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# Magneto-Mechanical Surfaces Design

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*This article is dedicated to Prof. Eduardo Ruiz Hitzky in recognition for his work at the time of his retirement.*

magneto-mechanical

magnetic nanoparticles

magnetic polymeric composites

nano/micro-structuration

Magnetic force on the magneto-mechanical active surface

Magneto-mechanically active surfaces (MMAS) represent a new family of nano/micro-structured surfaces in which motion is induced by an external magnetic field. Under the name of “artificial cilia”, “biomimetic cilia”, “magnetic actuated patterns”, “nanopillars”, etc., published works in this area continue their quick growth in number. Notwithstanding their potential application in microfluidic, chemical sensors, catalytic processes and microelectronics to increase device perfomances, there is still a lot to do in the development of these materials. Improvement and optimization of the performance of these structures are

essential tasks in order to fulfil their complete development. Along this article, a critical review involving the main aspects in the design of the patterned nanocomposites will be presented.

## 1. Introduction

Wireless induced motion by an active flexible surface (without the necessity of any kind of engine, gear system or electrical wires) has generated great interest in microscale applications for fluidics,[1--5] electronics,[3] chemical reactors,[6,] bioengineering,[8,9] and energy storage.[7] In a more general sense, any field with interest in the motion of fluids in the microscale range can be a suitable objective for these structured active surfaces.

Nowadays, the application of an external magnetic field on a patterned superparamagnetic material (i.^e. MMAS) is the preferred option. Magnetic actuation is more reliable than electric actuation. Magnetic fields suffer less interferences as they are no affected by surface charges, pH, ionic concentration or temperature.[211] In addition, there is a wide range of tunable parameters (rigidity, viscous coefficient, density, saturation magnetization and magnetic susceptibility) as a consequence of the different combinations of superparamagnetic particles and polymeric matrix which compose the MMAS.

The mechanical response of MMAS is conditioned by the intensity of the magnetic force. Its intensity is directly proportional to the magnetic susceptibility ($\chi_m$) of the MMAS. For high values of magnetic field intensity (H), the magnetization of the magnetic element becomes equal to the magnetization saturation ($M_s$). Usually, these surfaces are excited with high enough intensity to reach the saturation level. In consequence, $M_s$ takes a highlighted position against the magnetic susceptibility in the material selection. In addition, if a high frequency movement is required the $\chi_m$ will be an important property to achieve the desired velocity in the mechanical response.

Once the magnetic force is applied, a movement in response to that force will be observed in the patterned magnetic material. The rigidity and viscous coefficient of the material will be part of the mechanical impedance against this force. The interaction with the surrounded fluid is also a crucial aspect of the final mechanical response.

In addition to the materials selection, the fabrication method also takes a crucial role in the final performance of the MMAS. The three-dimensional pattern created on the surface is the main responsible of the interaction with the surrounding fluid. Its geometry constricts the mechanical response of the structure as well as the fluid pressure field generated by the active surface. This nano/micro-structuration of the surface can be obtained by a large number of different techniques. They can be classified in three categories: self-assembly (SA), mould casting (MC), and direct manufacturing (DM). In SA methods a self-ordering process is initiated by external conditions. If a casting or pouring process is part of the fabrication, that procedure will be classified as MC. Finally, the DM techniques are those in which the surface structuration is achieved by the selective elimination, deposition, heating or deformation of the starting material.

Although some laboratories have been working on MMAS's since the early 2000s there is still a great gap between the technology requirements and the current performance of these MMAS devices. In response to the interest of scientific community and industry, the main parameters involved in the design of MMAS have been compiled and described.

## 2. Magnetic Materials for Magneto-Mechanical Actuation

Structured surfaces are a powerful solution employed in nature for a multiple variety of different problems. The bidimensional repetition of a specific pattern allows a high level of interaction with the surrounding media. The control of the surface geometry implies the control of that interaction. Incorporating the last advances in microfabrication, patterned nanocomposites have been used for the fabrication of the MMAS. Nanocomposites are dispersions of magnetic nanoparticles (MNP) in a typically polymeric matrix. The range of available MNPs is in permanent growth, from new rare earth magnetic compositions[9,12] to novel superparamagnetic particles with functional coatings,[13--15] or even particle clusters of controlled size and multifunctionality[16,17] Table^^1<tabr1/o> summarizes some of the most common magnetic nanoparticles employed for this purpose.

