

An overview on nanomaterials with magnetic properties used in the textile sector

DOI: 10.35530/IT.073.03.202176

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ABSTRACT – REZUMAT

An overview on nanomaterials with magnetic properties used in the textile sector

Nowadays, the world of materials around us has reached a new step in evolution. New materials with amazing properties and functions are innovated in our attempt to make our lives easier and turn the world into a better place for the future. The current generation of textile materials is based on innovative technologies and modern fibres, making them smarter and more technical than ever, giving to people the possibility to adapt to the conditions and evolution of this century.

Nanotechnology is a big contributor to the wide expansion of textile applications through the offered benefits and functionalities. It is used for the development of fabrics that are stronger, lighter, more durable or among others, capable of self-cleaning, self-repairing or resisting wrinkling.

The addition of magnetic nanomaterials, such as iron oxide or nanoparticles to textiles, either as coatings or as composite materials or as unique elements in industrial processes (e.g., in the dyeing process, in the wastewater treatment process), opens new possibilities for the improvement and future development of the textile sector.

This paper presents a summary of some of the latest developments regarding the types of magnetic nanomaterials, their functions, and applications in the textile industry and also the technologies used in different studies to manufacture textile materials with magnetic properties. Finally, the utility of the electrospinning technology to produce materials with full magnetic properties at the nano level and their usefulness in a series of applications proposed by researchers is demonstrated.

Keywords: magnetic nanoparticles, functionalities, electrospinning, nanofibers, advanced materials

O privire de ansamblu asupra nanomaterialelor cu proprietăți magnetice utilizate în sectorul textil

În prezent, lumea materialelor din jurul nostru a atins un nou pas în evoluție. Noi materiale cu proprietăți și funcții uimitoare sunt inovate în încercarea noastră de a ne face viața mai ușoară și de a transforma lumea într-un loc mai bun pentru viitor. Actuala generație de materiale textile se bazează pe tehnologii inovatoare și fibre moderne, făcându-le mai inteligente și mai tehnice ca niciodată, oferind oamenilor posibilitatea de a se adapta la condițiile și evoluția acestui secol.

Nanotehnologia este un important contribuitor pentru extinderea largă a aplicațiilor textile prin beneficiile și funcționalitățile oferite. Este folosită pentru dezvoltarea de țesături mai rezistente, mai ușoare, mai durabile sau, printre altele, capabile să se autocurețe, să se autorepare sau să reziste șifonării.

Adăugarea de nanomateriale magnetice, cum ar fi nanoparticulele de oxid de fier în textile, fie ca acoperiri, fie ca materiale compozite sau ca elemente unice în procesele industriei (de exemplu, în procesul de vopsire, în procesul de tratare a apei uzate), deschide noi posibilități pentru îmbunătățirea și dezvoltarea viitoare a sectorului textil.

În această lucrare, este prezentat un rezumat la unele dintre cele mai recente dezvoltări cu privire la tipurile de nanomateriale magnetice, funcțiile lor și aplicațiile din industria textilă, precum și tehnologiile utilizate în diferite studii pentru fabricarea materialelor textile cu proprietăți magnetice. În cele din urmă, este demonstrată utilitatea tehnologiei de electrofilare pentru a produce în întregime materiale cu proprietăți magnetice la nivel nano și utilitatea acestora într-o serie de aplicații propuse de cercetători.

Cuvinte-cheie: nanoparticule magnetice, funcționalități, electrofilare, nanofibre, materiale avansate

INTRODUCTION

Nanotechnology offers the textile field a huge potential for development, helping it to acquire great improvement and performance. The special properties of nanomaterials can provide high durable functions for fabrics and also efficiency and economic benefits. Nanotechnology can act in two ways on textiles, either the existing functionality of the textiles is improved or, entirely new properties or a combination of different functions can be attributed to them [1].

Special attention was directed to the nanoparticles (NP) of various complex topologies (e.g., nanorods, nanowires, nanotubes, nanocubes, etc.) that can be used as coatings on different textile structures or distributed in polymer matrices that are further processed into textiles. These NP can enhance the mechanical properties like toughness, abrasion resistance or tensile strength of the fabrics and [2] very importantly, do not affect the breathability or hand feel of the fabrics [3].

