

Review

Electrospinning: A Powerful Tool to Improve the Corrosion Resistance of Metallic Surfaces Using Nanofibrous Coatings

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Abstract: The use of surface engineering techniques to tune-up the composition of nanostructured thin-films for developing functional coatings with advanced properties is a hot topic within the scientific community. The control of the coating structure at the nanoscale level allows improving the intrinsic properties of the surface compared to bulk materials. A nanodeposition technique with increasing popularity in the field of nanotechnology is electrospinning. This technique permits the fabrication of long and continuous fibres on the micro-nano scale. The good control over fibre morphology combined with its simplicity, cost-effectiveness, easy exploitability and scalability make electrospinning a very interesting tool for technological applications. This review is focused on the use of the electrospinning technique to protect metallic surfaces against corrosion. Polymeric precursors, from natural or biodegradable to synthetic polymers and copolymers can be electrospun with an adequate control of the operational deposition parameters (applied voltage, flow rate, distance tip to collector) and the intrinsic properties of the polymeric precursor (concentration, viscosity, solvent). The electrospun fibres can be used as an efficient alternative to encapsulate corrosion inhibitors of different nature (inorganic or organic) as well as self-healing agents which can be released to reduce the corrosion rate in the metallic surfaces.

Keywords: Electrospinning; nanofibres; fibrous coatings; corrosion resistance; metallic surfaces; biocorrosion; composite coating

1. Introduction

The development of surface engineering techniques has made available many surface treatments and coatings to improve the corrosion resistance of metallic materials. Traditional techniques such as electrochemical plating [1], electrodeposition [2], anodizing [3] or chemical conversion [4] were the most employed for this purpose, although some of them involve the use of chromates, which are a very serious threat to human health and environmental. In consequence, different alternatives are object of investigation in order to overcome this problem.

The ability to design and to modify materials at the nanoscale is a promising alternative for this purpose, as the possibility of introducing nanoscale texture features on materials can increase the surface-to-volume ratio and provide additional functionalities. The development of nanostructures has

proved to be very successful against corrosion resistance and a great variety of deposition techniques have been employed to protect from corrosion metallic substrates, such as atomic layer deposition [5], spin-coating [6], sol-gel [7], Layer-by-Layer (LbL) [8], Chemical Vapour Deposition (CVD) [9] or Physical Vapour Deposition (PVD) [10,11].

Advances in the field of nanotechnology have allowed the fabrication of nanofibres with an excellent control of their morphology and architectural features for functional applications. In particular, a technique with increasing popularity in the last few years is electrospinning. It allows the deposition of ultrafine polymeric fibres, even nanometric, onto metallic surfaces. The electrospun fibres can act as an effective barrier coating and reduce the corrosion rate of the metal. In addition, the electrospinning technique is a simple, versatile, cost-effective, efficient, easily exploitable and scalable process [12], which can be applied onto a wide variety of materials (natural or synthetic) and can be used to improve the corrosion resistance of metallic surfaces.

As it can be observed in Figure 1, since 2002 the number of research works on electrospinning and corrosion resistance published in scientific journals has steadily increased, on account of the remarkable simplicity, versatility, easy functionalization and potential uses of this nanodeposition technique in the field of corrosion protection.

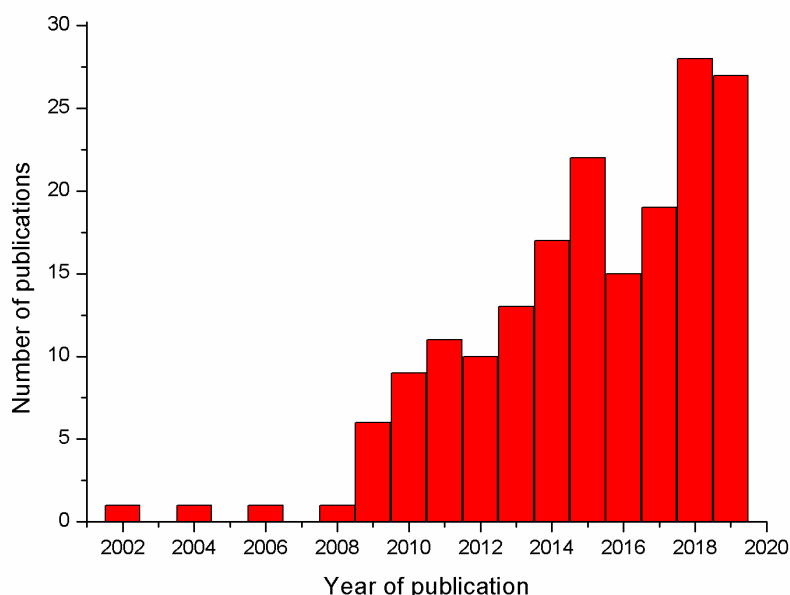


Figure 1. The annual number of publications (articles or conference papers) with the subject of “Electrospinning” and “Corrosion” in their title, abstract or keywords (source: Scopus).

This review is structured in three main sections. The first one is related to the fundamentals of electrospinning process, the effect of the operational parameters and the intrinsic properties of the polymeric precursor for obtaining fibres with well-controlled dimensions and morphology. The second one is devoted to demonstrate the potential of this nanodeposition technique in the design and development of corrosion protection surfaces. In this section, a review of all the polymeric precursors (biodegradable or synthetic origin) as well as the use of corrosion inhibitors or self-healing agents for improving the corrosion resistance of the metallic surfaces (namely steel, aluminium and magnesium alloys) is evaluated. In the third section, the possibilities of electrospinning to deal with a particular case of corrosion, biocorrosion, is discussed. This is a problem with a great transcendence in sectors such as biomedicine and offshore industries, for which electrospun nanofibrous coatings are particularly apt. To sum up, to the best of our knowledge, this is the first time that a review on the implementation of electrospun fibres for corrosion protection is presented in the literature.

2. Fundamentals of the Electrospinning Process

Electrospinning is a simple and versatile deposition technique that utilises electrostatic forces to obtain very fine polymeric fibres of variable size, from submicron down to nanometric scale [13]. In addition, this technique is a very powerful tool to fabricate materials with a high surface area [14]. Electrospun nanofibres (denoted as ENFs) can be made of different types of polymers such as synthetic [15], natural [16], biodegradable [17], copolymers [18] or polymer blends [19]. The nanofibres are fabricated by the application of a high voltage to a liquid polymeric precursor which is held at the end of a conductive capillary tube (needle) [20]. As a result, a continuous jet strand is accelerated from the eluting needle towards collector, usually grounded [21], as depicted in Figure 2. As the solution travels in the air due to the electric forces, the solvent is evaporated and ENFs are deposited onto the screen collector. Upon the action of the electric field, as the surface tension is balanced by the electrostatic forces, the droplets are gradually elongated, forming a characteristic conic shape on the tip of the needle known as the “Taylor cone”. Figure 3 shows the Taylor cone formed by a poly(acrylic acid) (PAA) precursor [22] and the final aspect of the electrospun coating composed of nanofibres onto a metallic aluminium alloy substrate.

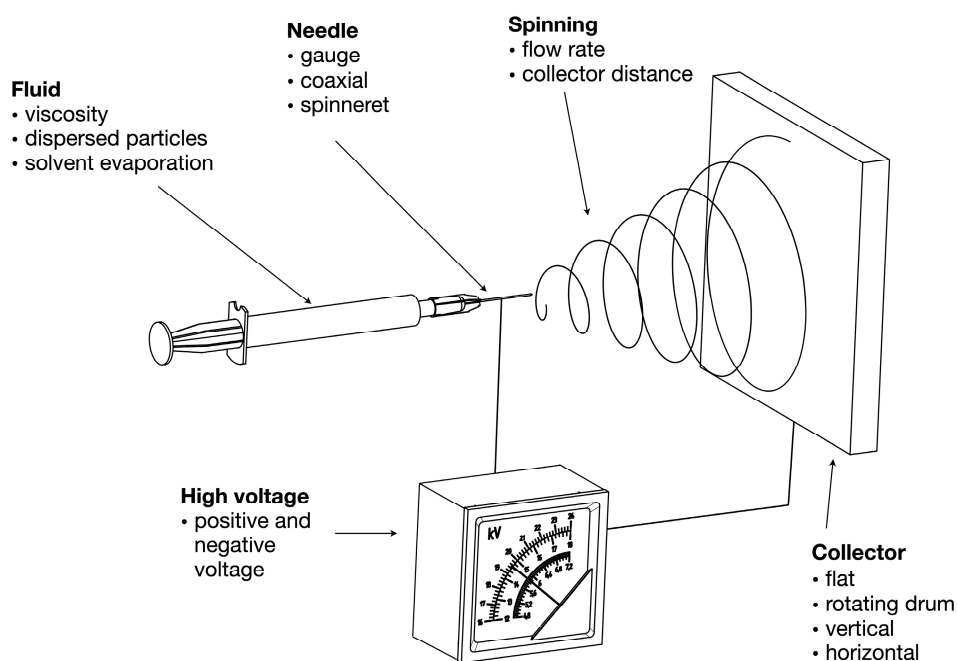


Figure 2. Schematic representation of a classical electrospinning setup for the fabrication of nanofibres as a function fluid properties (viscosity and polymer molecular weight), nature of the solvent, type of needle (coaxial, gauge, spinneret), high voltage applied, flow rate, collector distance and type of collector (flat, vertical, horizontal or rotating drum).

It is important to remark that the electrospinning process depends on the complex interplay of surfaces, shapes, rheology and electrical charge, and all these phenomena interact in different ways to create electrically charged jets of polymer solution [23]. In order to perform the electrospinning process, multiple parameters have to be controlled to generate nanofibres with the desired diameter and morphology, instead of droplets or beads. The first group are the properties of the polymeric precursor, such as molecular weight, chain entanglement, conformation of the polymeric chains, viscosity, molar concentration, surface tension, electrical conductivity and nature of the solvent, among others [24]. The second one is associated to the operational conditions such as the applied voltage, feeding or flow rate of the polymeric solution and distance between the capillary and collector [25]. The third set of parameters is related to the environmental conditions such as relative humidity and temperature and air flow inside the electrospinning chamber, associated to the solvent evaporation rate [26].