In general, the highest possible magnetization of saturation is desired. This value will be the limit of the magnetization intensity and will define the maximum force that can be

applied by an external magnetic field. The size of the particle should be small enough to present superparamagnetic behavior and to be equally well dispersed in the MMAS smallest feature.

Magnetic susceptibility ($\chi_m$), i.^e. the ratio between the intensity of the applied magnetic field (H) and the magnetization of the material (M), is in direct relation with the response time of the material. A higher $\chi_m$ implies a bigger magnetization at the same intensity of external magnetic field (H). Therefore, with a high susceptibility the material will be able to "follow" (to realign its magnetization) a high frequency excitation and this parameter should also be included in the magnetic load selection analysis. Some reference data (relation with temperature, quantitative values, methods of measure, etc.) can be found in literature.[23-25]

The final magnetic response of the material is strongly conditioned by the magnetic load distribution. Some investigators are currently exploring the possibilities of controlling the magnetic response through the control of the magnetic load distribution. Thereby, the agglomeration mechanics of this magnetic particles becomes another point of interest for the MMAS design.[26,27]

<?IMA tlsb=-2%?>Turning the focus on the matrix in which the particles will be dispersed, some mechanical aspects must be discussed. First of all, a flexible enough material is required to be deformed by the magnetic force action. However, the matrix also has to be rigid enough to pump the surrounding fluid. Therefore a big distinction between applications in air (negligible friction coefficient) and devices in liquids should be considered. Young's modulus, density and the viscous coefficient will be the key parameters in the matrix selection and modeling.

Young's modulus for active surfaces in contact with water should range between 0.1^^MPa (high frequency motion, low pressure generation) and 3^^GPa (low frequency motion, high pressure generation).[2,28] These values are useful for the majority of the microfluidic and biomedical setups since, in both cases, water based solutions are used.

Regarding organic solvents, the viscosity values are not so different to produce a change in the selection criteria.

Weight of the structures will begin to gain relevance in the same way as the importance of gravity force in the final device. In general, the magnitude of these forces is low enough in comparison to magnetic or friction forces, therefore the specific gravity usually plays a secondary role in the matrix (and particles) selection.

Another relevant criterion is the friction coefficient of the cured composite, i.^e. its friction with the surrounding media. If the interaction is too strong, not only the pressure applied to the fluid would be bigger but also the viscous drag. On the other hand, if the interaction is too low it will be quite difficult to reach high pressure values.[2]

Usually, the selected material might be immersed in a moving fluid that, depending on the application, could be more or less chemically aggressive: a good chemical resistance must also be considered.[29] In the particular case of biomedical applications, the developed surfaces, besides being as chemical inert as possible, should be biocompatible.[30]

Based on the mechanical-chemical requirements, a polymer matrix stands as the best option. Particularly, elastomers (e.^g. polydimethylsiloxane, PDMS) are the preferred choice because of their great capacity of elastic deformation. Despite of this, some thermoplastics and thermosets (e.^g. PMMA, PU, PS, Epoxy, etc.) can be found in the literature acting as MMAS matrix.[2,28]

Processing of the polymeric composite is a key aspect to achieve the desired performance. The three main fabrication methods are: melt-mixing, in^^situ polymerization and solution processing.

