized using a facile one-step method. The reported strong magnetorheological responses

highlighted the feasibility of a conformance control fluid for making a solid-like structure to block the high permeable zone in oil reservoirs[38].

Magnetostrictive lightweight materials

The most cited paper regarding the application of magnetostrictive lightweight materials was published in 1999 by Lim *et al*.[39]. A high value of magnetostriction (536 ppm) at a magnetic field of 1.1 kOe, combined with a high maximum slope in the magnetostriction-applied magnetic field curve of 1.3 ppm/Oe (16.3 nm/A) was verified for the Terfenol-D composite fabricated with an average particle size of 137.5 μm, a phenol content of 3.1 wt.%, and a compaction pressure of 0.5 GPa. At the same time amorphous ribbons of an alloy with the composition $(Tb_{0.33}Fe_{0.67})_{0.98}B_{0.02}$, which exhibits good magnetostrictive properties at low magnetic fields, were bonded with a phenol-based binder to fabricate bulk composites [40]. A magnetostriction of 493 ppm (at a magnetic field of 1.1 kOe) was achieved on the lightweight composites, together with a high $d\lambda/dH$ (magnetostriction sensitivity with the applied magnetic field) of 1 $ppm.Oe^{-1}$.

As in the previous case of magnetorheological materials, gels have been also produced in order to develop magnetostrictive lightweight materials[41]. Such materials were based on silicon gel with 80 wt.% of 3.8 μm embedded carbonyl iron particles. Under a magnetic field of 0.44 T the compression modulus reaches a value of 861 kPa, which represents a 100% increase from the case at B=0 T. Such properties can offer potential applications as variable stiffness components, large strain actuators, electro-magnetically active damping elements and artificial muscles[41].

In the context of wearable Internet of Things devices, magnetostrictive wire/polymer composites were developed by embedding Fe–Co wires in an epoxy matrix (Figure 4), and their inverse magnetostrictive characteristics were evaluated. It was reported that the output voltage (≈10 mV) of this composite in the compression mode strongly increased with increasing stress-rate, opening new application perspectives for the development of lightweight, robust, and efficient magnetoactive energy harvesting devices[42].

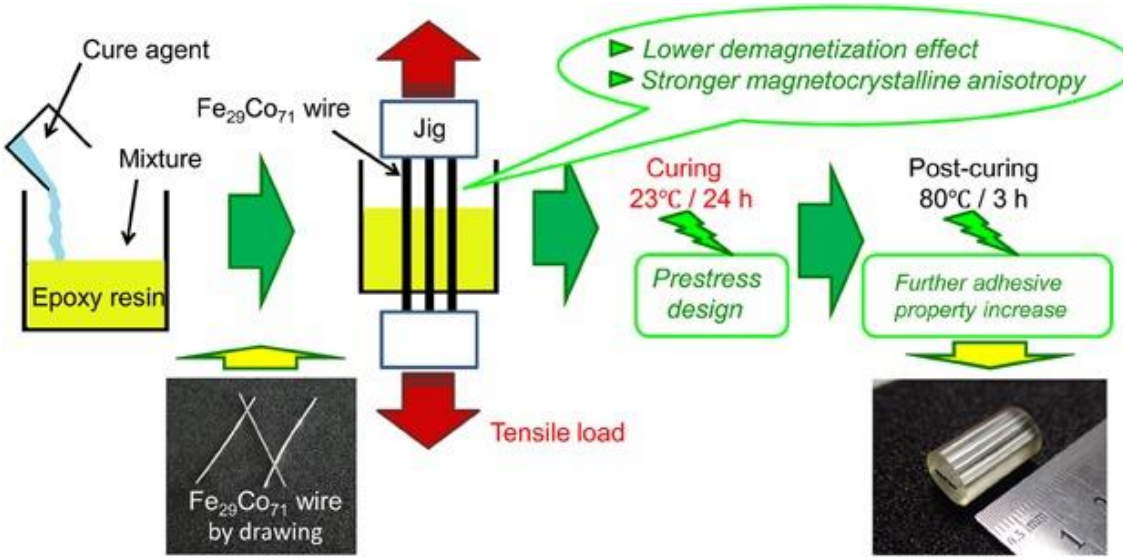

Figure 4. Schematic representation of the sample manufacturing procedure of Fe–Co wires/epoxy composites. Taken with permission from[42].

Spherical, granular and flake-type powders were also used to produce polymer-bonded composites with a Fe–Co based alloy, being observed that their magnetostrictive sensitivity at low applied fields was optimized for the composites fabricated with flake-type powders[43]. Additionally, a high magnetostriction of 200 ppm was obtained under an applied magnetic field of 4.3 kOe[43].