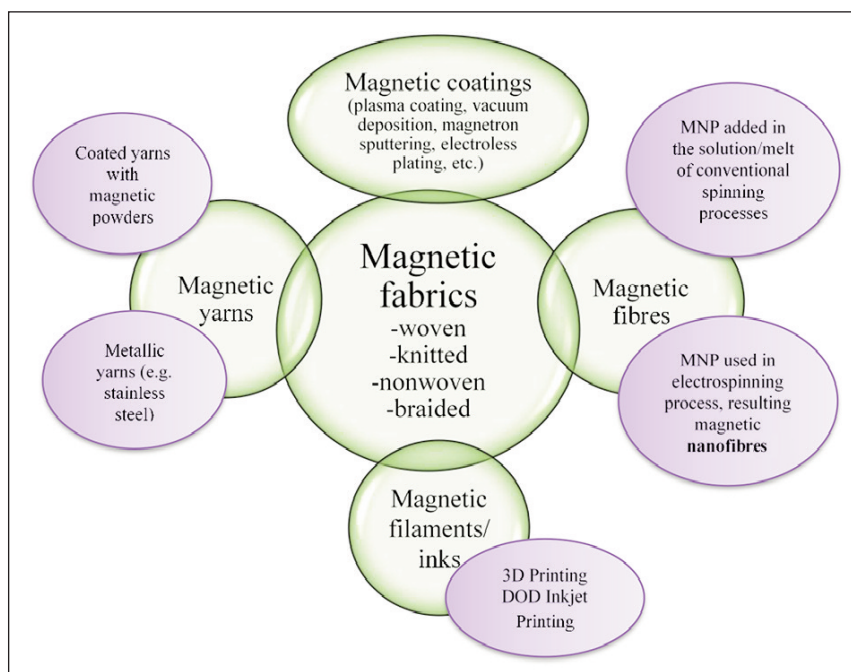


Fig. 1. Different methods for manufacturing textiles with magnetic properties

Magnetic nanoparticles (MNP) are a special class of nanoparticles that are based on pure metals, metal oxides, bi-component alloys or composites (metal core – protective metallic or non-metallic shell) and pose very impressive properties that offer the possibility to connect the textile field with many others like medical, energy, environment, agriculture, electro-technical (actuators, EMI shields, memory devices), safety and defence sectors, and so on.

It is well known that the dying process of the textiles generates a strong negative impact on natural water pollution, people's health, the environment and ecosystems, thus a special contribution of these MNP to the textile industry is related to their ability to be used efficiently in the removal of harmful organic compounds such as dyes found in industrial wastewater.

There are several different approaches involved in obtaining textiles materials (woven, knitted, nonwoven) with magnetic properties, as shown in figure 1. This research paper focuses on summarizing and making a short presentation on the fundamentals reported recently on different types of magnetic nanoparticles and their properties, the involvement of these nanomaterials with magnetic properties in the field of textiles, the generated properties, and methods of obtaining textile materials with magnetic properties.

NANOPARTICLES WITH MAGNETIC PROPERTIES

Nanoparticles (NPs) present interest because represent a bridge between bulk materials and molecules and structures at the atomic level [4]. Nanoparticles are quasi-dimensional (0D) elements with an order of

magnitude between 1 and 100 nm. They can be synthesized from a number of materials, such as metals, metal oxides, carbon or polymers.

Nanoparticles with magnetic properties (MNPs) are a class of nanoparticles that can be manipulated using magnetic fields. They possess several unique properties and configurations such as large surface sizes, shape and size-dependent catalytic properties, superparamagnetic behaviour, small size, biocompatibility, the possibility of chemical modification of their surface and a high surface-to-volume ratio, which leads to different better properties compared to bulk materials [5]. Different factors are contributing to the magnetic properties of

nanoparticles, including chemical composition, type of crystal lattice and its degree of deficiency, particle size and shape, morphology, particle interaction with the environment (the matrix) and adjacent particles (the magnetic interaction between particles) [6].

In fact, it should be noted that three major contributions, sometimes interconnected, offer the specific and remarkable properties of magnetic nanoparticle systems: intrinsic properties of components, size effects and interphase or intercomponents interactions [7].