In melt-mixing processes a thermoplastic, previously loaded with nanoparticles (NPL), is heated and then mechanically mixed. Common fabrication techniques are extrusion, injection molding and blow molding.[31-33] If the viscosity of the mix is too high for achieving a good homogeneity, in^^situ polymerization can improve the dispersion and integration of the NPL in the matrix.[32] NPL are dispersed in the prepolymer solution before the polymerization reaction begins. This process can be applied to elastomers and thermoset

polymers, which cannot be processed by melt-mixing. The last category, solution processing, takes advantages of the previous dispersion of both components in a proper solvent. The low viscosity solution allows the use of more effective dispersion techniques such as high power ultrasound. As disadvantage, the solvent has to be eliminated after the mix is complete.[33]

Another fundamental aspect of the optimum processing of the nanocomposite is the surface modification of nanoparticles. The functionalization of the nanoparticles surface allows a better interaction with the polymer matrix along with the tuning of the nanocomposite mechanical rigidity,[34,35] rheological properties,[36] and even the glass transition temperature.[37]

## 3. MMAS Structuration

Structured surfaces offer the possibility of increasing the contact surface between the composite and the fluid. Moreover, its geometry can modify the mechanical response to the magnetic excitation. As consequence, MMAS patterning methods play a position of privilege in the final design of the device. An overview of the accessible current procedures for the preparation of these patterned surfaces is presented in Table^^2<tabr2/u>.

“Self-Assembly” (SA) methods are those in which the material is structured in a nano/micro scale range due to the action of an external force which initiate the local self-ordering process. Therefore, there is no need of any rigid solid to shape the material with its geometrical restrictions. Three main SA techniques will be discussed: electrospinning, molecular self-assembly, and magnetic self-assembly.[40,44]

### 3.1. Electrospinning

It is one of the most common techniques for the fabrication of large quantities of fibers in the nano- and micro-scale ranges.[40] In this technique, an electric field is used as the external force that will produce the self-assembling of the material. The polymer solution is dropped from a millimeter-sized capillary and exposed to an electric field. The applied voltage can decrease around 4--5^^orders the fluid jet diameter.[41] In the last step, the jet is solidified and collected in an electrode. It is able to produce different kinds of filamentous

morphologies (Figure^^1<figr1/u>) with diameter sizes down to a few nanometers.[40] However, the control of a regular diameter size below the 100^^nm requires a single jet state, i.^e. there is not splitting,[41] and an optimization process of the electrospinning parameters. Two of the more significant characteristics, regarding to fiber diameter, are the viscosity of the polymer solution (the higher concentration of polymer, the higher viscosity and therefore, bigger fiber diameter) and the applied voltage (higher voltage will increase the quantity of fluid in the jet and therefore, bigger fiber diameter will be spun).[40,41,55]

### 3.2. Molecular Self-Assembly

It comprises all the structuration techniques driven by secondary forces, such as hydrogen bonds, van der Waals, electrostatic interactions, or hydrophobic effect.[40] Depending on the chosen system (initiator molecule and self-assembly developer) the minimum diameter size can reach values lower than 5^^nm.[40,44] Usually, it is difficult to find a magnetic molecule able to reproduce a molecular SA process. One possibility is to arrange the magnetic nanoparticles inside a nanotube as it was already published by Yan et^^al.[70]

Once the magnetic filament is finished, it has to be attached to a substrate in order to obtain the final desired MMAS. However, there are already reported methods in which the 1D structure is directly assembled on the surface. For example, Massey et^^al.[71] developed a method to create self-assembled nanoscopic micelle arrays of poly (ferrocenyldimethylsilane-*b*-dimethyl-siloxane), which could act as precursors of MMAS (so the filaments will grow directly on the surface).

### 3.3. Magnetic Self-Assembly

Magnetic SA involves the use of a magnetic field to fix the desired geometry in the material. In this method, magnetite polymeric beads[47--49] and magnetite emulsion droplets[47] have been employed as precursor materials for the creation of flexible chains. The general procedure is straightforward: spreading the particle dispersion in the desired container (usually two flat surfaces), applying the magnetic field (magnetic particles will align with the external field), and fixing the chain morphology. The bonding between particles can consist of a simple polymerization of some compatible coating substance. Another possibility is the

modification of the ionic interactions to physically aggregate the particles by van der Waals forces.[47]