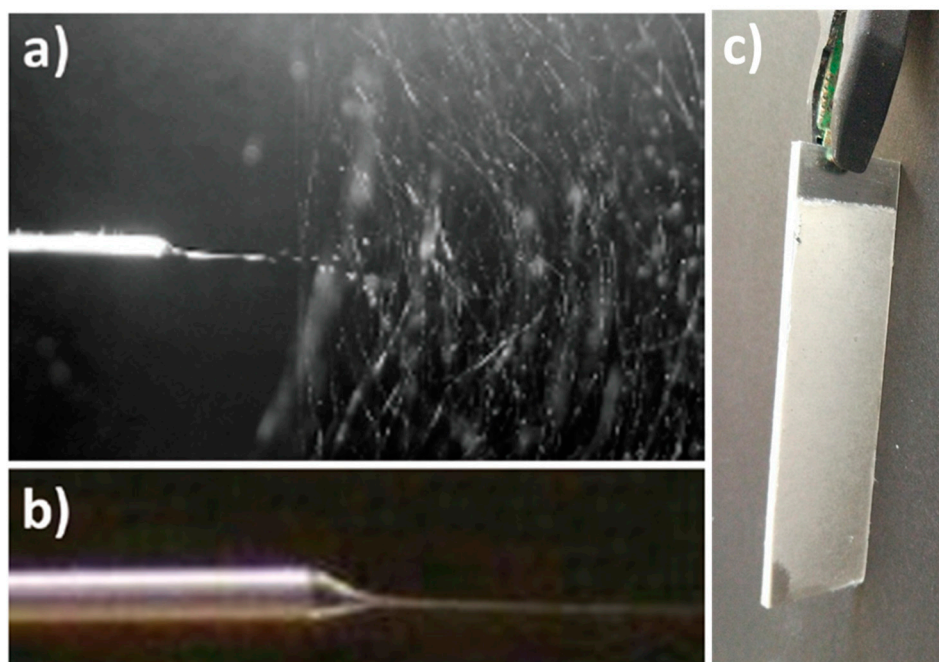


Figure 3. (a,b) The aspect of the fibres being electrospun towards the cathode from the needle which contains the polymeric solution and a detail of the Taylor cone formed at the tip of the needle; (c) The aspect of the final coating based on the electrospun fibres onto the reference metallic substrate (6061-T6). Reprinted with permission of [22].

The coordinated control of all these parameters makes possible to tune the diameter and morphology of the resultant fibres. Several research articles can be found in literature focused on the effect of the processing variables on the fabrication of fibres with specific properties. A minimum voltage is needed to eject the polymer solution from the tip of the Taylor cone. High electric potential is not desired as it is associated to bead formation or defects in the nanofibres [27]. The applied voltage on the electrospinning process greatly depends on the polymer used. Some works corroborate that high voltage promotes the formation of fibres with a larger diameter because there is more polymer ejection [28,29]. Contrarily, other research works found that the effect of increasing the applied voltage produces narrower fibres due to the production of a higher electrostatic repulsive force on the fluid jet [30,31].

The adequate selection of the polymer molecular weight as well as the employed solvent also are key factors to ensure that the polymer travels to the collector in the form of a continuous jet and is deposited in the form of nanofibres. When the polymeric jet is disintegrated into droplets, the process is denoted as electrospraying instead of electrospinning [32]. Solution concentration strongly affects fibre morphology. An increase in the fibre diameter is observed for high solution concentrations, which was characterized by a power law relationship [14,30]. The use of volatile solvents facilitates the drying of the nanofibres during the trajectory to the collector surface due to their lower boiling temperature and rapid evaporation rate [25]. It has been demonstrated that the fibre diameter decreased when solvents with higher density and boiling point were used [33]. A representative study can be found in [34] where the effect of varying the solvent concentration (acetic acid) from 10 up to 90 wt% for the preparation of electrospun chitosan fibres is studied. Experimental results show that the formation of thinner fibres is associated to an increase in solvent concentration. Other parameters to be controlled are the physical properties of the polymeric precursor. An increase in the polymeric viscosity promotes the formation of nanofibres with higher diameter, whereas an increase in the conductivity and surface tension of the polymer solution produces a reduction in diameter [24].

Flow rate and tip-collector distance also affect fibre diameter. The use of low feeding rates is desirable to let enough time for the solvent to evaporate before the fibres reach the collector. As the

flow rate is increased, the available polymer volume is higher, producing an increase on the nanofibre diameter [25,35] and mean pore size [30]. Nonetheless, it was observed that excessively high flow rates can produce beaded fibres due to the unavailability of a sufficient drying time of the solvent when the collector is reached [33]. The distance from the tip to the collector must be enough to give time to the fibres to dry before they reach the collector. Generally, a longer distance between the tip and collector induces the formation of thinner fibres [36], although too short or too far distances can lead to the formation of beads [30] or lots of droplets [37], respectively. The effect of atmospheric conditions such as relative humidity on the electrospinning process have been also investigated and the production of electrospun polymer microfibres with a nanoporous surface texture is possible in the presence of humidity. Density, shape and depth of the pores greatly depend on relative humidity [38]. Surface features and pores become more evident when the process is performed in an atmosphere with more than 30% of relative humidity. An increase in humidity produces an increase in the number, diameter, shape and distribution of the pores [39]. Once the multiple operational parameters involved in the electrospinning process, to design of nanofibres with desired morphology, have been examined, the following section is devoted to an exhaustive study of electrospun, functionalised coatings with anticorrosion properties.

3. Electrospun Coatings for Corrosion Protection

In this section different strategies used for the fabrication of anticorrosive surfaces are reported. The first subsection reviews coatings made of entirely polymeric fibres. The role of polymer selection, the resultant surface properties and hydrophobicity are discussed. In the following subsection, the immobilization and encapsulation of corrosion inhibitors or self-healing agents of different nature (organic or inorganic) inside electrospun fibres are presented. In the final subsection, some hybrid approaches that combine electrospinning with other deposition techniques are examined.

3.1. Electrospun Coatings of Entirely Polymeric Fibres

The role and importance of biodegradable materials have continuously increased in the field of medical implants in comparison with conventional materials. Magnesium alloys are metallic substrates widely used for bone and cardiovascular stent implants, although their high galvanic corrosion and degradation in physiological environment are important constraints for clinical applications. The accelerated corrosion causes the generation of hydrogen gas and as result, a degradation of the mechanical integrity of the alloys is observed. To overcome these drawbacks associated to the Mg-based alloys, the development of specific deposition techniques coupled with biodegradable materials is investigated, being electrospinning one of the most promising alternatives. Polymers deposited via electrospinning are poly(ϵ -caprolactone) (PCL), poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) (PHBV) and poly(L-lactic acid) (PLLA) due to their biocompatibility and biodegradability [40]. Castro et al. [41] evaluated the corrosion behaviour of electrospun PHBV coated magnesium alloy for biodegradable implant applications, proving that the electrospun coated sample showed better corrosion resistance than the bare metal. In addition, electrospinning technique also allows the fabrication of porous coatings that resemble the extracellular matrix of the body, promoting cell growth for tissue healing or used as drug releasers for infection control [42]. Nafi et al. [43] studied the corrosion behaviour of pure magnesium and magnesium alloy (AZ91) coated with PLLA electrospun fibres. The experimental results confirmed that this surface treatment produced a reduction in the corrosion rate assessed by hydrogen evolution volume and weight loss after immersion in Hank's solution. A similar work can be found in [44], where electrospun PCL nanofibres are deposited onto a magnesium alloy (AZ31) previously treated with HNO₃ solution to provide a good adhesion between the coating and the metallic substrate. The results obtained by weight loss and corrosion immersion tests corroborate that the combination of HNO₃ pre-treatment and PCL electrospun coating are very effective in controlling the degradation rate with an enhancement in bioactivity. Hanas et al. [45] also corroborated that PCL electrospun coatings successfully protects the surface of a fine grained

AZ31 magnesium alloy from chloride ion attack, avoiding the pitting corrosion when the samples are exposed to supersaturated simulated body fluid (SBF 5x). Other work studying the influence of electrospinning and dip-coating techniques on the degradation of Mg-based alloy can be found in [46]. In this work, the implementation of both deposition techniques using a degradable polymer such as poly(lactic acid) (PLA) strongly enhances the corrosion resistance of the Mg substrate (die casting AM50) for short immersion times. Rezk et al. [47] presented a bifunctional composite coating composed of polycaprolactone and synthesised hydroxyapatite nanoparticles (HA-NPs) loaded with simvastatin deposited onto magnesium alloys (AZ31) to enhance corrosion resistance in simulated body fluid (SBF) and improve osteointegration.

