

A Review on the Latest Developments of Conducting Polymer and Composite Coatings for Enhancing Biocompatibility and Corrosion Resistance of Metallic Biomedical Implants

Mohammed Razzaq Mohammed, Safaa Hashim Radhi, and Ahmed Namah Hadi

Abstract — The utilisation of metals and alloys in the biomedical field was and is still of immense importance for human life. Typically, the materials used for metallic biomedical applications, particularly those are implanted *in vivo*, provide appropriate mechanical and biological properties that allow them to accomplish the purpose for which they are used. Nonetheless, there are some inherent limitations impede the optimal use of these materials. One of the most crucial determinants is corrosion, which results in several other problems such as the formation of toxic substances that can not only cause necrosis of the cells attached to the implant, these toxins could also be carried by blood into body tissues and organs. This in turn leads to dire consequences on patient's life. Although a wide variety of approaches may be available to address the corrosion issue, it is alleged that coating these metals and alloys with polymers, especially the conductive ones, is among the best strategies in this regard.

This review will highlight the latest developments in using conductive polymers including polypyrrole, polyaniline, polythiophene and their composites in order to enhance biocompatibility, mechanical properties and most importantly corrosion protection performance of metallic implants. The findings obtained from coating 316L stainless steel, titanium and magnesium alloys, which have been widely manipulated in biomedical field as long and short-term implants, will be evaluated.

Key words — Biocompatibility, Composites, Conducting Polymers, Coating, Corrosion, Metallic Implants.

I. INTRODUCTION

Metallic materials have an essential role to play as biomaterials due to the fact that they can regenerate or replace the damaged tissue and some of the body parts. Compared to polymers or ceramics, metals have appropriate tensile properties and superb fracture toughness which make them highly applicable for load-bearing applications, for instance [1-3]. Even so, some disadvantages are still accompanied with using of metallic materials. These include the likelihood of releasing ions that could negatively impact compatibility, human tissues and causes inflammation in the course of the rehabilitation [4]. Furthermore, when the implant is placed inside the body, it is subjected to ongoing degradation by an

electrochemical attack as a result of the presence of greatly oxygenated, saline, electrolytic environment of the body. Various corrosive substances present in the blood and other components of body fluids such as water, amino acids, plasma [5], various anions, cations, organic substances of low and high molecular weight matter and dissolved oxygen are caused such degradation [6], [7]. Corrosion of metal implant is also considerably related to the changes in the pH value where this could extremely be reduced because of a number of factors such as diseases and infections, leading to implant failure. Implants with mobile components can develop accelerated corrosion by the mechanical wear; longevity of a hip replacement is shown to be no further than a decade, for example [8].

The use of implantable medical devices and orthopaedic implant is being growing recently in which the orthopaedic biomaterial market recorded more than one third of the total biomaterial products market [9]. The metallic materials that have been broadly utilised as metallic implants are 316L stainless steel (316L SS), pure titanium (Ti) and Ti alloys, and cobalt-chromium alloys (Co-Cr) (Fig.1). Generally, the biocompatibility, high mechanical strength and corrosion resistance of these metallic materials have promoted their use in biomedical applications, particularly in orthopaedic and orthodontic implants. Some of metallic implants and their applications in human body is presented in Fig.1.

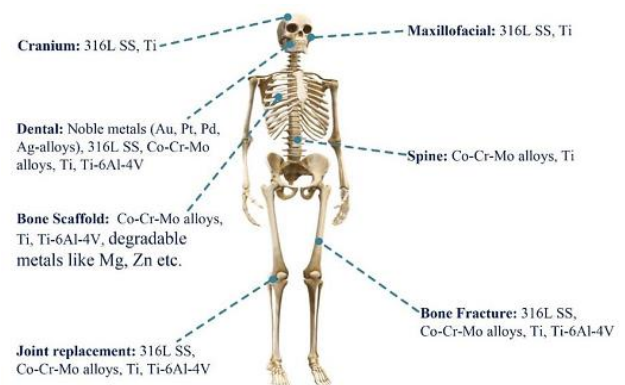


Fig. 1. Some of metallic implants and their applications in the human body [10].