Self-assembly methods in which a rigid solid imposing its geometrical constrictions is not required has been presented hitherto. When a mould is employed, the fabrication method is classified as “Template Casting” or “Mould Casting” (MC). By using these preparation procedures for the MMAS fabrication, a magnetic nanocomposite is poured into a mould. Attending to the differences in material preparation, material pouring and mould fabrication, three main groups of MC fabrication techniques can be found: porous template casting, photolithography mould casting, and additive-manufacturing mould casting.[45]

### 3.4. Porous Template Casting

The casting of fiber-like structures is carried out through the use of a porous layer. The thickness of this layer would be the total length of the filaments and the porous diameter would be the filament diameter, since the magneto-composite is cured inside the porous of the mould. Characteristic ratios (length/diameter) up to five[56,72,73] and fibers diameters around 20^^nm[53,55] have been obtained in air with low collapse probability. For higher ratios, collapse because of contact between each other or with the ground usually appears due to the evaporation of the solvent. The use of a suitable solvent, which can be a strong base for alumina templates, or an organic solvent for polymeric templates, is a price to pay for the elimination of the solid template.[8,73]

The preservation of the pattern after the elimination of the porous template layer, along with the total consumed time in the different steps, are the main disadvantages of this method. On the other hand, high accurate and regular structures can be obtained if the demoulding stage is successfully done.

### 3.5. Photolithography

It is the most common lithographic process used in the fabrication of moulds for magneto-mechanical structured surfaces. Typically, the same accuracy and metrology quality as porous template casting are obtained while the demoulding process becomes easier. In this

method a photoresin is exposed to UV-light following a specific pattern in order to fabricate the mould. The non-exposed volume of polymer is removed from the substrate by the action of an organic solvent (developer). After this step, a post-curing stage is done to reach the final mechanical strength value. In this mould the magnetic nanocomposite is poured and cured. During the polymerization inside the mould, the magnetic material will obtain the final shape of the MMAS.

The resolution limit is imposed by the photomask used in the UV exposition stage (Figure^^2<figr2/u>), which can have problems in patterns with features sizes below 20^^nm. There are several examples in the literature employing different polymers, nanoparticles, and some variations in the mould fabrication process.[38,45,57,74]

### 3.6. Additive Manufacturing (AM) Mould Casting

The recent advances in AM techniques have made possible their use for MMAS mould fabrication. For instance, the two-photon stereolithography, which can be seen as a 3D photolithography process[58--61] may reach spatial resolutions under 30^^nm.[60] Other more popular AM techniques, like selective laser sintering or 3D printing, work with resolutions limits around 50^^μm.[75] Despite not all the AM options can reach submicron features, micrometrical accuracy can be enough for a wide range of applications. However, cost issues are a big drawback for their use. The fabrication of a mould by AM is only justified in the case of a real complex geometry. This capacity of geometrical freedom is the main advantage of AM techniques.

### 3.7. Imprinting

The family of imprinting techniques comprises all those methods in which a pattern is fixed on a substrate material via direct (physical) contact between a stamp and the substrate. Nanoimprinting lithography (NIL) is the highest resolution technique in this area.[45,76] There are two variations: thermal NIL and UV-NIL. In the first one a hot mould is pressed against the substrate, which is then cooled down to preserve the pattern morphology.[62,64] In the second one the mould is pressed at room temperature against a photosensitive liquid material, meanwhile it is exposed to the UV-light in order to fix the pattern. The usual feature limit of

this technique is around 5^^nm, although there are some published works in which 2^^nm features have been reported.[77] An interesting use of NIL for the fabrication of different filaments tips is reported by Jiand et^^al.[8] Furthermore, Wang et^^al. developed a high velocity production technique (decreasing the resolution level) named as “the continuous roll pulling method”.[78]

### 3.8. Direct Deposition

Different approaches in direct deposition techniques have been successfully used for the fabrication of nanostructures. Robotic deposition,[45] 3D printing,[79] additive manufacturing (AM),[75] or rapid prototyping (RP)[80] are the most common names chosen by the industry and research laboratories for the different fabrication techniques based on the 3D direct deposition. The first step is to have a computer-aided design (CAD) model of the desired object. To fabricate the model, the precursor material can be deposited from the melt or it may be consolidated through several physical-chemical processes: sintering, polymerization, etc. As with the AM for mould casting, the freedom of geometry is its main advantage and the fabrication cost its main disadvantage. There are other direct deposition techniques, like the recently developed 3D-bioprinting, in which a submicron resolution is combined with the possibility of fabricating layers alternating different materials.[68,69,81]