Synthetic polymers such as water-soluble polymers, conducting polymers, hydrophobic polymers and superhydrophobic polymers can be also used for the fabrication of electrospun micro or nanofibres with anticorrosion properties. In work [48], polyaniline (PANI) microfibres blended with poly(methyl methacrylate) (PMMA) are electrospun onto Q325 carbon steel. In a first step, the PANI dosage (up to 25%) was optimised, reaching the best anticorrosion properties when the substrate is exposed in 0.1 M H₂SO₄ solution. The experimental results corroborate that this PANI dosage in the PANI/PMMA coating provides the maximum corrosion protection efficiency (99.99%), nearly 500 times higher than the one obtained by traditional drop-casting PANI/PMMA coating. Moreover, the efficiency of the corrosion protection remained as high as 99.96 even after 20 days of immersion in acidic solution. The anticorrosion behaviour could be explained by the released H₂ gas occupying holes of the PANI/PMMA coating and as a result, H⁺ diffusion the carbon steel surface was blocked, providing a cathodic protection. In addition, the trapping of H₂ in the holes can also limit the diffusion of the anodic reaction produced by Fe²⁺ ions through PANI/PMMA coating to the H₂SO₄ solution. As a result, the anodic reaction is retarded. A similar anticorrosion coating composed of electrospun conductive polyaniline (PANI) and poly(methyl methacrylate) (PMMA) is evaluated in [49], although in this work the electrospun coating is exposed to 3 wt% NaCl. The best anticorrosion performance of the electrospun PANI/PMMA film is achieved with a dosage of 25 wt% PANI, associated to an extraordinary compact microstructure. The resultant electrospun coating acts as an efficient barrier and facilitates the formation of a protective passive layer on the surface of the metallic surface. This is in agreement with the experimental results and very satisfactory anticorrosion properties with specific corrosion protection efficiency of 99.98% were obtained. However, the presence of voids between microfibres are unfavourable for anticorrosion protection. In order to overcome this problematic, a new topcoat of polystyrene (PS) is applied onto the PANI/PMMA fibres, as described in work [50]. The resultant PS topcoat has been fabricated by different preparation methods such as electrospinning, spray-coating and drop-casting. However, the best corrosion protection results have been obtained from the combination of PANI/PMMA (primer) and sprayed PS (topcoat): the protection efficiency was kept at 99.95% after immersion of 720 h in 3% NaCl solution. This excellent protection is associated to the good shielding performance of sprayed PS and the anodic protection of PANI/PMMA primer.

Another relevant result is found in [51] where the design of Al₂O₃ coatings on zinc alloys for anti-corrosion in alkaline solution by using electrospinning process is presented as an efficient alternative in metal-air batteries in renewable energy devices where the zinc is one of the most widely used electrodes. A schematic representation of the fabrication process can be observed in Figure 4: the electrospun fibres are firstly obtained and deposited onto the metallic substrate. A thermal treatment is then performed to obtain Al₂O₃ coatings with different thicknesses. The precursor solution is a mixture of poly(acrylonitrile) (PAN) and aluminium nitrate (Al(NO₃)₃·9H₂O) dissolved in dimethylformamide (DMF). The aspect of the fibres before and after thermal treatment can be observed in Figure 5. The nanofibres first display a smooth surface and an average diameter of around 400 nm before thermal treatment, whereas the nanofibres became a little rougher and thinner with an average diameter of around 220 nm after thermal treatment.

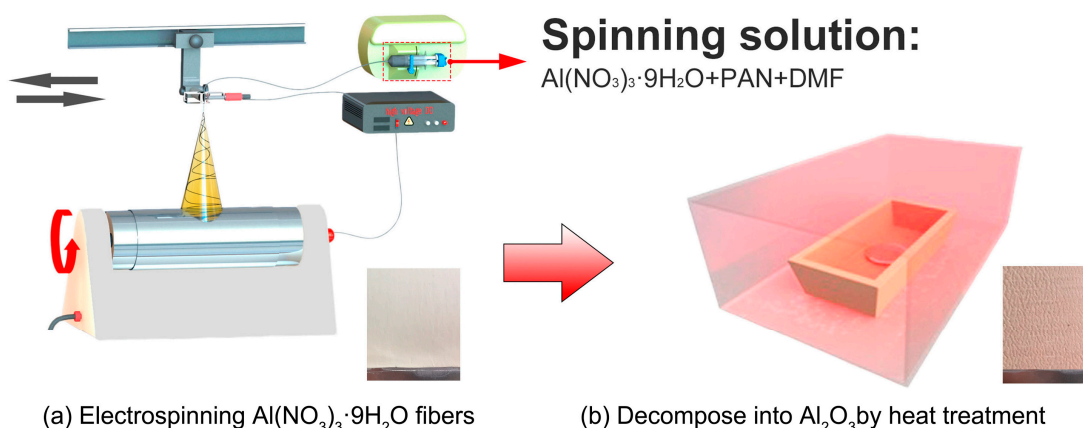


Figure 4. Electrospun $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, polyacrylonitrile (PAN) and N,N-dimethylformamide (DMF) mixed solution on zinc substrate (a). Heat treatment of the electrospun films in muffle furnace in an atmospheric environment to obtain Al_2O_3 coatings (b). Reprinted with permission of [51].

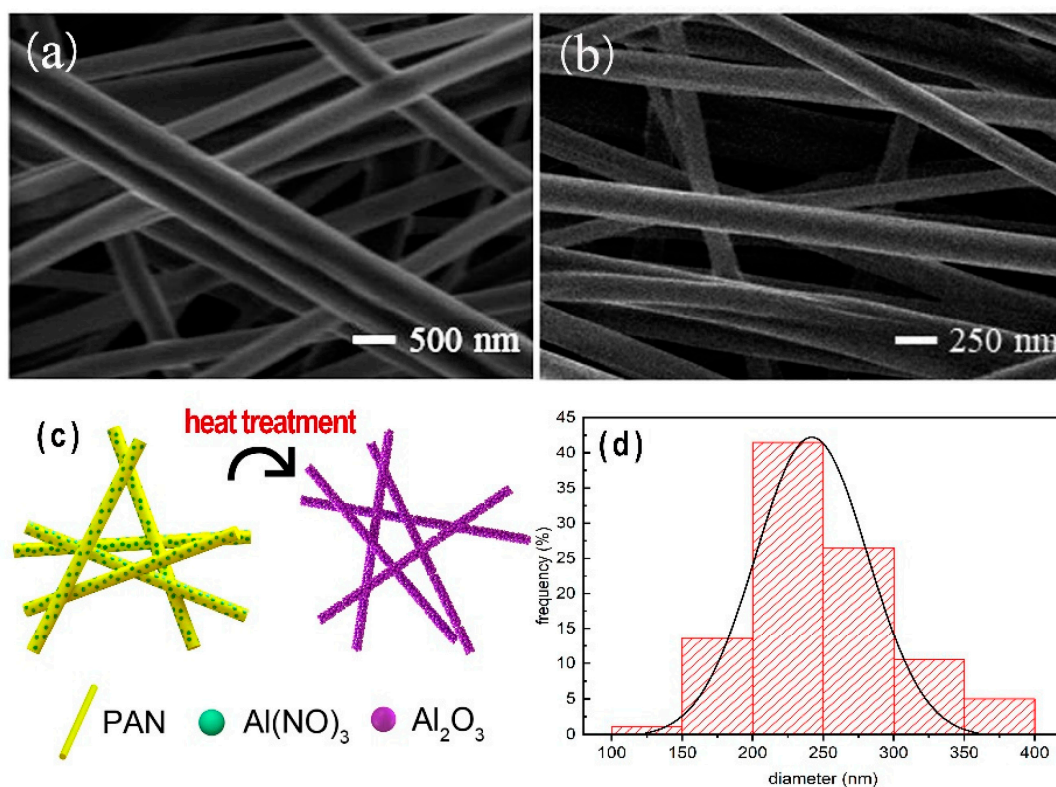


Figure 5. SEM images of Al_2O_3 coatings made by electrospinning technique before (a) and after heat treatment (b). Sketch illustrating the formation mechanism of the Al_2O_3 nanofibre coatings (c). The diameter distribution of Al_2O_3 nanofibers after thermal treatment (d). Reprinted with permission of [51].

The anticorrosion properties of Al_2O_3 coatings with different thicknesses (6 μm , 12 μm and 18 μm , respectively) have been assessed by means of hydrogen evolution. Suppressing hydrogen evolution is critical for zinc in alkaline solutions. The Al_2O_3 coatings prevent the direct contact between zinc and the alkaline solution, minimizing the hydrogen evolution. Figure 6 shows the volumetric amount of hydrogen spontaneously evolved from zinc substrate modified with Al_2O_3 coating in 4 M KOH during 1.5 h at 298 K. The bare zinc substrate has the highest H_2 evolution rate in comparison with other samples coated with Al_2O_3 in variable thicknesses (see Figure 6a). It can be also observed that

the volume of H_2 gas decreased with an increase of coating thickness and the zinc modified with 18 μm Al_2O_3 showed the best hydrogen evolution rate. In addition, Nyquist plots derived from Electrochemical Impedance Spectroscopy (EIS) results (see Figure 6b) have the shape of a capacitive loop in all the cases. The decrease in capacitance with increasing coating thickness observed is consistent with the decrease in porosity. All the experimental results derived from EIS data indicated that the thicker Al_2O_3 coatings the better anticorrosive properties.

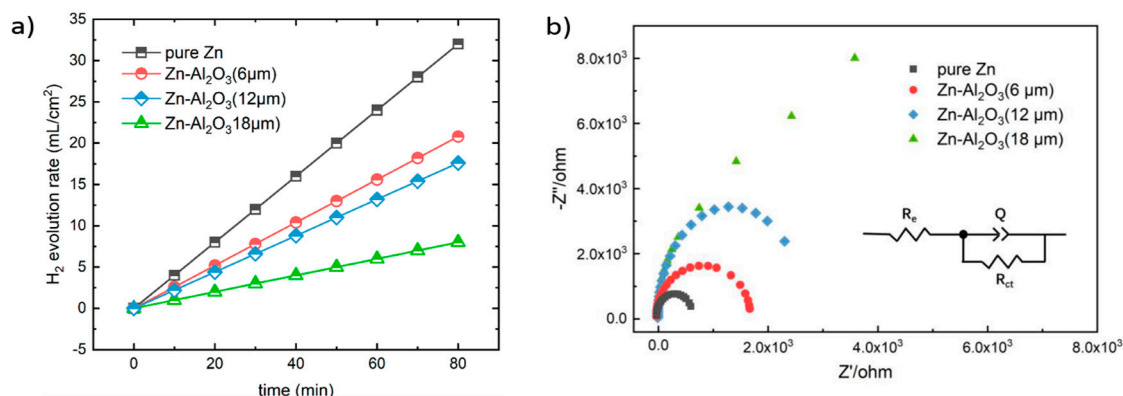


Figure 6. (a) Hydrogen evolution rates of bare and Al_2O_3 -coated zinc substrates with various coating thicknesses in 4 M KOH solution; (b) Nyquist plots obtained by Electrochemical Impedance Spectroscopy (EIS) for bare and Al_2O_3 -coated zinc substrates in 4 M KOH solution. Inset corresponds to the equivalent circuit model for fitting the impedance data. Reprinted with permission of [51].