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M. R. Mohammed, Department of Mechanical Engineering, College of Engineering, University of Misan, Iraq.

(e-mail: mohammedrazzaq14@uomisan.edu.iq)

S. H. Radhi, Department of Materials Engineering, College of Engineering, University of Kufa, Iraq.

(e-mail: safaa.radhi@uokufa.edu.iq)

A. N. Hadi, Department of Biomedical Engineering, College of Engineering, University of Babylon, Iraq.

(e-mail: ahmed.hadi.eng@uobabylon.edu.iq)

Ease of formation, moderately low price and corrosion resistance of stainless steel make this material to be regarded as one of the most satisfactory metallic biomaterials. The 316L SS is generally utilised in orthopaedic, long-term implants, non-permanent implants and dental applications [11]-[13]. Not only bare 316L SS biocompatibility is still a concern despite being approved by the US Food and Drug Administration [14], [15], both permanent and provisional implants have also been developing such biocompatibility issue [16]. Furthermore, the presence of alloying elements including chromium and nickel can be enormously dangerous causing serious issues such as immunoreactions and inflammatory responses since some of these materials are toxic and carcinogenic [13], [17], [18]. In order to overcome this problem, the surface modifying or coating is of great importance to increase the biocompatibility of the 316L SS implants. Applying protective coatings can be an effective method to protect the surrounding tissues from the harmful corrosion products that could be released from the implant. In this respect, several materials have been utilised as coatings for 316L SS implants; while some of these contain metal oxides [19]-[21], others comprise of organic materials and also conducting polymers [22], [23].

From corrosion resistance perspective, 316L SS alloy is protected by a passive film produced on its surface; nevertheless, this biomaterial is susceptible to localised attack make it potentially undergoing corrosion in strong chloride solutions. Therefore, the use of these alloys can be highly influenced by such localised corrosion [24], with even further implications in the biomedical field [25], [26] (Fig.2). Conducting polymers is one of a number of approaches that have been utilised to create additional protective interfaces on 316L SS [27]-[29].

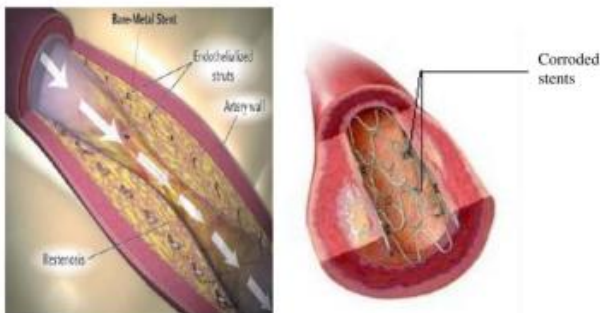


Fig. 2. Metal stent corrosion [30].

Another substantial class of biomaterial that has been extensively utilised, particularly in orthopaedic and dental related applications is titanium (Ti) or Ti-based alloy [31], [32]. Ti and its alloys have good ductility, biocompatibility and lower corrosion rate in comparison with SS and Co alloys [33]. Despite causing no unfavourable biological reaction, the long-run stability of Ti-based implants cannot be thoroughly affirmed. The deficiency of surface stability due to corrosion could form several undesirable effects. Alloying of Ti implants with other metals such as aluminium (Al) and vanadium (V) or Al and niobium (Nb) can improve corrosion resistance. For example, the low corrosion rate, durability, low modulus of elasticity and high osseointegration of the Ti-6Al-4V alloy make it frequently used in both orthopaedic and orthodontic implants [34]-[36]. Nevertheless, studies have

revealed that the alloy's components can result in a number of serious health problems including peripheral neuropathy. The presence of toxic V, on the one hand, and the release of Al and V ions from the alloy cause such deleterious health issues [37].