The Dip-Pen Nanolithography (DPN) is located outside layer by layer fabrication techniques but it is a direct deposition method. In DPN an atomic force microscope tip is used for the direct deposition[65--67] or for the local reaction of a target precursor.[82]

## 4. Characterization Methods and MMAS Design Optimization

The quantification of the physicochemical properties of the structured nanocomposite and its components (nanoparticles and the matrix) is an essential stage in which is based the complete design of the magneto-actuated surface. The experiments needed for a complete description of its behaviour will be cited below in relation with the quantification feature in which it is involved.

### 4.1. Geometrical Characterization

The analysis of the characteristic lengths and the morphology of the surface pattern and motif is one of the most critical and time consuming characterization task of the nanocomposite.

Through the analysis of nano/micrographies, the complete geometry of the system can be characterized. It also provides the required information for the study of the distribution of the magnetic reinforcement. Optical microscopy,[20,83--85] scanning electron microscopy (SEM),[8,20,56] transmission electron microscopy (TEM),[20,86,87] and atomic force microscopy (AFM)[34,88,89] are the most common techniques for this purpose.

Some features, as the particle size, can be also measured by dynamic light scattering (DLS),[90--92] x-ray diffraction (XRD),[93,23,94] or even vibrating sample magnetometer (VSM).[94,95] The previous cited techniques also give information about the particle clusters formation, colloidal stability, crystalline structure, magnetic behaviour, etc.

### 4.2. Coating Characterization

The control of the distribution of nanoparticles inside the matrix is one of the most compromising aspects of the MMAS fabrication. There is a notable difference in the magnetic response of a homogeneous distribution of magnetic nanoparticles and another one in which there is a strong gradient in some spatial direction. Therefore, in an attempt to synthesize smaller and narrow sized distributions of desired morphologies, magnetic nanoparticles are usually coated with a fatty acid or some other surfactant.

The particle coating efficiency can be analyzed by means of infrared spectroscopy. Fourier transform infrared spectroscopy is the most reliable and used technique for this analysis.[96--98]

### 4.3. Magnetism

Magnetization curves of nanoparticles and magnetic composites are required in order to obtain their response against an external magnetic field. This information can be obtained through vibrating sample magnetometer (VSM)[14,15,19] or superconduc-ting quantum interference device magnetometer (SQID) experiments.[13,34,93] Magnetization *versus* external

magnetic field (MH) graphs, along with zero field cooling (ZFC) and field cooling (FC) plots, are obtained. Through the analysis of these curves, the superparamagnetic behaviour is checked and the magnetic properties are quantified.

In the case of a mixture of iron oxides, there is also the possibility of quantifying the amount of magnetite in the sample. The Verwey transition[99] is a visible phenomenon in the ZFC-FC plot as a step in the magnetization curve against temperature. Verwey transition for a 100^% pure magnetite powder takes place around 125^^K. If the sample has a lower percentage of magnetite, the Verwey temperature ($T_V$) would be lower allowing thus magnetite quantification. In Figure^^3<figr3/u> the ZFC and FC plots of a magnetite sample with a $T_V$ of 121^^K (0.35^% of deviation from pure magnetite) is presented. .[100--102]

For the characterization of the external magnetic field applied to the surface, the density of magnetic flux may be measured using a gaussmeter.[39,103]

### 4.4. Mechanical and Thermal Response

Young's modulus, strength, and shear modulus among other parameters are obtained from mechanical tests: tensile, three-point bending, compression, and hardness are the most common ones.[104] Rheology and Dynamic mechanical thermal analysis (DMTA) are usually employed for the measurement of the viscoelastic parameters: storage modulus, loss modulus, and loss tangent;[105--110] DMTA also gives information about thermal transitions such as glass transition temperature, which can be also measured through differential scanning calorimetry DSC.[37,109] The later can be used to obtain information about the residual polymerization heat, which may be useful to determine the extent of the polymerization process.