Superparamagnetism is an important property of magnetic nanomaterials, which occurs in nanoparticles composed of a single magnetic domain. This is possible when their diameter is between 3 nm and 50 nm, according to the material [8]. This property prevents the agglomeration of nanoparticles [9], a phenomenon that causes poor corrosion resistance, high solubility and phase change of nanomaterials, and further damage. The smaller the particle size, the slower the agglomeration phenomenon will take place, but they do not always retain their original size after their synthesis, often requiring the encapsulation of nanoparticles [10].

This step of NPs encapsulation is designed not only to prevent agglomeration but also to prevent oxidation, corrosion, toxicity, and to improve the stability and solubility of nanoparticles, or to increase the biocompatibility and specificity of the target, characteristics generally required in the case of medical applications [11].

Therefore, they can be encapsulated in either magnetic or non-magnetic materials to: stabilize them chemically and colloidal, provide a modified surface that can be further functionalized, or modify the magnetic properties [12].

Types of magnetic nanoparticles (MNP)

Pure metals

Most magnetic materials used in current technology are either metals or metal oxides. Iron (Fe), nickel (Ni) and cobalt (Co) are the most important metallic MNPs because they present high magnetic properties and a good capacity to control and adjust their size, composition and shape [13]. However, the biggest drawback they face is the fact that they are not stable in air and are slightly oxidized, resulting in the change or loss (complete or partial) of their magnetization [14].

Metal oxides

The magnetic properties of metal nanoparticles are dependent on the degree of oxidation of the surface. Therefore, true knowledge of the degree of oxidation of nanoparticles is necessary to assess the magnetic characteristics of the materials obtained.

Among the most important and used oxides with magnetic properties are iron oxides, such as hematite (Fe_2O_3), magnetite (Fe_3O_4), ferrites (ex. MnFe_2O_4 , MgFe_2O_4 , $\text{SrFe}_{12}\text{O}_{19}$, GdFeO_4), wustite (FeO). Iron oxides have received increasing attention due to their significant advantages contributing to the expansion of their applications. Magnetic iron oxide nanoparticles have low production costs, have sufficient physical and chemical stability, as well as biocompatibility and are environmentally safe [15].

Magnetic bi-component alloys (Fe-Co, Fe-Ni, Fe-Pt, Co-Pt)

The magnetic properties of these metals improve considerably when mixed to form alloys, especially Fe-Co nanoparticles attracting considerable attention [16, 17, 18]. The use of bimetallic NPs is of great interest due to their increased stability, oxidation inhibition and increased reactivity [19].

Composites

Because stability is a crucial requirement when exposed to air, especially in the case of pure metal particles, the metal core of magnetic nanoparticles can be passivated by light oxidation, surfactants, polymers, precious metals, silica or carbon for various applications. These coatings not only help to protect the core but are also used as functionalizers; The magnetic properties of these structures can be controlled by varying the relative concentrations of the used magnetic nanoparticles and coatings [19, 20].

Morphologies of magnetic nanoparticles

In general, nanoparticles are considered spherical, isometric materials, but they can never exist in practice because they are crystalline and have preferential crystallographic planes on the surface. Research has revealed other types of nanoparticle structures, anisometric, created by different methods: NP in the form of cubes, nanoworms, nanostars, nanotrapods, nanoprisms, nanotubes, nanowires, elongated NP (spindles, nanobelts, nanorods, nanowhiskers, nanorice), disks, nanoflowers, hollow structures [21–26].

The shape strongly influences both the magnetic properties and the surface chemistry of the MNPs. For example, MNP that possess different shapes can be used in sensors development for three essential purposes: improving the magnetic response time, adjusting the anisotropy-controlled signal, or creating additional functionality [27].

Dimensions

The properties of nanoscale materials are unusual compared to the properties of bulk materials. For example, transparency, colour, or melting point may differ significantly from the properties of the latter. Gold nanoparticles are red at the nanoscale, not yellow, as we are used to at the macro scale. From the perspective of magnetic NP dimensions, they can be classified as follows:

- Large particles (>30 nm): particles around the monodomain-multidomain dimension, with high remanence and coercivity;
- Small particles: superparamagnetic nanoparticles, without magnetic remanence and no coercivity.
- Very small particles (<2 nm) known as clusters [12].