Since the majority of the *in vivo* utilised metals are bioinert and have diminutive degradation levels [38], [39], they developed some negative issues including the stress shielding, lack of supporting the surrounding tissue to grow and body inflammation [39], [40]. Meanwhile, as metal implants are heavy [41], [42], Mg alloys could be a proper candidate in this respect because of their high specific strength, degradability and cytocompatibility [42], [43]. Owing to having comparable density and modulus of elasticity to that of bone, Mg alloys does not experience stress-shielding phenomenon [44], [45]. The innocuous degradable products that are excreted in urine eliminates the need for a second operation to remove the biodegradable Mg-based implant; consequently, this greatly reduces the financial burden and patient concerns. These alloys can be even more appropriate for bone tissue applications due to the comparable mechanical properties as well as to the capability of these materials to promote bone growth and adjust neuromuscular activity [46], [47]. Despite such merits, enhancing the cytocompatibility and controlling the degradation rate of Mg alloys to be utilised for bone tissue regeneration need further work to be done [48]-[50]. Moreover, lack of control over degradation may lead to profound negative consequences such as failure of the implanted part and could even threaten patient life [51], [52]. Additionally, the mechanical properties and the growth of the neo-tissues are also greatly related to the balanced degradability of such alloy [53]-[55]. Like some other metallic implants, improving bioactivity, biocompatibility and corrosion resistance of Mg implants can be achieved by alloying, surface treatment, and coatings. From financial point of view, the surface treatment and coating procedures have received increased attention compared to the alloying method [56], [57]. Even though diverse kinds of polymer and ceramic coatings have been available to reduce the corrosion rate and improve bioactivity and biocompatibility of Mg alloys [57], corrosion resistance obtained using ceramic coatings as not high as that achieved using polymer coatings [58]-[60]. More merits can be offered by biodegradable and resorbable polymers in comparison with coatings of metals or ceramics, particularly in terms of ease of manufacture and lower levels of possible infection and implant rejection [61]-[65].

II. CONDUCTING POLYMER AND ITS COMPOSITE COATINGS

In the last few decades, the interest in using polymers has increased remarkably in various biomedical fields such as tissue engineering [66], [67], drug delivery [68], [69], and dental technology [70], [71]. Among the different types of polymers, there is a class, which is called conductive polymers or conducting polymers (CPs), has some unique characteristics allowing it for use in distinctive applications that conventional polymers may not be able to achieve. The electrical conductivity in CPs is attributed to π - electron backbone; single and double bonds alternate all over the

polymer chain [72]. π -conjugated systems structural and morphological disorder is decreased when they are doped. This can open the door to develop a wide range of CPs that their conductivity could be tuned easily from the insulating to the metallic spots. As illustrated in Fig.3, undoped polymers have conductivity is in the region between semiconductor and insulator. Interestingly, the conductivity of undoped polymers can be folds improved through doping in which these polymer conductivities following doping can be comparable to those of some metals [73], [74]; therefore, they are regarded as a proper material to be used in electronic applications [75].

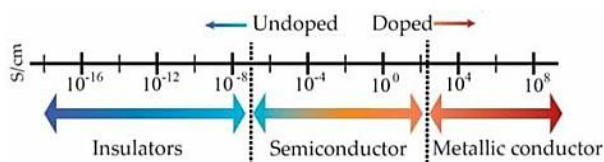


Fig. 3. CPs conductivity range [75].

In the biomedical field, beside to biosensors [72], [76] drug delivery [76], [77], CPs have been widely utilised in area of engineering human tissues including nerve tissue [78], [79], cardiac tissue [78], [80], skin tissue and wound healing [78], [81]. The use of CPs as a coating for preventing metal corrosion was first described by DeBerry in 1985 when polyaniline was used to coat stainless steel [82]. Because of their appropriate properties including easy fabrication, high conductivity, eco-friendly nature, affordable price and nontoxicity, these materials have been evaluated substantially [83], [84]. Despite being some debates about their protective mechanism, CP coatings are thought to improve anticorrosion of metals [84]-[86] by establishing a physical barrier, inhibition and passive oxide layers [85]. With suitable dopant molecules, CPs can be electropolymerised on substrates, leading to a conductive and electroactive film that can have distinctive redox reactions with the metal [83]. A number of mechanisms have been provided to clarify CPs corrosion regulation due to the presence of various kinds of CPs and dopants. The utilisation of dopant released from the CP, a barrier layer, shifting of the electrochemical interface and anodic protection are some of these mechanisms [83], [84], [87]. It is also pointed out that CPs can serve as a self-healing coating through protecting exposed areas of the substrate electrochemically [88], [89].