The importance of the crosslinkage of electrospun fibres is evaluated by [52]. In this work, polyvinyl alcohol (PVA) is used as polymeric precursor for the fabrication of electrospun fibres. In order to avoid PVA disintegration in aqueous environments, an exhaustive study with several crosslinking procedures using glyoxal was carried out. The crosslinked PVA mats showed improved properties (mechanical and thermal) compared to electrospun fibres without crosslinker. The crosslinked fibres can protect aluminium alloys substrates (AA6082) against corrosion as demonstrated by electrochemical impedance tests. The resultant crosslinked PVA/glyoxal fibres thermally treated at 120 °C for 60 min provided significant corrosion resistance (26 k Ω) in comparison with the blank alloy (about 3.8 k Ω) after long immersion time (270 h) in 3 wt% NaCl. The importance of highly crosslinked fibres is also evaluated in [53]. In this work, electrospun fibres of poly(acrylic acid) (PAA) crosslinked with β -cyclodextrin (β -CD) and titania (TiO_2) nanoparticles have been deposited onto aluminium substrates. The use of this crosslinker (β -CD) for the fabrication of coatings is of great importance, as the resultant electrospun fibres showed a high degree of insolubility after immersion in water for a long period of time, compared with uncrosslinked fibres (only PAA), as it can be observed in Figure 7.

Another long-term anticorrosive protection strategy is based on the use of polymers with intrinsically ultrahigh hydrophobicity or superhydrophobicity. Polyvinylidene fluoride (PVDF) is a well-known polymeric precursor with highly hydrophobicity which also has excellent antioxidation and anticorrosion properties, favourable thermal stability and good mechanical behaviour [54]. Work [55] describes the fabrication and deposition of polyvinylidene fluoride (PVDF)/stearic acid (SA) nanofibres onto aluminium sheets for long-term anticorrosive protection. Pure PVDF nanofibres show a highly hydrophobic behaviour (WCA of $130 \pm 1^\circ$), whereas the incorporation of stearic acid (SA) into the PVDF nanofibrous coating produces an enhancement in water repellence behaviour with a superhydrophobic surface (WCA of $151 \pm 1^\circ$). PVDF/SA nanofibres exhibited bigger impedance and lower corrosion current density in comparison with PVDF nanofibres after 30 days of immersion in a 3.5 wt% NaCl solution. The study concludes that superhydrophobic PVDF/SA nanofibres showed a superior anticorrosion performance for long-term metal substrate conservation.

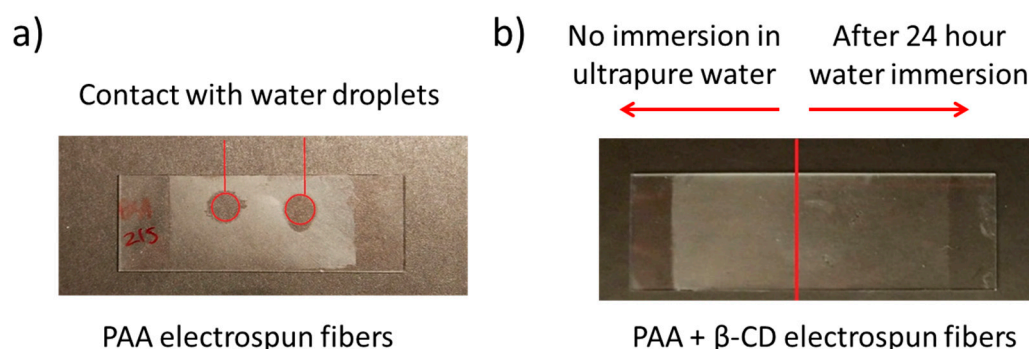


Figure 7. (a) Aspect of the poly(acrylic acid) (PAA) electrospun fibres onto glass slides, showing a total remove of the coating after contact with water droplets; (b) aspect of the PAA + β -cyclodextrin (β -CD) electrospun fibres where the coating remains totally unaltered after 24 h immersion in water. Reprinted with permission of [53].

Another interesting approach based on the development of superhydrophobic surfaces is presented in [56] where the protection properties of PANI/PS micro/nanostructures are increased along with their water repellence. Good anticorrosion properties were obtained with a PANI-PFOA/PS coating based on a drop cast of a mixture of polyaniline (PANI) and perfluoro caprylic acid (PFOA) deposited onto polystyrene (PS) microfibrils. This PANI-PFOA/PS coating has a contact angle value of 153° and anticorrosion efficiency of 99.48%. In work [57] the corrosion passivation of brass surfaces with nanofibre coatings fabricated by electrospinning of polymers with a superhydrophobic behaviour such as polyvinyl chloride (PVC) or polystyrene (PS) is studied. The experimental data confirm that the protected brass surface shows a less corrosion current and corrosion rate in comparison with the uncoated samples with an increase in their corresponding polarization resistance. In work [58] electrospun polymer nanofibre coatings of PVC as corrosion inhibitor were deposited onto aluminium, steel and brass surfaces. The fibres had diameters of 80 to 100 nm and lengths of 3 to 5 μm , being compact and entangled with each other. Nanofibre coatings of PVC with variable diameters used for corrosion passivation are presented in work [59].

One interesting and innovative work on surfaces with superhydrophobic behaviour can be found in [60]. In this work, anticorrosive superhydrophobic polystyrene-coated mesh (PSCM) has been fabricated by electrospinning and then folded around a three-dimensional (3D) miniature box which can remove oils (heavy and light) from water with a high efficiency (99.92%), even in harsh environments (strongly acidic, alkaline, hot water or hypersaline solution). The potentiodynamic curves corroborate the excellent corrosion resistance of this PS-coated aluminium surface. This approach could be an ideal alternative to solve the issue of pollution due to oil spills in sea water.

The use of the same polystyrene (PS) polymeric precursor is also investigated in [61]. In this work, the effect of coating parameters together with the composition of polystyrene (PS)-aluminium oxide (Al_2O_3) precursor on the morphology, surface roughness and wettability of the fibres is evaluated. The experimental results show that highly porous superhydrophobic nanocomposite coatings provided better corrosion resistance, higher than uncoated aluminium substrate by three orders of magnitude (exposed to saline water). The addition of Al_2O_3 nanoparticles produced an increase in surface roughness with higher water contact angle (WCA) values. Generally, Al_2O_3 nanoparticles and the combination of micro beads with nanofibres make possible this increase in roughness and WCA in comparison with pure PS electrospun fibres, as it can be seen in Figure 8. A SEM/EDX (Scanning Electron Microscopy/Energy dispersive X-Ray) mapping of the PS/ Al_2O_3 coating has been performed to corroborate the presence and dispersion of these Al_2O_3 nanoparticles on the beaded PS fibre structure, as reproduced in Figure 9.

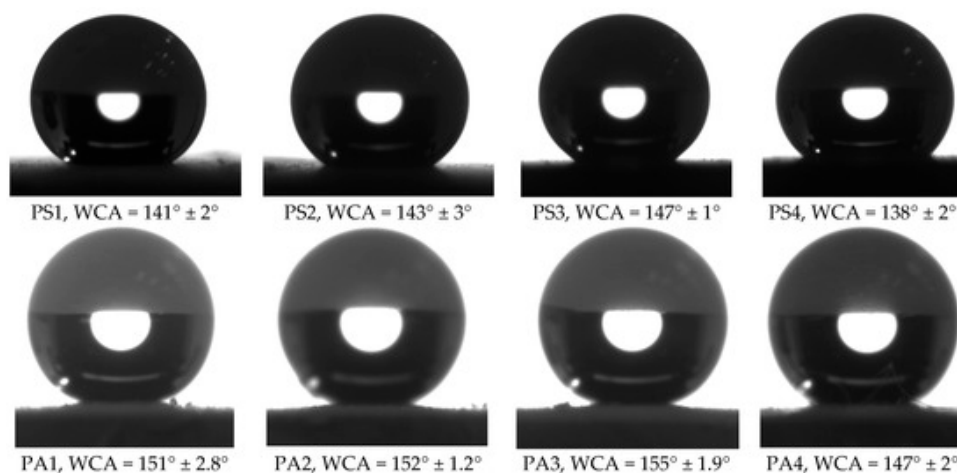


Figure 8. Snapshots of the measured water contact angle of only polystyrene (PS) fibres (PS1, PS2, PS3 and PS4) and PS/Al₂O₃ fibres (PA1, PA2, PA3 and PA4). Reprinted with permission of [61].