Other applications of magnetostrictive lightweight multifunctional materials include sensing of ultrasonic waves, actuators, biomedical materials, sensors for magnetic fields and electrical currents, vibration isolation and active control, magnetoelectric sensors and devices, stress sensing and health monitoring[44].

Magnetocaloric lightweight materials

Most of the applications developed from magnetocaloric lightweight materials have been developed over the past decade. A good example was reported by Fujita *et al.* [45] in 2009, showing the control of the magnetocaloric effect by partial substitution in itinerant-electron metamagnetic $La(Fe_xSi_{1-x})_{13}$ for applications in magnetic refrigeration.

Li et al. [46] explored the concepts of magnetocaloric effect and lower critical solution temperatures (LCST) in order to develop magnetothermally-responsive nanocarrier for magnetothermal drug release under alternating magnetic field (Figure 5)

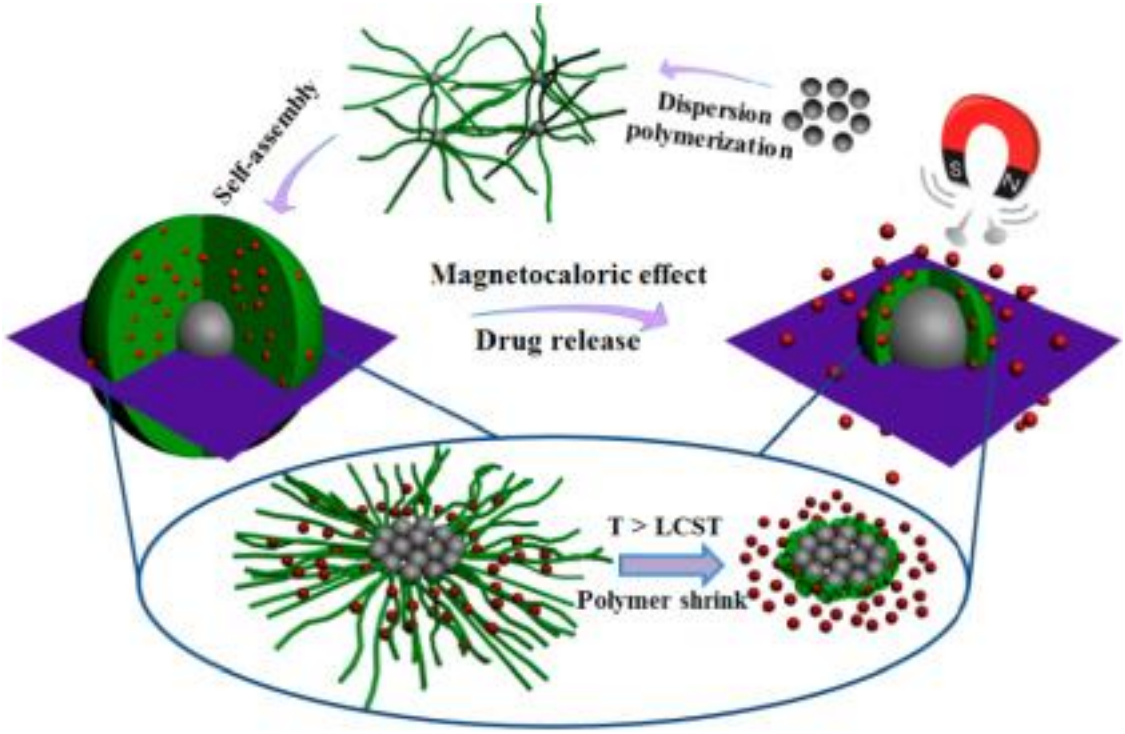

Figure 5. Schematic illustration showing the preparation process of the nanocarriers and mechanism of magnetothermal drug release. Taken with permission from [46].

For that, $Mn_{0.2}Zn_{0.8}Fe2O_4$ nanoparticles with low Curie temperature (T_C) were dispersed in a polymeric matrix consisting of N-Isopropyl acrylamide (NIPAAm) and N-hydroxymethyl acrylamide (HMAAm). A maximum self-heating temperature of 42.9 °C was achieved by optimizing the nanoparticle content (8wt.%) in the polymer matrix. Additionally, a good biocompatibility and efficient therapeutic effects in cancer treatments were observed, presenting high potential in clinical systemic therapeutics.