A. Polypyrrole (PPy) and PPy-based Composites

PPy has high electrical conductivity and can be easily fabricated and modified. Besides, it has good biocompatibility with mammalian cells; therefore, it is alleged to be the most examined conductive polymer for biomedical applications [90]-[92]. PPy has the capability to promote cell adhesion and ingrowth of various cell types [93]-[95]. The biocompatibility of PPy film coated implants has been confirmed in a variety of studies both *in vitro* and *in vivo* [96]-[99]. Along with the biocompatibility and because of the stability of PPy, which preclude the electron exchange between the metallic material and the biological materials, PPy coating has an exceptional corrosion resistance [98]. PPy has been employed for several biomedical applications such as tissue engineering [90], [93], drug delivery [100], and

biosensors [72]. PPy can straightforwardly be produced in large quantities in different solvents [101]-[103]. Nonetheless, inadequate mechanical strength, lack of ductility, processability and PPy bone bonding capability are required to enhance. Pristine PPy is barely utilised in most biomedical applications by reason of the difficulties in its processing once fabricated since it is brittle, rigid, and insoluble [90], [104]. To overcome these limitations, developing composites based on natural and biodegradable polymers with proper conducting substrates is a common procedure [105], [106].

The enhancement of corrosion resistance and biocompatibility is being considerably crucial in recent implant technology. Improving surface properties for biomedical implants can be successfully achieved using biocompatible nanocomposite coatings where hybrid implant coatings with various chemistry, functionality, and biocompatibility components have been drawn remarkable attention in a variety of biomedical applications. Cyclic voltametric technique was used to prepare PPy/zirconia nanoparticles (ZrO_2) nanocomposite coatings electrochemically on 316L SS in aqueous solution of oxalic acid for orthopaedic implants. Owing to their hydrophilic, smooth, compact and less porous surface morphology compared to nanoparticles-free PPy coatings, the PPy/ ZrO_2 coatings had superior biocompatibility and reduced corrosion rate on 316L SS [106]. PPy was also strengthened with functionalised multi-wall carbon nanotubes (CNTs) that was deposited on 316L SS by means of electrochemical method. Dispersion of the CNTs within the nanocomposite was relatively uniform. The hardness and surface wettability of the PPy/CNTs coatings were shown to enhance. 316L SS coated with PPy plus CNTs displayed corrosion potential better than uncoated 316L SS when both alloys placed in simulated body fluid (SBF) [107]. Kumar *et al.* fabricated PPy/graphene oxide (GO) nanocomposites by electropolymerisation to be applied on 316L SS implants. Dispersion of the GO nanosheets within the PPy matrix was verified, and enhancements in surface protective and biocompatibility of MG-63 human osteoblast cells of PPy/GO coatings on 316L SS implants were clearly achieved [108]. Bilayer coatings by electropolymerisation of PPy on 316L SS followed by the electrodeposition of porous strontium hydroxyapatite (Sr-HA) were successfully developed. The PPy/Sr-HA bilayer coated 316L SS could have the highest Rp value, and could reduce both the release of metal ions and corrosion rate for the implant for a longer period. Besides, owing to their chemical and biological resemblance to the bone tissue, and the presence of pores that can promote cell proliferation and differentiation, the porous coating may stimulate fixation of implants to host bone [109].

In order to increase biocompatibility and corrosion resistance of 316L SS for orthopaedic and dental applications, the substituted hydroxyapatite (I-HAp)/silica nanotube (SiNTs)/PPy coating on 316L SS was formed by electrophoretic deposition procedure. An efficient anticorrosion rate in SBF solution of this alloy by this bilayer composite coating was verified. The I-HAp plus SiNTs coating diminished metal ions dissolution ratio. Good mechanical properties of the composite were obtained due to the presence of SiNTs while the I-HAp improved the

formation of apatite that was confirmed in the SBF for different time points of incubation. *In vitro* MG-63 cells attachment and viability were higher for the I-HAp/SiNTs/PPy compared to that ppy-coated free substrates [9]. In another work, coatings of PPy and TiO₂ were electrochemically produced on 316L SS in oxalic acid solution. 316L SS coated with PPy/TiO₂ nanocomposite displayed greater biocompatibility and improved corrosion performance compared to the alloy coated with pristine PPy coatings [110]. In a study by Kumar *et al.*, PPy/Nb₂O₅ nanoparticles composite coating was synthesised and coated on 316L SS by electrochemical deposition. The existence of these nanoparticles was shown to strongly influence the surface nature of the nanocomposite coated 316L SS along with improving its microhardness. The electrochemical and biocompatibility studies in SBF and on MG63 osteoblasts, respectively indicated that the coatings displayed proper corrosion protection and biocompatibility by contrast with PPy modified 316L SS [11].