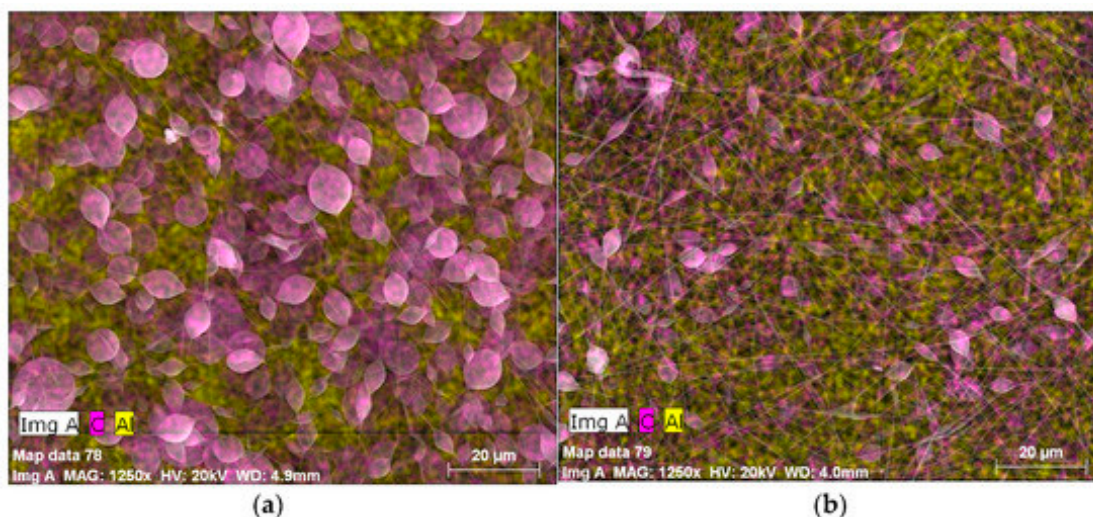


Figure 9. The SEM/EDX mapping micrographs of the as-prepared superhydrophobic coatings of PS/Al₂O₃ for PA1 sample (a) and PA3 sample (b). Reprinted with permission of [61].

An anticorrosion coating for magnesium alloys based on electrospun superhydrophobic polystyrene/SiO₂ composite fibres is presented in [62]. SiO₂ nanoparticles have been synthesised by sol-gel technology and hydrophobilised with a fluorosilane precursor. The modified nanoparticles (denoted as mod-SiO₂) were then used as additives in the polystyrene fibres by electrospinning technique. The resultant PS/mod-SiO₂ fibres showed a maximum WCA value of 165° and more than 13 times lower corrosion current density than only PS fibres coating. Finally, the corrosion protection efficiency of the fibrous coating was found to be greater than 99%, showing a highly protective nature of the composite fibres.

Other work using the electrospinning of a fluorinated diblock copolymer solution to obtain superhydrophobic aluminium surfaces with an excellent corrosion resistance and good adhesion is reported in [63]. The diblock is composed of poly(heptadeca-fluorodecylacrylate-co-acrylic acid) (PFDA-co-AA) random copolymer as the first block and polyacrylonitrile (PAN) as the second one. The fluorinated block promotes hydrophobicity of the metallic surface by reducing the surface tension, whereas the carboxylic functional groups makes possible the anchoring of the polymer onto to aluminium surface after annealing at 130 °C. The PAN block ensures the stability of the structure during the thermal treatment of annealing due to the infusible character of PAN.

3.2. Electrospun Protective Self-Healing Coatings

Electrospun coatings can self-heal by releasing corrosion inhibitors encapsulated by micro/nanocontainers incorporated into the electrospun fibres. The polymeric precursor poly(vinyl alcohol) (PVA) has been used in [64] to produce self-healing coatings for light alloys. Two different cerium salts and corrosion inhibitors, cerium nitrate and cerium acetylacetone, have been added to a PVA precursor and deposited onto aluminium alloy substrates by electrospinning. The resultant nanofibrous coatings have been evaluated for healing of generated defects, and the coatings doped with these corrosion inhibitors showed a remarkable corrosion resistance. A self-healing effect has been observed in the sample doped with cerium acetylacetone, providing a significant recovery of the corrosion resistance due to the formation of cerium hydroxide on the defective zone. The same PVA precursor was used by [65] to obtain long-term active corrosion protection of damaged coated aluminium alloy by embedded electrospun inhibiting nanonetworks. In this work two corrosion inhibitors such as cerium chloride and lithium carbonate have been used. Polymeric PVA fibre mats have been crosslinked with glutaraldehyde (GA) and crosslinked fibres mats showed a fibre diameter with a slight swelling effect in comparison with non-crosslinked PVA fibres. In addition, the coated panels have been scratched and exposed to NaCl solutions for a month. The protective properties were continuously evaluated electrochemically in order to confirm the release of the corrosion inhibitors. The experimental results confirmed the release of inhibitor from the inhibiting nanonetworks and subsequent formation of protective cerium oxides and hydroxides at the scribe surface, reducing the natural aluminium corrosion process. In work [66], cerium oxide nanoparticles (ceria NPs) are embedded in situ in PVC nanofibres, providing good corrosion resistance as demonstrated by EIS experiments.

Dong et al., in reference [67], report the self-healing capability of inhibitor-encapsulating polyvinyl alcohol (PVA) and polyvinylidene fluoride (PVDF) coaxial nanofibres loaded in epoxy resin coatings. The inhibitor 2-mercaptobenzothiazole (MBT) has been blended with PVA to serve as the core structure, whereas PVDF has been chosen as the shell structure for being a hydrophobic fluoropolymer with low surface energy. The PVD@PVDF nanofibre membrane was coaxial electrospun onto the surface of the metallic surface (Q345 carbon steel). The electrochemical tests indicate that the nanofibre membrane could inhibit the penetration of the corrosion media for a certain time. In addition, the Electrochemical Impedance Spectroscopy (EIS) and the Scanning Kelvin Probe (SKF) data showed that the corrosion at the scratched area in the electrospun coating has been inhibited by the release of the corrosion inhibitor and the formation of a thin inhibitor film on the scratched substrate.

Work [68] presents the use of coaxial electrospinning for the development of self-healing coatings composed of electrospun core-shell fibres to protect steel. The liquid healing agents are contained in two types of fibres, type A and B. The core material of type A contains a mixture of poly(dimethylsiloxane) (PDMS) and the crosslinker poly(diethoxysiloxane) (PDES), whereas the core material of type B fibres contains the crosslinking catalyst dibutyltin dilaurate (DBT), respectively. In both types of fibres, PVA was used as the shell structure. The performance of the healed coatings is evaluated electrochemically using linear polarization when the samples were exposed to corrosive environment. The results corroborate that the self-healing electrospun coating has lower corrosion current in comparison with control sample, resulting in 88% corrosion inhibition efficiency. A similar approach is presented in [69] where a pH-responsive self-healing core-shell electrospun nanofibres coating encapsulating oleic acid (OA) and benzotriazoles (BTA) is used for corrosion protection of carbon steel. In this work, the shell of electrospun nanofibres is PVA, whereas the healing agents OA and BTA are used as core materials to reseal a damaged region. A maximum inhibition efficiency of 83.4% after 5 days of immersion in corrosion media was observed and characterised by electrochemical measurements. [70] also used the same corrosion inhibitor of benzotriazole (BTA) embedded in nylon 6-6 to fabricate electrospun fibres for copper corrosion protection.

The use of metallic oxide nanoparticles as corrosion inhibitors combined with synthetic hydrophobic polymeric precursors is another novel approach used for the development of long-term

anticorrosive surfaces. Zinc oxide nanoparticles (ZnO NPs) embedded into polymeric precursors such as polyvinylidene fluoride (PVDF) [71], polyvinyl chloride (PVC) [72] or polystyrene (PS) [73], have been investigated. It has been commented that the electrospinning technique is an ideal strategy for constructing superhydrophobic surfaces on a large scale, being an increasingly hot research topic for a wide number of industrial applications [74]. In addition, the presence of ZnO NPs into the electrospun fibres can offer an additional multifunctionality as an efficient corrosion inhibitor and even additional advantages such as antibacterial properties, nontoxicity and anticancer behaviour [75].

In work [71], it is presented a superhydrophobic PVDF-ZnO nanocomposite coating fabricated by one-step electrospinning process, showing a water contact angle (WCA) of $155 \pm 2^\circ$. It has been observed that by using electrospinning, a better distribution of the ZnO NPs has been obtained in the coating without using any dispersing agent in comparison with other deposition techniques such as spray coating. In addition, the presence of ZnO NPs produces an increase in the surface roughness (R_a value) from 20 nm (only PVDF coating) up to 40 nm (PVDF-ZnO coating) which has been corroborated by atomic force microscopy (AFM). Finally, the addition of ZnO NPs to PVDF has led to the formation of voids at the polymer surface which retards the penetration of the aggressive ions within the nanocomposite coating due to the presence of trapped air.

Polyvinyl chloride (PVC), a polymer with highly water repellent behaviour, is used in work [72], in combination with ZnO NPs for the development of anticorrosion electrospun fibres. In Figure 10 are shown the optical images of the water contact angles related to both only PVC and PVC-ZnO electrospun fibres, respectively. Figure 11 shows the 2-dimensional (2D) atomic force microscopy (AFM) image of the PVC-ZnO nanocomposite coating with its corresponding roughness profile, showing surface morphology with an average roughness R_a of 427.5 nm.

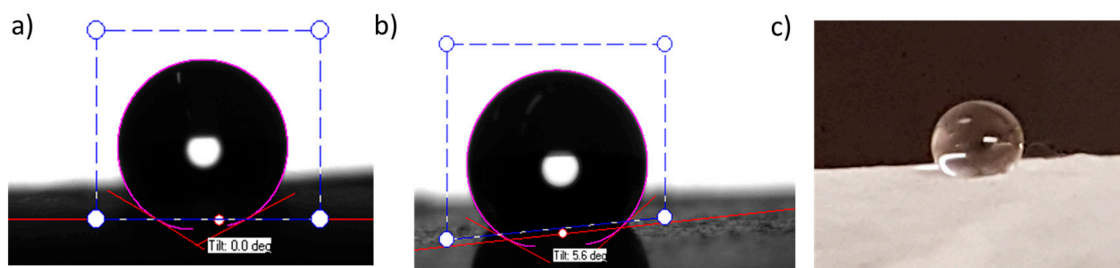


Figure 10. Optical images of the water contact angle values on the polyvinyl chloride (PVC) sample with a value of 151.73° (a); PVC-ZnO samples with a value of 146.39° (b); aspect of the water drop deposited onto a surface coated with the electrospun fibres. Reprinted with permission of [72].