### 4.5. MMAS Design Optimization

The optimization of the materials, MMAS fabrication and magnetic actuation, is a complex task in which computer simulation can be a very useful tool. Finite elements based programs, such as Comsol Multiphysics,[111--113] computer assisted design,[114] mathematics programs,[52] and other computing tools, have been used for the magnetic force calculation in the structures along with the mechanical-fluid stress and pressure simulations. The good use

of those models is translated into shorter times in the materials selection process, an effective optimization of the surface pattern, as well as a better external magnetic excitation design. An example of a model for the calculation of the bending angle of a magnetic cilia can be found in the work of Evans et^^al.[52]

## 5. Conclusions

The industrial and scientific interest in MMAS is still growing. The materials and methods employed need to be more efficient, and moreover, to be able to operate in the submicron scale.

A compilation of the key parameters of the MMA surface fabrication and design is provided in this article. A complete description of the most interesting materials, fabrication techniques and analysis methods that are being used or that can be employed in the development of MMA surfaces has been concisely presented.

As it has been exposed, there is a bright future for magnetic actuation in microfluidics, biomedical an electronic applications. Based in the number of published articles, in the next years, the popularity of MMAS will keep growing.

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Table^^1 Magnetic Nanoparticles.<W=1>

| Composition | Sat. Mag. $M_s$ [emu/g][a] | Size range [nm] | Ref. |
|---|---|---|---|
| Pure Fe | 190--220 | <20.0 | [12,18] |
| $Fe_3O_4$ | 58.6--88 | 7.8--14.0 | [19,20] |
| $Fe_2O_3$ | 48--72 | 2.7--8.7 | [12,21] |
| Ni-NiO | 25--58 | 2.2--3.2 | [22] |
| $CoFe_2O_4$ | 44 | 60.0 | [15] |

[a] Saturation of magnetization per unit of mass.

Table^^2 MMA surfaces structuration methods.

| Family | Name | Morphology[a] | Size[b] | Ref. |
|---|---|---|---|---|
| SA[c] | Electrospinning | Fibers | 50^^nm | [38--43] |
| SA | Molecular | Fibers | 1--2^^nm | [40,43--46] |
| SA | Magnetic assisted | Fibers | 500^^nm | [2,47--51] |
| MC[d] | Porous template casting | Fibers | 5^^nm | [35,43,52--55] |
| MC | Photolithography mould casting | Free cross section fibers | 30^^nm | [45,56,57] |
| MC | Additive Manufacturing MC | Free cross section fibers | 30^^nm | [58--61] |
| DM[e] | Imprinting techniques | Free cross section fibers | 5^^nm | [8,56,62--64] |
| DM | Direct deposition tecniques | Free cross section fibers | 1^^μm | [45,65--69] |

(a) Morphology of the structured surface: a distinction between the free cross section shape fibers and those with limitations is presented.

(b) Minimum size resolution of the structures which compose the texturized surface.

(c) Self-Assembly (SA) family of fabrication methods.

(d) Mould Casting (MC) family of fabrication methods.

(e) Direct Manufacturing (DM) family of fabrication methods.

Figure^^1 Electrospinning morphologies. (a) Circular cross section fibers. (b) Flat fibers. (c) Porous fibers. (d) Spindle-type disturbances fibers. (e) Fractal shape fibers. (f) “Barbed” nanofibers. Reproduced with permission from ref.[40]

Figure^^2 Photolithography procedure scheme. (a) Spin coating of the photoresin on the silicon wafer surface. (b) Soft-Bake. (c) UV-light exposure. (d) Post exposure bake. (e) Development in ultrasonic bath. (f) Hard-Bake. (g) Photoresin final mould on silicon wafer.

Figure^^3 Verwey transition in a ZFC/FC plot of magnetite under an external field of H=10 Oe. Reproduced with permission from ref.[102]