Combinations of natural biodegradable and synthetic polymers can be useful in developing advanced biomedical materials. Composites were formed from PPy/chitosan via electrochemical polymerisation in oxalic acid solution for potential use in coating 316L SS implants. Because of the presence of chitosan within PPy, surface hydrophilicity was observed to improve. The coatings exhibited improved corrosion protective performance in comparison with pristine PPy. The composite containing equal amounts of these materials was noticed to be biocompatible which was confirmed through the growth of MG-63 cells on this composite [111]. Electrodepositions of a PPy film and a coating of CaP doped with different Si concentrations were investigated under steam sterilisation conditions when these multilayer coatings were used on 316L SS. Relying on sterilisation resistance and good biocompatibility, this multilayer coated 316 L SS biomaterial could be proper for orthopaedic and dental applications [112].

Conductive polymer coatings are not only used with steel alloys but have also been utilised to improve the properties of many other alloys. In order to enhance osteointegration performances of Ti–Al–V substrates, De Giglio *et al.* utilised PPy film as protective coatings [99]. PPy/calcium phosphate (Ca-P) and PPy/ poly(sodium-4styrenesulfonate) (NaPSS)/Ca-P coatings were produced by electrochemical deposition of PPy and PPy/PSS onto Ti alloy. Following immersing in SBF solution for 24 h, the corrosion resistance of PPy/PSS/Ca-P coating was influenced by structural alterations of coating owing to the potential interactions between PSS- and Ca²⁺. Moreover, PPy/Ca-P coating promoted osteoblast cell viability, and the amount of Ca-P deposited on the coating was displayed to control the osteoblast metabolism [113].

The Ti-6Al-V alloy that containing high percentage of V has a higher corrosion resistance than that having lower content. However, as depicted from SEM/EDX analyses (Fig. 4), the surface of Ti-6Al-4V alloy after two days of immersing in SBF solution was shielded with corrosion related substances that had some flower shaped-like morphology on the surface. The percentage of Ti was much lower (62.70%) than that of its original presence in the alloy (86%) due to the surface coverage with corrosion products. It was revealed that Ti-6Al-4V had V and O percentages of

4.50% and 19.98%, respectively which are as higher as those of Ti-6Al-2V alloy, resulting in a strong probability of oxide film generation [114]. Therefore, the corrosion rate in implantable Ti-6Al-4V alloy needs to be decreased; coating it with CPs could be an effective strategy in this respect. Martinez *et al.* used sodium salicylate-contained solution to produce PPy films potentiostatically as a coat on this alloy for dental implant applications. The immobilisation of Zn species was carried out either after the PPy electropolymerisation or during the electrosynthesis process. The coating acquired by the latter technique presented antibacterial resistance against *Staphylococcus aureus*. Artificial saliva at pH 4 was utilised as electrolyte to simulate the intraoral condition; coating the electrode with neat and modified PPy illustrated an appropriate corrosion behaviour. The steady state current densities and Ti and V ions release were revealed to decrease following the coating process. After the samples had been immersed in AS solution, they were intact where no corrosion related appearances were distinguished [115].

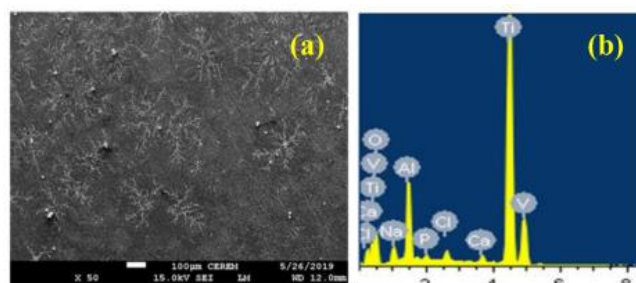


Fig. 4. (a) SEM images and (b) Energy Dispersive X-Ray for the Ti-6Al-4V alloy that was immersed in SBF for 2 days prior to stepping the potential to 500 mV (Ag/AgCl) for 30 min [114].