An innovative mode of radical polymerization (by the assembly of "host" β-cyclodextrin (CD) and "guest" N-vinylimidazole (VI)) was demonstrated by Yu *et al.*[47], which was accomplished through the magnetocaloric effect, aiming to fast fabricate (5 min) novel host–guest supramolecular gels. The resulting Fe_3O_4-doped gels were found to have self-healing properties spontaneously induced when damaged and under an applied magnetic field (450 kHz). Such strategy might open a promising way for accelerating the use of host–guest assemblies to quickly build bio-inspired robust materials.

Radulov *et al.*[48], recommended the use a particle sizes larger than 200 μm, a compaction pressure of 0.1 GPa and approx. 5 wt.% of low viscosity epoxy adhesive (silver based epoxy H27D and Epoxyharz L) $La(Fe,Mn,Si)_{13}H_x$ composite for optimized magnetocaloric properties (ΔT=4.8 K for a $\Delta\mu_0 H$=1.9 T), suitable for magnetic refrigeration at room temperature.

Multifunctional hydrogels with both vivid colour change and shrinking-swelling response (with clear and fully reversible colorimetric sensing ability in the temperature range 15–32 °C and NaCl concentration from 200 to 1200 × 10^{-3}M (ion strength), respectively) to external stimulus such as temperature, ion strength, and alternating magnetic field were produced trough magnetic assembly[49], with potential applications such as target medical therapy, tissue engineering, wound healing, and *in vivo* drug delivery studies.

Still in hydrogels, Yu *et al.*[50], demonstrated the fabrication of quadruple stimuli-responsive hydrogels with self-repair capacity via rapid interface-directed frontal polymerization. The as-prepared hydrogels, composed of 2-hydroxypropyl acrylate (HPA), 1-vinyl-2-pyrrolidinone (NVP) and graphene oxide, revealed auto-healing without the assistance of any external stimuli and the addition of graphene oxide can lead to better performance in toughness and healing efficiency (91.5%), being the magnetocaloric effect used to contribute to the ignition process in the oil phase.

Epoxy (Amerlock Sealer)-bonded La–Fe–Co–Si magnetocaloric plates were presented by Pulko etl al.[51]. The resulting assembly fabricated in the form of stacked epoxy-bonded plates was fabricated and tested on an experimental magnetic cooling device, being reported a maximum temperature span of approximately $\Delta T=10$ K under magnetic field change of $\mu_0 H=1.15$ T and a long-term cyclic loading, which is essential for its application in device applications such as magnetic refrigerators.

Polymer-based (our two-dimensional heterometallic Cu-Ln coordination polymers based on 2-methylenesuccinic acid (H_2MSA) ligand, $\{[Ln_2Cu(MSA)_4(H_2O)_6]\cdot 2H_2O\}n$(Ln = La (1); Gd (2); Tb (3); Dy (4))) composites were also developed by Li *et al.*[52], in order to develop magnetic refrigerants for low temperature applications. The existence of weak magnetic interactions (antiferromagnetic Gd···Gd and ferromagnetic Cu···Gd couplings) and a large magnetocaloric effect ($-\Delta Sm = 36.05(1)$ J K^{-1} kg^{-1}) for a $\Delta H=7T$ is reported.

4. Final remarks and future perspectives

In the last decade, the use of lightweight magnetoactive materials has grown both in volume and diversity. The materials development must meet challenging and demanding requirements. This has led to an enhancement in the understanding of the characteristics which are responsible for the individual material magnetoactive properties. In this scenario, both basic knowledge and device integration and applications have stimulated

each other so that a large volume of scientific and technological work has been performed[53].

Experimental research must explore a wider range of compounds, taking advantage of a high number of candidate lightweight materials available, with a clear predominance of polymer-based magnetoactive materials. This strategy would allow to structure the magnetic knowledge in magnetoactive materials, leading to fresh insights of the microscopic behaviour that should be determined by the strength of the exchange interactions and uniaxial anisotropy[4]. Additionally, future experiments will require considerable technical development on the fillers optimization and new composite ideas to probe magnetism quantitatively on very small length scales and in the conditions of very large demagnetization fields[4].

The *magnetic field into multifunctional lightweight materials* considerations taken in this chapter reveals that there are many different directions for future works. The promising results reported over the past years represent the starting point of a new field in which major applications/developments are expected. At this stage, the main questions that are being discussed are essentially of fundamental nature, but as soon as lightweight magnetoactive materials can be reliably produced with the use of additive manufacturing techniques, based on environmental friendly particles, polymers and solvents, as well as with low particle-to-composite magnetic energy loss, applications based on those materials will be a reality.

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