APPLICATIONS OF MAGNETIC NANOPARTICLES IN THE TEXTILE INDUSTRY

Magnetic nanoparticles have a high potential to be used in the textile industry. Magnetic nanoparticles can be used either alone or as coatings on the surface of the textile or as basic elements in composite materials by embedding them in suitable matrices even during spinning processes. The most important uses of these nanoparticles in the textile industry are discussed below.

Textile actuators based on magnetic nanoparticles

The most recent and essential development of the textile field is the creation of intelligent textile systems capable to react to stimuli of different origins (actuators) with the help of stimuli-responsive materials like shape-memory polymers (SMP), electroactive polymers (EAP), electrochromic materials, or with the help of magnetic nanoparticles.

With great potential in conductive devices for wearable electronics, strain sensors, smart actuators or bioelectrodes, graphene oxide sheets grafted with Fe_3O_4 nanoparticles were used by a group of scientists to coat a cellulose woven fabric through a multi-dipping-drying treatment. The graphene oxide sheets were assembled layer-by-layer magnetic-field-induced onto the surface of cellulose fabrics many times. The well-aligned alternating ordered structures showed good thermal and electrical conductivity of coated cellulose fabrics and also excellent water laundering durability during tests [28].

Furthermore, cellulose nanocrystals decorated with magnetic nanoparticles reinforced in fibrous scaffolds have recently been used to make actuators with a role in the functional regeneration of tendons in

response to magnetic stimulation [29]. Also, nanoparticles like CoFe_2O_4 have been used in conjunction with PVDF, for the production of electrospun magnetic nanofibers useful in actuation systems, biosensors or tissue engineering systems due to their magneto-electric properties [30].

Electronic devices have become essential components that can be integrated into the structure of textiles to create smart textiles that can improve the quality of daily life. However, a key factor for user acceptance of these wearable devices is the comfort appropriate to the type of physical demands we are exposed to. In addition, a still existing problem related to the use of nanotechnology and wearable smart fabrics is the stability in time, as clothes need to be periodically washed and electronics despise water. Moreover, nanomaterials can be transferred in this process to the wastewater and further in the environment, affecting, in the end, people's lives.

Electromagnetic interference (EMI) shielding

Another use of magnetic nanoparticles is in electromagnetic wave control systems, an important action because electromagnetic interference (EMI) can disrupt electronic devices, equipment and systems used in critical areas such as telecommunications, industry, defence, security, military and medicine and also affect our daily lives by utilising the wifi, mobile phone, computers, tablets, television, electric network, etc. [31]. By simply applying metals to the surface of textiles, structures with electrical and magnetic properties can be created to prevent electromagnetic noise through different methods. Recently, nickel nanoparticles have been deposited on the surface of a polyester material by a less expensive and simple method, called "click finishing". The results showed a considerable improvement in magnetic properties and shielding studies on a frequency range of 8.4–12.4 GHz indicated a 100% shielding for nickel-treated fabric [32].

Water treatment and catalysis

The textile industry uses huge amounts of dye and water to colour textiles, and so, complex residues are released with wastewater, having negative impact on natural water pollution, people's health, the environment and ecosystems. In this context, MNP or MNP-treated fabrics are a promising solution for decomposing organic pollutants from the wastewater and quick and facile recovery of the catalysts.

A composite magnetic coagulant (CMC) based on alum ($\text{Al}_2(\text{SO}_4)_3$)-coated ferromagnetic nanoparticles of Fe_3O_4 has been mixed with wastewater from the textile industry for successful residue removal [33]. A DBD (dielectric barrier discharge)/ $\gamma\text{-Fe}_3\text{O}_4$ treated cotton fabric also showed good removal properties for pollutants from the wastewaters [34]. Also, MNP used as support for catalysis substances in the chemical recycling of synthetic fibres like PET allows the catalyst to be recovered [35].

A different method of approaching the problem of pollution due to the conventional dyeing processes of the textile industry was developed by impregnating dyes into magnetic nanoparticles (skin-core structure) to help dye textiles and so, being easily collected from wastewater with a magnet, significantly simplifying the wastewater treatment process and indicating a more ecological approach in the dyeing process of textiles [36].