PPy/polyethylene glycol (PEG) composite film was prepared to improve the corrosion rate and biocompatibility of Ti6Al7Nb alloy. PEG resulted in additional stable composite films on the Ti alloy with lower corrosion rate and higher hydrophilic behaviour compared to the neat film. Regarding the cellular activity, incorporating PEG within PPy had no significant increase in G292 human osteoblasts viability and proliferation [116]. Ungureanu *et al.* incorporated torularhodin into PPy to make composite film for modification of Ti-based implants surfaces. This composite was revealed to act as an anticorrosion coating and has antibacterial activity and no detrimental impact on cell viability [117]. Rikhari *et al.* used potentiostatic method to deposit PPy/CHI composite coating on Ti. They found that the improvement of hydrophilicity, microhardness, corrosion resistance (protective efficiency of 95%), growth of HAp and biocompatibility of Ti implant could be achieved by PPy/CHI composite coating, suggesting greater potential for bone implants [118]. Pectin was added to PPy to form multifunctional composite coatings that can be used to increase the biocompatibility, antibacterial behaviour and corrosion resistance of TiNbZr. These composite coatings laden with gentamicin (GM) and deposited on TiNbZr. Effective antibacterial performance and controlled degradation of the composite were achieved because of the release of GM, and compared to other formula, incorporating 10 wt. % of GM in these composite coatings displayed favourable results in terms of lowering corrosion rate in SBF, improving biocompatibility and antibacterial performance

[119]. The higher surface roughness and the increase in adhesion strength and the lower wettability of PPy/GO composite-coated were confirmed. Moreover, a higher polarisation resistance (R_p) and corrosion protection for this coating were displayed. The PPy/GO coating demonstrated a higher impedance in SBF and a higher resistance whereas the biocompatibility of PPy/GO coating was evaluated *in vitro* using MG-63 cell culture studies [120]. In another research, a composite coating of PPy/ZnO was developed by Guo *et al.* [121] to protect biodegradable Mg alloys for orthopaedic implants. Corrosion rate, antibacterial property and cytocompatibility were shown to enhance for the composite coating. PPy/gelatin (Ge) composite coatings were also developed to enhance the biodegradability and corrosion of AZ31 Mg by anodisation and electrodeposition. Corrosion analysis showed that the anodisation layer powerfully enhanced the corrosion resistance behaviour of modified AZ31 Mg [122]. PPy coating was also revealed to be effectually contributed to a reduction in the corrosion rate of WE43 Mg alloy and production of H_2 gas after nearly a week of immersion in m-SBF [123]. In a study by Kumar *et al.*, the surface of AA2024 alloy was coated with PPy/ CeO_2 nanocomposite through the electrochemical polymerisation. Thermal stability of the formed nanocomposite was confirmed to improve. Potentiodynamic polarisation and electrochemical impedance spectroscopic (EIS) for the electrochemical corrosion behaviour revealed that a high loading of CeO_2 in the composite could lead to a larger shift of E_{corr} in the positive direction. Furthermore, EIS studies also indicated that incorporating of these nanoparticles in the PPy coatings improved corrosion protection efficiency of PPy/ CeO_2 coatings with higher charge transfer resistance, and lower CPEDl in comparison with CeO_2 -free PPy coating [124].

B. Polyaniline (PANI) and PANI-based Composites

Over the last few decades, PANI has received substantial attention in numerous industrial and biomedical areas because of its uncomplicated fabrication, extraordinary electrical conductivity, biocompatibility and low toxicity [125], [126]. Besides, PANI has extensively been studied in the field of anticorrosion [127]-[129]. However, PANI has some disadvantages that restrict its application including the difficult solubility in the majority of the available solvents, and poor processability [130], [131]. Even though studies indicated that PANI promotes cell ingrowth and proliferation, recent studies showed an opposite behaviour. For instance, increasing the ratio of PANI incorporated into PCL was revealed to reduce the viability of hADSC cells on this scaffold (Fig.5) [132]. Additionally, PANI electrical conductivity reduces in a long-term [131] and the weak thermostability and mechanical integrity [133], [134]. A number of strategies including re-doping with the functionalised organic acids, polymer copolymerisation, and the fabrication of the blends and composites with several materials have been established to overcome the reported limitations [135].