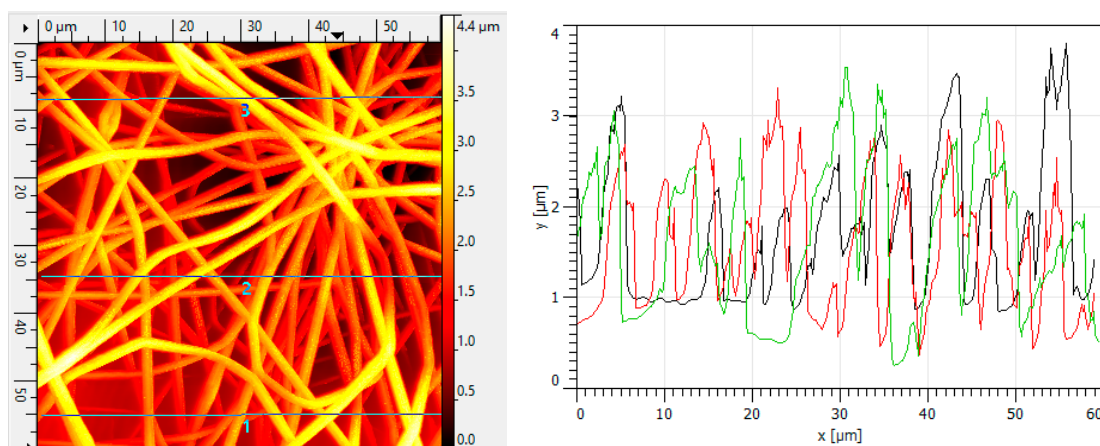


Figure 11. On the left: 2D AFM image of the PVC-ZnO sample. Image dimensions: $60 \times 60 \mu\text{m}$. On the right: roughness profiles corresponding to the three evaluation lines indicated on the left. Reprinted with permission of [72].

By using the same corrosion inhibitor, ZnO NPs, work [73] presents a comparative study of multifunctional coatings on electrospun fibres as a function of two different polymeric precursors with highly hydrophobic nature: poly(vinyl chloride) (PVC) and polystyrene (PS). The novelty of this work is that a specific thermal treatment of 20° higher than glass transition temperature (T_g) allows obtaining an excellent and better anticorrosion properties. This may be explained by a better distribution of the ceramic ZnO NPs due to the movement of the polymeric chains above the resultant T_g . Figure 12 shows the morphology of both types of fibres on scanning electron microscopy (SEM). A dense structure of entangled threads of variable thickness between 2 and 4 μm was observed in PS samples (Figure 12a,b), whereas thinner electrospun fibres in a submicrometric range was observed in PVC sample (Figure 12c,d) with a thickness diameter between 500 and 700 nm. In addition, the cross-section SEM images in Figure 13 reveal a notorious difference in the thickness coating, being of 25 μm (PS sample) and 70 μm (PVC sample).

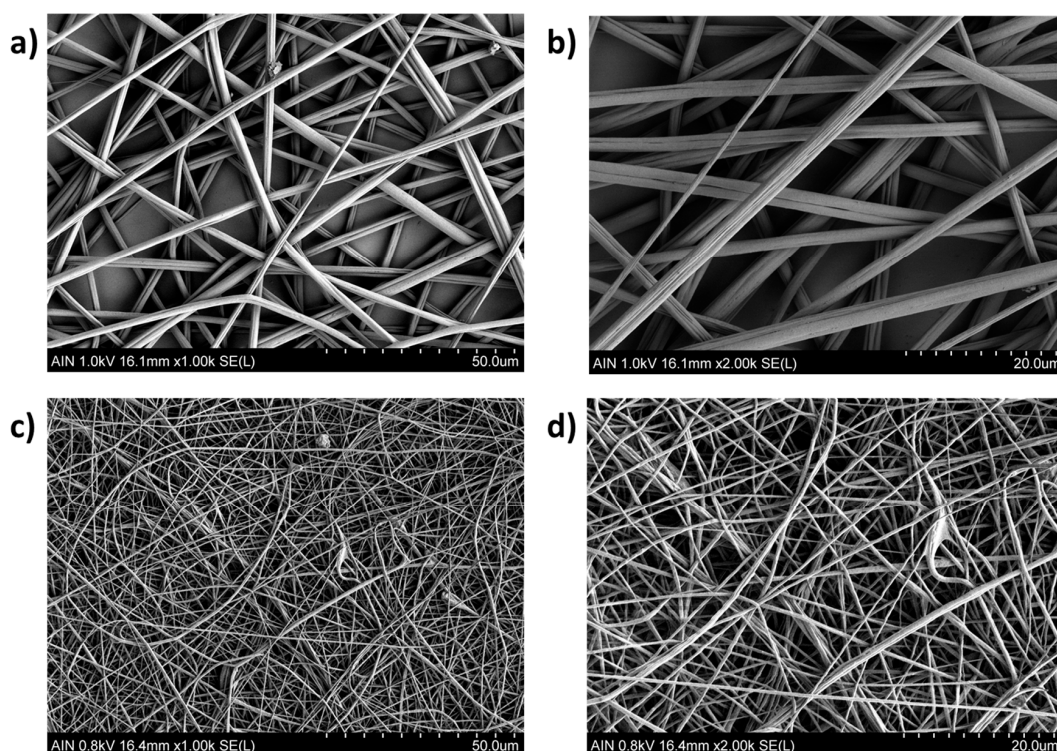


Figure 12. SEM images of the PS electrospun fibres (a,b) and PVC electrospun fibres (c,d) at different scale bar. Reprinted with permission of [73].

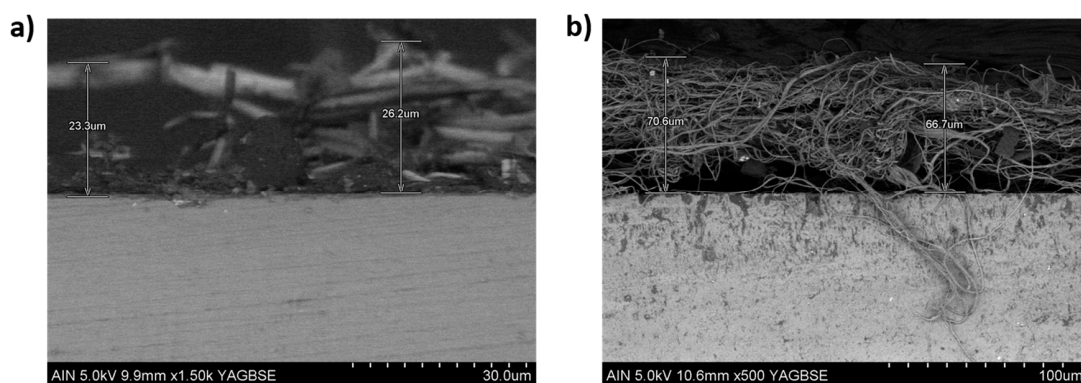


Figure 13. Cross-sectional SEM image of the PS (a) and PVC (b) electrospun fibre coating with their corresponding thickness. Reprinted with permission of [73].

As it was previously commented, firstly, a thermal treatment has been performed up to the glass transition temperature (T_g) in order to improve the adherence of the electrospun fibres and the underlying metallic substrate. Secondly, a thermal treatment up 20 °C higher than the T_g was also performed in order to promote the movement of the polymeric chains, leading a better distribution of the ZnO NPs along the electrospun fibres [76]. The experimental results derived from corrosion tests are presented in Figure 14 where it is shown the Tafel polarization curves of aluminium reference substrate (6061T6), PS-ZnO fibres and PVC-ZnO fibres thermally treated at T_g and $T_g + 20$ °C. First of all, it can be observed that electrospun coatings with ZnO inclusions produce an enhancement in the corrosion resistance of the aluminium substrate. All coatings have reduced the corrosion current density in two orders of magnitude, from a value of $1.107 \mu\text{A}\cdot\text{cm}^{-2}$ (bare aluminium substrate) to a minimum of $0.010 \mu\text{A}\cdot\text{cm}^{-2}$ (PS-ZnO) or $0.009 \mu\text{A}\cdot\text{cm}^{-2}$ (PVC-ZnO) for the samples thermally treated ($T_g + 20$). In addition, the protection efficiency of the PS-ZnO and PVC-ZnO coatings heat-treated to the glass transition temperature of the polymer was found to be 93.95% and 95.12%, respectively. However, when the samples were heat treated 20 degrees over T_g ($T_g + 20$), maximum values of 99.10–99.19% have been obtained. To sum up, a heat treatment over T_g improves anticorrosion capacity associated to a better distribution of the ZnO NPs between the interstices of the fibre mat.

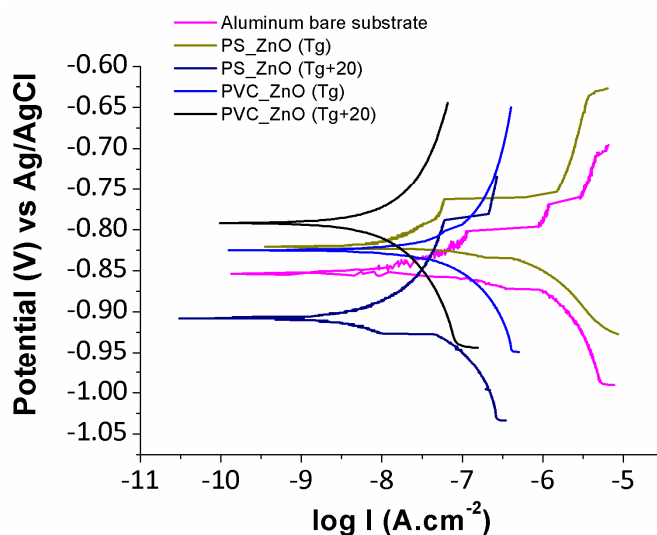


Figure 14. Tafel plots corresponding to the Al bare substrate and the Al samples coated with electrospun PS-ZnO and PVC-ZnO electrospun fibres which have been thermally treated and tested in 3.5 wt% NaCl aqueous solution. Reprinted with permission of [73].