Oil recovery

Also, in the context of industrial wastewater pollution or marine pollution with oil spills, scientists have developed some solutions recently to counteract the negative impact of pollution. Thus, one study proposes a method based on in situ coprecipitations to manufacture superhydrophobic cotton fabrics functionalized with Fe_3O_4 magnetic nanoparticles, which could be controlled to absorb the oil from water as oil absorbents, even in hot water. Increased separation efficiency and facile operation procedures were demonstrated as also remarkable mechanical durable properties of the created fabric [37].

Another study proposes using a mixture of magnetic Fe_3O_4 nanoparticles and dodecylamine (DDA)-modified TiO_2 to coat a textile material which by changing the pH value of the surface achieved switchable wettability the magnetism allowed easy recovery of the textile from the environment. The results indicated very good oil/water separation efficiency, high oil flux, good reusability and high-temperature resistance of the material. So, the proposed method is environmental-friendly and besides oil/water separation, it can also be used for sewage purification, as mentioned by the authors [38].

Biomedical and antimicrobial applications

Because abdominal hernia is a frequently encountered health problem, surgical mesh implants are proper solutions and act as reinforcement for the weakened or damaged tissue and support tissue restoration. But postoperative problems like pain, mechanical mismatch, infection and non-acceptance of the implant by the surrounding tissues are serious issues that endanger the patient's life. In this sense, scientists proposed the designing of meshes with appropriate textile structures made of warp-knitted polypropylene (PP) and covered with electrospun polycaprolactone (PCL) nanofibers or PCL-gelatine nanofibers that better mimic the performances of the human abdominal wall and improve tissue restoration [39, 40]. Furthermore, for a better and non-invasive revision of the implant after surgery, the incorporation of small superparamagnetic iron nanoparticles into the polymer allows visualization and tracking of the implant's behaviour over time using magnetic resonance imaging (MRI) [41].

Polycarbonate-urethane (PCU) nanofiber tubes, including magnetic nickel (Ni) nanoparticles also manufactured through electrospinning technology, were developed for their potential use in biomedical

applications as magneto-active components (stents, heart patches or artificial nerve guides), capable of being deformed under the application of a controlled external magnetic field [42]. Functionalized textiles with MNP can also be used as dressings and materials for the care of wounds that can cause infections or treat postoperative infections, and a number of studies demonstrate this. Thus, magnetite MNPs offer a high potential for use in the medical field and have been used against the actions of several bacteria or fungi, such as *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Candida albicans*, *Escherichia coli* [43–45]. Also, magnetite nanoparticles synthesized by an eco-friendly process from a lemongrass extract are effective as antimicrobial agents by coating textiles [46]. ZnO nanoparticles were also applied directly to 100% cotton textiles by a 'pad-dry-cure' method for antibacterial treatment [47].

Agriculture applications

An implemented project (MagPlanTex) by a team from Poland, in the context of the ClimateLaunchpad competition, consisted of a new method to grow lettuce with the help of a green knitted textile mat with magnetic properties. By using textile technologies combined with drop-on-demand (DOD) printing technology with functionalized inks, the resulted textile mat could produce plant growth intensification by the action of magnetic fields. This method is suitable to be further explored because it could greatly influence the stimulation of food production [48].

With the introduction of nanoscience and nanotechnology in the textile industry, several properties of textiles can be controlled and improved. The figure below exemplifies these properties.

ELECTROSPINNING – AN UNCONVENTIONAL TECHNOLOGY USED FOR PRODUCING MAGNETIC TEXTILE NANOFIBERS

If the aim is to obtain an entire textile structure with magnetic properties at the nanoscale, the very well-known method of electrospinning can be used to manufacture a fibrous nonwoven nanostructure with the help of MNP.



Fig. 2. The influence of nanotechnology on textiles

This process is based on using a high electrical voltage to create an extrusion force on a solution or melt. The basic electrospinning system consists of a high voltage source, a spinneret, and a grounded collector. By applying an electric field of adequate intensity to the solution or melt, a strand of fibres is obtained and deposited on a collector forming a nonwoven fibrous layer [49].

Electrospinning is the most common and widely used technique for manufacturing nanofibers due to its advantages: simplicity, applicability on a wide range of materials, and low costs. Electrospinning has also the advantage of allowing the preparation of large-scale nanofiber networks in a short time, without the need to use a clean room, very sophisticated equipment or very toxic material and is therefore often used to prepare nanofibers.