PANI nanocomposites are among the most favourable CPs composites displaying an electrical conductivity by integrating PANI with nanofillers. Shabani-Nooshabadi *et al.*

used the galvanostatic method to fabricate PANI-montmorillonite (MMT) nanocomposite coatings to be assessed on 316L SS surface in terms of anticorrosion performances. What they found was that, in an acidic environment, the PANI-MMT nanocomposite was shown to be an excellent potential to protect 316L SS against corrosion [136]. An Ag-contained poly(amide-amine) dendrimer was used as a dopant for the polymerisation of PANI on Ti for potential using in the coating of hard tissue repairing implants. The antibacterial behaviour of the resulted PANI coating against *E. coli* and *S. aureus* was observed to be much higher to that of pure Ti. From biocompatibility perspective, this coating not only promoted the proliferation and differentiation of MC3T3, the alkaline phosphatase activity and intracellular calcium content of the cells were displayed to rise [137]. In another study, PANI was added to TiO_2 nanotubes then this composite was used to coat Ti implant. PANI-2/TNTA nanocomposite exhibited lower corrosion current density and higher R_p , resulting in reduced corrosion rate in physiological environment. PANI-2/TNTA nanocomposite promoted cell adhesion and proliferation of MG-63 osteoblasts, increased antimicrobial activity and reduced implant-associated infections [138].

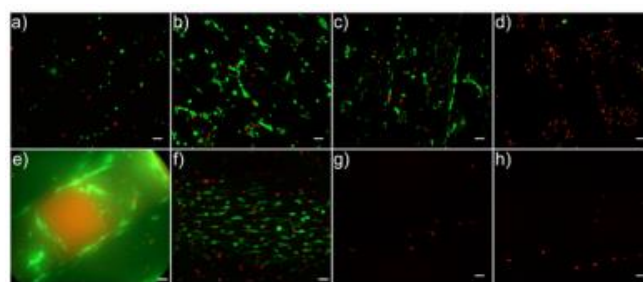


Fig. 5. Live/dead staining of hADSCs on PCL/PANI scaffolds. At day 1 of cell culture (a) pristine PCL, (b) PCL/0.1 wt% PANI, (c) PCL/1 wt% PANI, and (d) PCL/2 wt % PANI (scale bar = 100 μ m); and at day 21 (e) pristine PCL, (f) PCL/0.1 wt% PANI, (g) PCL/1 wt% PANI, and (h) PCL/2 wt % PANI. Live cells (green) and dead cells (red) (scale bar = 50 μ m) [132].

C. Polythiophene (PTh) Derivatives and Composites

Polythiophenes could have comparable characteristics to those of PPy and sometimes even better [139], [140]. Owing to its great electrical conductivity, chemical and environmental stability, excellent biocompatibility [141]-[146], and the variety of its forms including nanofilms and nanofiber mats, poly(3,4-ethylenedioxythiophene) (PEDOT) is regarded as the most successful PTh derivative to be utilised in biomedicine and biotechnology [147]-[149]. A striking application for PEDOT is in orthopaedic implantable devices [145], [146], [150], [151].

Electrochemical corrosion outcomes confirmed that the electropolymerisation of PEDOT coatings on near- β Ti-20Nb-13Zr (TNZ) substrates were displayed to develop barrier protection performances in SBF [152]. Catt *et al.* found that coating Mg implants with PEDOT/GO composite by electropolymerisation could decrease rates as was confirmed by a number of techniques including electrochemical methods. Moreover, the neuronal biocompatibility of the Mg samples coated with PEDOT/GO was illustrated to improve [153]. Bilayer coatings by electropolymerisation of PEDOT on 316L SS followed by the electrodeposition of Sr and Mg substituted porous