3.3. Combination of Electrospinning Process with Other Deposition Techniques

One of the main advantages of the electrospinning technique is its great versatility, making possible to combine it with other deposition techniques for improving the corrosion resistance. An interesting approach based on the implementation of two different deposition techniques to improve corrosion resistance and bioactivity can be found in [77]. In this work, cellulose acetate (CA) nanofibres have been deposited onto the metallic surface (304 stainless steel). A composite of hydroxyapatite (HAP) nanoparticles and chitosan (CHI) was then deposited by dip-coating. As a result, the CA nanofibres were completely embedded in the HAP/CHI coating, which was densely packed and uniform onto the substrate. Finally, the electrochemical polarization and impedance tests were performed in simulated body fluid (SBF) confirmed that the presence of CA nanofibres significantly increased the corrosion resistance of the metallic substrate. In addition, this type of coating can be implemented onto medical implants, being a promising material for long-term stability in biomedical applications. A novel approach for self-healing applications is found in [78] where poly(caprolactone) (PCL) was electrospun onto metallic substrate and further infiltrated with a shape memory epoxy matrix using a spin coater.

The experimental results corroborate that the coating provided an excellent thermally induced crack closure and protection against corrosion.

Other novel work using hybrid sol-gel coatings with electrospun nanofibres doped with ceria nitrate and ceria particles is presented in [79]. The coating is deposited onto aluminium alloys (AA2024-T3). The hybrid sol-gel matrix is composed of both inorganic-organic precursors such as tetra n-propoxyzirconium (TPOZ) and 3-glycidoxypolytrimethoxysilane (GPTMS), whereas the electrospun nanofibres are obtained from poly(vinyl alcohol) (PVA). The presence of these nanofibres into the hybrid sol-gel coatings provides good barrier properties, making possible an increase in the corrosion resistance of the metallic substrate at longer exposure times in saline media (demonstrated by electrochemical impedance measurements).

Finally, a novel coating is presented in work [53], using a combination of electrospinning and chemical vapour deposition (CVD-silanization) techniques in order to create functionalised films with an enhancement of both corrosion resistance and hydrophobicity. In a first step electrospun fibres of poly(acrylic acid) (PAA) crosslinked with β -cyclodextrin (β -CD) and titania (TiO_2) nanoparticles have been deposited onto aluminium substrates. The presence of TiO_2 NPs into the electrospun fibres enables an important enhancement in the corrosion resistance of the coatings (demonstrated by cyclic potentiodynamic curves) because the sample composed of TiO_2 NPs exhibits the least negative potential (-532.6 mV) in comparison with the bare substrate (-642.2 mV) and the crosslinked PAA/ β -CD electrospun fibres (-617.2 mV), as it can be observed in Figure 15. In a second step, to increase the hydrophobicity of the surfaces, a chemical vapour evaporation of 1H,1H,2H,2H-Perfluorodecyltriethoxysilane has been performed. The hydrophilic head of this molecule is oriented towards the hydrophilic surface of the electrospun fibres and the hydrophobic tail is oriented up to the outer surface, producing a considerable change of the resultant wettability. The morphology of the coatings has been analysed before and after CVD-silanization process, and an important change in the topographic surface has been observed because an increase in the surface roughness has been clearly obtained after CVD-silanization process, corroborated by AFM images. The roughness (RMS) before silanization (as prepared electrospun fibres) was 152 nm, whereas the roughness value after CVD-silanization process was 337 nm.

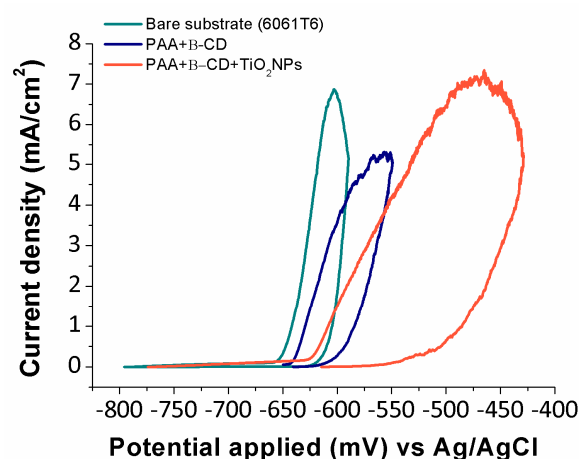


Figure 15. Cyclic polarization curves in 3.5% NaCl solution of aluminium bare substrate (black line), crosslinked PAA+ β -CD electrospun fibres (blue line) and crosslinked electrospun fibres with metal oxide nanoparticles (PAA+ β -CD+ TiO_2 NPs) (orange line). Reprinted with permission of [53].

4. Emerging Trends of Electrospun Coatings: The Case of Biocorrosion

Electrospinning, due to the ability of combining surface texturing with compounds encapsulation, has started to being regarded as a very promising technique for preventing a specific type of corrosion caused by microorganisms, biocorrosion. In this final section, some clues and examples of this

incipient application are gathered. Corrosion processes can be influenced by the metabolic activity of some microorganisms [80,81]. This type of corrosion, termed microbial induced corrosion (MIC), or biocorrosion, affects most of the systems exposed to a biological environment, including marine structures [82,83], offshore oil and gas industries [84,85], water distillation and other separation processes [86–88] and biomedical devices [89–91], where the proliferation of microorganisms can provoke implant-associated infections [92,93]. From the US \$2.2 trillion of annual cost of corrosion worldwide estimated by the World Corrosion Organization [94], the economic burden imputed to biocorrosion could be getting on for 20%, that is \$440 billion yearly [95–98].

Microorganisms act on the corrosion reactions by oxidation or reduction of the passivation layers, production of acids and corrosive compounds, protein secretion (catalysers, enzymes) and the formation of extracellular polymeric substances (EPS) that modify the interface between the metal and the medium [99,100]. Chemolithotrophic organisms obtain energy from the oxidation and/or reduction of inorganic compounds [101,102], namely iron, sulphur and manganese [103,104]. Nevertheless, microorganisms can interact with other elements such as chromium, molybdenum, vanadium, technetium, polonium, uranium, neptunium, plutonium and other rare earth elements [103,105–107]. The role of microorganisms on corrosion is modulated by multiple factors and their effects cannot be attributed to a specific organism or chemical reaction: some microorganisms and biofilms have been proved to have inhibitive effects on corrosion [108]. This is a very promising corrosion control approach yet still restricted, as the growth of microorganisms and biofilm formation are still hard to control and predict in operating, non-laboratory conditions [102]. The complex interactions of corrosion reactions with the metabolism of microorganisms make MIC a particular type of corrosion that needs dedicated, cross-cutting approaches. Most of the current approaches rely on two general strategies: killing the microorganisms in planktonic state before they adhere to the surface by releasing active compounds and texturing of the surface to prevent bacterial adhesion and biofilm formation. The principal advantage of the electrospinning technique is the possibility to control both active compound release and surface texturing in a precise and simple way.

4.1. Release of Active Compounds

An approach to prevent MIC is to use antimicrobial agents to kill the microorganisms in planktonic state before they adhere to the metal surface. Electrospun fibres provide matrices in which active compounds can be incorporated. Fibres with a core-shell structure fabricated via coaxial electrospinning can be loaded with a core of antimicrobial compounds [109,110], as well as corrosion inhibitors and self-healing agents [111]. The shell of the fibres will serve to protect and control the release. Alternatively, nanoparticles can be used to carry active compounds [90]. Widely used in the biomedical sector for tissue engineering scaffolds fabrication, electrospun fibres have been successfully used as a protective barrier to enhance the biocompatibility of magnesium alloys whilst improving the corrosion resistance. The good mechanical resistance-to-weight ratio, mechanical properties close to human bone, good biocompatibility and biodegradation properties, which permits avoiding surgeries for removal, makes Mg alloys good candidates for medical prostheses [112]. Nevertheless, their in-vivo corrosion rate and degradation, which causes hydrogen release and alkalization of the pH, are hard to predict and are up to this time a challenge [90,113]. Surface modifications and coatings can often be needed [114].

Bakhsheshi-Rad and collaborators coated Mg-Ca (1 wt%) specimens with poly-L-lactic acid electrospun nanofibres and Åkermanite (AKT) nanoparticles. The coated specimens exhibited a higher corrosion potential (−1594 mV) in the Tafel curves compared to bare Mg samples (−1724 mV). The EIS analysis suggested a formation of a protective layer on the metal surface (CPE in the equivalent circuit) when the AKT was present in the fibres. The PLLA-AKT fibres successfully preserved the mechanical properties (compression test) of the Mg specimens after immersion in simulated body fluid for 7 days. In a further step, the PLLA-AKT fibres were loaded with an antibiotic (Doxycycline). The resulting coating considerably increased antibacterial response compared to fibres with no doxycycline and maintained a good biocompatibility with low concentrations of doxycycline (5 wt%) [90]. This

study is an illustrating example of how electrospun nanofibres can be enriched with active compounds to modulate corrosion processes and microorganism activity. Electrospinning can be combined with other coating techniques to design nanostructured coatings. With the aim of improving the corrosion and antibacterial properties of Mg-Zn-Ca alloys, the team of Bakhsheshi-Rad designed a bi-layer coating composed by a first compact layer of tantalum pentoxide deposited by magnetron sputtering covered by electrospun PCL (poly (ϵ -caprolactone)) nanofibres with embedded magnesium oxide-silver nanoparticles. The Ta₂O₅-PCL coating improved the anticorrosion performance on the potentiodynamic polarization test, with $E_{\text{corr}} = -1549$ mV, compared to the approximately -1800 mV of the bare metal. The addition of the PCL fibrous coating with magnesium oxide-silver nanoparticles significantly reduced the bacterial growth compared to both uncoated alloy and Ta₂O₅ coated samples [115]. Analogously, in work [116], poly(ϵ -caprolactone) fibres and zinc oxide nanoparticles (ZnO NPs) composite coatings have been also applied on magnesium alloys (AZ31) to improve the corrosion resistance and biocompatibility of this metallic alloy. Polyetherimide (PEI) is used as a protective barrier for corrosion, notably for biomedical applications, given its good biocompatibility [117]. The electrospinning technique can be used improve the surface properties of the PEI coatings and to obtain hydrophobic surfaces ($\text{WCA} > 115^\circ$) with good resistance to chemical attack (DMF-ethanol) [97]. Artifon et al. were also able to improve the resistance of these fibrous PEI coatings against bacterial colonies by embedding ZnO powder (10–50 wt%), an antibacterial agent and corrosion inhibitor [118,119], into the polyetherimide (PEI) fibres. The ZnO-PEI scaffolds fabricated by electrospinning furnished good inhibition against *S. aureus* and *E. coli* in harsh environments. Other examples of the use of ZnO in combination with TiO₂ prove the good antibacterial properties of this strategy [120].