Micro- and nanofibers produced using electrospinning have many extraordinary properties, such as high surface-to-volume ratio, high porosity, extremely small diameters, along with interconnected micro-nanostructure and surface functionality [50]. But, rate and scale of production are serious limitations in some applications that require large-scale production of these nanomaterials and in this sense, several modifications have been made over time to the classical process to improve its effectiveness. Figure 3 shows different technology configurations depending on specific criteria (collector shape, number and arrangement of needles, etc.).

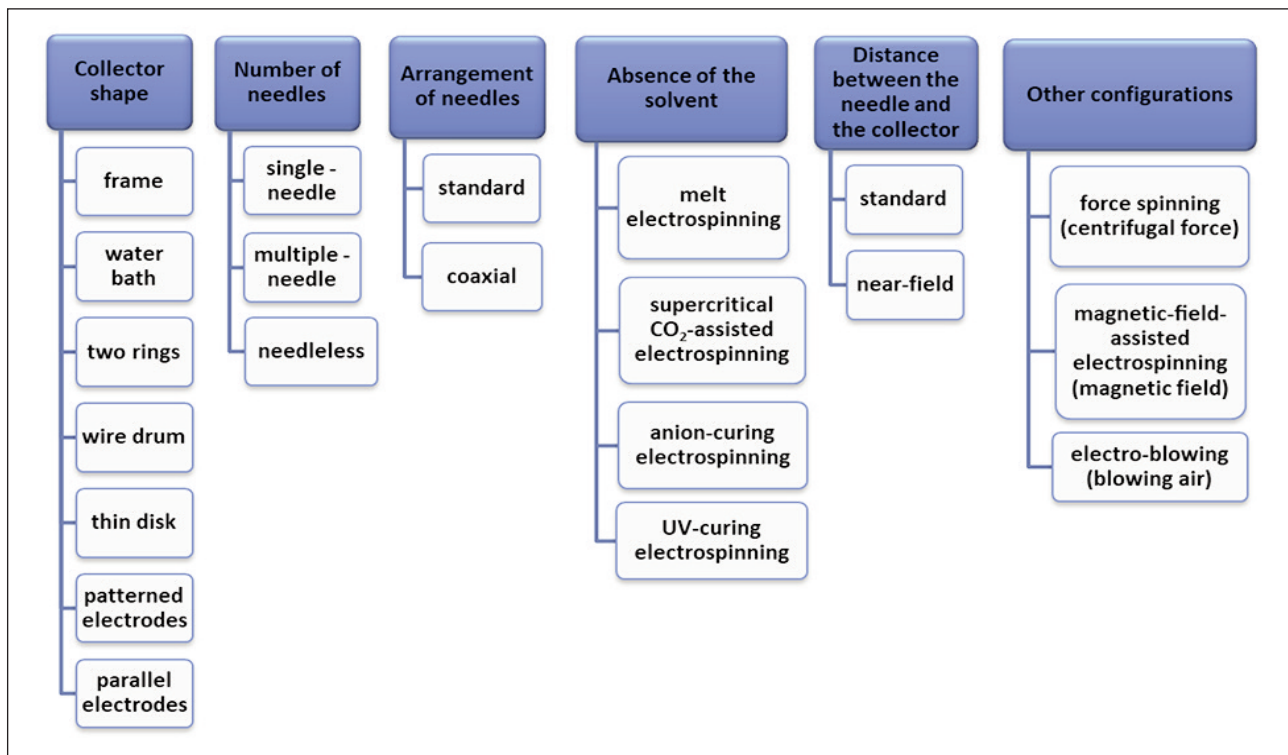


Fig. 3. Types of electrospinning technologies [51]

Table 1

RESEARCH ON COMPOSITE NANOMATERIALS MADE OF ELECTROSPUN NANOFIBERS WITH MNP FOR DIFFERENT APPLICATION AREAS					
Polymer	Solvent	Nanoparticles	Use form	Application	Reference
PVP	DMF	CoFe ₂ O ₄	Membrane(calcined nanofibers after electrospinning)	Microwave absorption	[53]
PCL	TFE:DMSO (90:10)	Fe ₃ O ₄	Bandage	Skin cancer treatment	[54]
Methacrylic acid/methyl methacrylate copolymers	water	Iron oxide (SPION) and carmofur (an adjuvant in chemotherapy for colon cancer)	pH-responsive fibres for oral administration	Magnetic resonance imaging (MRI) for drug release	[55]
Recycled polyester	TFA/DCM (3:7)	Fe ₃ O ₄ (magnetite)	Magnetic mat	Antibacterial applications	[56]
Silk fibroin	Formic acid	CoFe ₂ O ₄	Magnetoactive scaffolds	Tissue engineering	[57]
PVDF-HFP	DMF:acetone (1:1)	NiFe ₂ O ₄ and nanoclay	Magnetolectric fibre mat	Energy harvesters, data storage, sensors, actuators	[58]
PVDF/PBI (5:1)	DMF:acetone (2:1)	Fe ₃ O ₄	Composite nanofibers	Electronic devices (overheating phenomenon)	[59]
PVB	methanol	Fe ₂ O ₃	Membrane	Removal of iron ions from groundwater	[60]
PVB	Ethanol:isopropyl alcohol (4:1)	Fe ₃ O ₄	Magnetic yarn	Radiofrequency electromagnetic field shielding	[61]
PVP	DMF	NiZnFe ₂ O ₄	Film (calcined nanofibers after electrospinning)	Electromagnetic interference shielding	[62]

There are four methods involved in the production of magnetic nanofibers through the electrospinning process, depending on the used raw material [52, 15]:

a) Magnetic nanofibers produced from polymeric solutions and metal salts. Through the chemical reaction in the gas phase, the metal salt in the polymeric nanofibers is subsequently converted into magnetic nanoparticles.

b) Magnetic nanofibers produced from polymer solutions and nanoparticles, mixed in an appropriate proportion to obtain composite MNF with uniformly dispersed MNP, thus, particle surfaces are protected from oxidation, dispersibility is improved, and chemical stability is also improved and toxicity is reduced.

c) Pure magnetic nanofibers obtained by calcination of electrospun composites to remove polymeric matrix;

d) Magnetic nanofibers are produced by using a polymeric intermediate that will be electrospun, then making a magnetic coating on the surface of electrospun NF.

CONCLUSIONS

By using nanotechnology, new materials are further developed by many research groups. Nanotechnology offers improved properties over bulk materials due to its specific structure. There is a very important phenomenon called the size effect, that when the material scale is reduced from micro to nanoscale, the fundamental properties of the materials can be changed, for example, strength or electrical and thermal conductivity.

Also, nanomaterials with magnetic properties in the form of nanofibers/membranes/films/yarns and obtained by electrospinning technology have been increasingly studied during the last two decades in applications such as microwave absorption, skin cancer treatment, magnetic resonance imaging (MRI) for drug release, electromagnetic interference shielding, energy harvesters or data storage sensors and actuators.

One easy way of producing these types of nanomaterials discussed in this paper is the introduction of nanoparticles with magnetic properties in the electro-

spinning solutions so that the obtained nanofibers have already incorporated these nanoparticles in their structure. The most used nanoparticles in different studies are magnetite and iron oxides in general due to their low price, physical and chemical stability, biocompatibility and environmental safety.

Electrospinning is a remarkable technology by its simplicity, flexibility, and versatility, meaning that a variety of materials can be used in this process to obtain nanofibers. But, in general, some limitations regarding this process occur and are needed to be solved in the future. The rate and scale of production are limited in some applications that require large scale or massive quantities of the electrospun nanofibers and are relatively time-consuming. However, significant steps have been taken in this regard by reconfiguring the classical electrospinning equipment by using, for example, multiple needles.

In order to be used to efficiently create advanced materials that are widely accepted by the consumer public, extremely challenging tasks related to nanotechnology will have to be further solved and ensured: manufacturability, affordability, usability, maintainability, durability and safety.

Therefore, nanotechnology is a bridge between several domains, it can bring many benefits and can be used to achieve increased functioning of almost everything in the world, but we must be careful with how it is used and controlled because it can be unpredictable and there are still some unknown effects of it.

ACKNOWLEDGMENTS

The research presented in this paper was prepared in the INCDTP laboratories. Funds support this work from MCID, National Project "Composite materials with electroconductive properties, based on 3D polymeric array for sensorial monitoring system and electromagnetic waves attenuation (3D ELECTROTEX)", Contract PN 19 17 01 01.

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