The use of antimicrobial compounds has been widely used to prevent biocorrosion, of what the presented cases are examples. This approach has nonetheless evident limitations associated to the resistance of microorganisms to the antimicrobial compounds. Biofilms not only concentrate most of the corrosion sites, but also increased substantially the resistance to antimicrobials, compared to microorganisms in planktonic state [121,122]. Higher concentrations of the antimicrobial are thus needed, which will cause more resistance of the microorganisms in a long term. In addition, high concentrations of antimicrobial agents, together with deficient release control result on cytotoxicity and damage to non-related organisms. It is of interest then, to prevent microorganisms to adhere to the surface and form biofilms in a way that the use of biocides is limited, if possible.

4.2. Surface Texturing: Antifouling Surfaces

Chan et al. showed the ability of electrospun gelatine coatings to hamper pH alkalization and ion release of Mg-Zn-Ca biomedical alloys without embedding further bactericide agents. The pH measurements were lower on Mg samples coated with crosslinked gelatine fibres compared to bare Mg ($p < 0.05$) at 0.03% CO₂ concentrations. The release of Mg⁺² was also significantly mitigated at the three CO₂ concentrations compared to bare samples ($p < 0.05$). The gelatine coated samples showed no indirect toxicities in the cytotoxicity assay and provided for cellular attachment with good viability [89]. Indeed, hydrophobic coatings obtained by electrospinning are able to trap air within the gaps between the hydrophobic electrospun membranes and the electrolyte. Studies with PVDF-based coatings successfully prevented organisms and pollutants in seawater to be deposited on the surface [87]. Nevertheless, it is also reported that high hydrophobicity can have a deleterious effect on protein adsorption. Chitosan coated PVDF-HEMA electrospun nanofibrous membranes ($\text{WCA} = 72^\circ$) absorbed less than half of concentrated BSA than the more hydrophobic PVDF-only membranes ($\text{WCA} = 132^\circ$) [123]. The morphology of polymers with good biocompatibility as PVA can be tuned with the electrospinning technique to obtain surfaces that prevent bacterial adhesion [86], making it a strategy to generate biocompatible and antibacterial coatings. Moreover, nature is also a model for the design of bioinspired coatings. Looking at the adhesion mechanism of marine mussels, Son et al. bonded silver nanoparticles to catechol-grafted PVA fibres and obtained fibrous coatings with potential antibacterial properties [124].

Despite the youthfulness of this field of application, clear trends can be drawn from the current use of electrospun nanofibre coatings for the prevention of microbial influenced corrosion. The combinations of polymer precursor, fibre shape, release of corrosion inhibitors and release of biocides, combined with surface texturing, permit to adapt the technique to a wide range of user requirements. Moreover, its consolidated presence in fields such as tissue-engineering, from which an important know-how can be learnt, puts this technique in a very advantageous position for future coating development.

5. Summary Table

To sum up, in order to have a better understanding of the different anticorrosive coatings analysed in this document, a summary of the different coatings employed as well as the corrosion tests performed onto different metallic substrates is shown in Table 1.

Table 1. Summary of the different sensitive electrospun coatings, the metallic substrates used and the resultant corrosion tests for the development of new and innovative protective coatings with good anticorrosion properties.

Coating	Metallic Substrate	Corrosion Tests	Reference
PHBV	Magnesium alloy (AZ31)	Tafel polarization curves and immersion test	[41]
PLLA	Pure magnesium and Magnesium alloy (AZ91)	Hydrogen evolution after immersion test in Hank's solution	[43]
PCL	Magnesium alloy (AZ31)	Weight loss and immersion test	[44]
PCL	Magnesium alloy (AZ31)	Immersion test	[45]
PLA	Die casting magnesium alloy (AM50)	Tafel polarization curves, immersion test and weight loss in SBF	[46]
PCL/HA-NPs/simvastatin	Magnesium alloy (AZ31)	Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[47]
PANI/PMMA	Q325 carbon steel	Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[48]
PANI/PMMA	Q235 carbon steel	Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[49]
PANI/PMMA (primer) and PS (topcoat)	Q235 carbon steel	Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[50]
PAN-Al ₂ O ₃	Zinc sheet	Hydrogen evolution, Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[51]
PVA/glyoxal	Aluminium alloy (AA6082)	Electrochemical Impedance Spectroscopy (EIS)	[52]
PVDF/SA	Aluminium sheets	Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[55]
PANI-PFOA/PS	Q235 carbon steel	Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[56]
PVC PS	Brass	Cyclic potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS)	[57]
PVC	Aluminium, copper and brass	Cyclic potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS)	[58]
PVA PVC	Aluminium	Cyclic potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS)	[59]
PS	Aluminium	Potentiodynamic polarization curves	[60]
PS/Al ₂ O ₃	Commercial aluminium foil	Electrochemical Impedance Spectroscopy (EIS)	[61]
PS/mod-SiO ₂	Magnesium alloy (AZ31)	Potentiodynamic polarization curves	[62]
(PFDA-co-AA)-b-PAN)	Aluminium alloy (AA2024T3)	Acetic acid salt spray test	[63]
PVA/glyoxal doped with cerium nitrate and cerium acetylaceton	Aluminium alloy (AA6082)	Electrochemical Impedance Spectroscopy (EIS)	[64]
PVA/GA doped with CeCl ₃ and Li ₂ CO ₃	Aluminium alloy (AA2024-T3)	Electrochemical Impedance Spectroscopy (EIS)	[65]

Table 1. Cont.

Coating	Metallic Substrate	Corrosion Tests	Reference
PVC/Ceria NPs	Aluminium	Cyclic potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS)	[66]
PVA@PVDF doped with MBT	Q345 carbon steel	Scanning Kelvin Probe (SKF) and Electrochemical Impedance Spectroscopy (EIS)	[67]
PDMS/PDES@PVA DBTL@PVA	Carbon steel	Linear polarization	[68]
PVA@(OA+BTA)	Carbon steel	Electrochemical Impedance Spectroscopy (EIS)	[69]
Nylon/BTA	Copper	Electrochemical Impedance Spectroscopy (EIS)	[70]
PVDF-ZnO	Aluminium alloy	Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[71]
PVC-ZnO	Aluminium alloy (AA6061-T6)	Tafel polarization curves and pitting corrosion	[72]
PVC-ZnO PS-ZnO	Aluminium alloy (AA6061-T6)	Tafel polarization curves and pitting corrosion	[73]
CA nanofibres and HAP/CHI solution by dip-coating	304 stainless steel	Electrochemical polarization curves and electrochemical impedance	[77]
PCL and epoxy resin by spin-coating	Carbon steel	Linear sweep voltammetry	[78]
TPOZ+GPTMS and PVA doped with Ce(NO ₃) ₃ and CeO ₂	Aluminium alloy (AA2024-T3)	Electrochemical Impedance spectroscopy (EIS)	[79]
PAA/ β -CD/TiO ₂ NPs and CVD-silanization process	Aluminium alloy (AA6061-T6)	Tafel polarization curves and cyclic potentiodynamic polarization curves	[53]
Sputtering Ta ₂ O ₅ and PCL/MgO-Ag	As-cast Mg-Ca-Zn specimen	Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[115]
Gelatin	As-cast Mg-Ca-Zn specimen	Metal ion concentration and pH monitoring	[89]
PLLA-AKT-DOXY	As-cast Mg-Ca specimen	Tafel polarization curves, Electrochemical Impedance Spectroscopy (EIS) and hydrogen evolution	[90]
PCL/ZnO	Magnesium alloy (AZ31)	Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS)	[116]

6. Conclusions

Electrospinning is a fast emerging technique which enables the fabrication of nanofibres with a desired morphology, attracting the attention in the nanotechnology field for the design and development of nanomaterials. The advantages associated to this nanodeposition technique such as simplicity, versatility, cost-effective and scalability make electrospinning of great interest for technological applications which can provide corrosion protection of metallic surfaces. The aim of this work is to present to the reader an overview of the possibilities that the electrospinning technique offers to the design of anticorrosion coatings. This exhaustive review presents different types of polymeric precursors used in the electrospinning process (natural, biodegradable, synthetic or copolymers), the encapsulation of corrosion inhibitors and self-healing agents as well as the different operational processing parameters that can be adjusted to obtain electrospun coatings with a desired morphology, porosity and topography. Finally, an emerging trend of the electrospun coatings in the field of biocorrosion is also presented, being of great importance in biomedicine and offshore industries. To sum up, this is the first time a review on the use of electrospun nanofibres to improve the corrosion protection of metallic surfaces is presented in literature.

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