hydroxyapatite (Sr, MgHA) were successfully developed. The resulted coatings were examined by electrochemical techniques where the findings of corrosion resistance were compatible with those accomplished from chemical analysis. Furthermore, greater adhesion strength was demonstrated when the PEDOT/Sr, Mg-HA bilayer was used compared to the Sr, Mg-HA coated 316L SS. The dual coating layer of Sr, Mg-HA was observed to be more bioactive in terms of cell adhesion in comparison with that of the mono substituted hydroxyapatite on the PEDOT coated 316L SS [154]. Electrochemical copolymerising of EDOT with GO, polystyrene sulfonate (PSS), or heparin (HEP) on SUS316L SS was used to form protection coatings to this alloy that could potentially utilised for cardiovascular stents. The surface morphology and roughness were examined by various techniques; for instance, AFM displayed increasing in roughness of substrate after modification (Fig. 6). The presence of negatively charged functional groups in GO resulted in higher anti-fouling ability of PEDOT/GO than that of PEDOT modified either with HEP or PSS. PEDOT/GO/HEP coating had the highest anti-fouling capability compared to other batches. PEDOT/GO/HEP illustrated also much longer blood clotting time than that of neat SUS316L SS [155]. It was also found that adding polydiallyldimethylammonium chloride into the PEDOT/GO generated anti-bacterial capability for this coating due to the positive charge of the obtained composite that can efficiently kill *Staphylococcus aureus* [156].

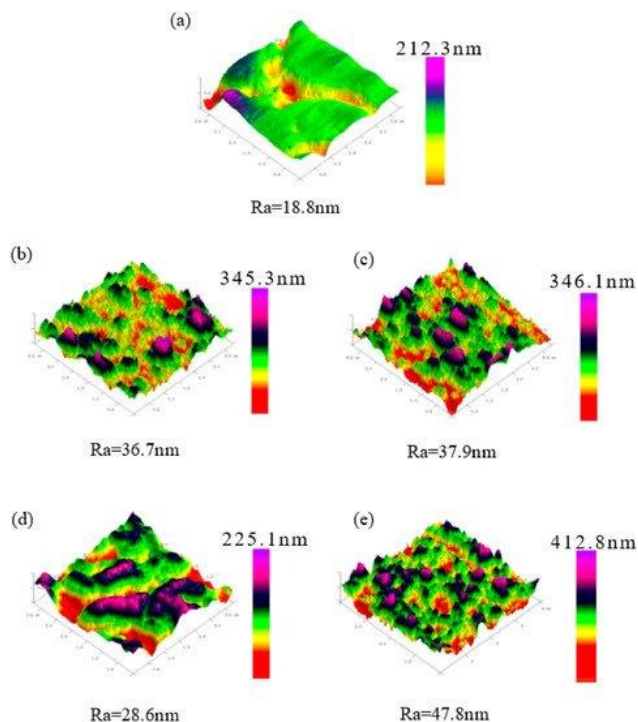


Fig. 6. Atomic force microscopy images of (a) unmodified SUS316L, (b) PEDOT/ heparin, (c) PEDOT/ polystyrene sulfonate, (d) PEDOT/ graphene oxide, and (e) PEDOT/ graphene oxide / heparin [155].

Poly(3,4-ethylenedioxyppyrrrole) (PEDOP) has also been utilised as a biomaterial and for coating implantable metals owing to its proper characteristics. These include superb conductivity, uncomplicated polymerisability and biocompatibility [84]. PEDOP; however, has some drawbacks including insufficient mechanical stability,

inferior bone-bonding capability and lack of long-run stability that impedes its uses as a coating material for protecting orthopaedic implants [157]-[160]. Due to compact film formation, it is pointed out that the copolymerisation improves several PEDOP films properties including corrosion resistance [161]. The electrochemical copolymerisation of thiophene and its derivative has been of interest to improve these materials properties [162]. P(EDOP-co-EDOT)/minerals substituted porous HA bilayer coated 316L SS was indicated to have high thermal resistance and anticorrosion. Moreover, it exhibited superior antibacterial property and promotion of MG-63 cells adhesion and viability with high capability of bone-like apatite formation [163].

III. CONCLUSIONS AND FUTURE PROSPECTS

The use of metals and alloys in biomedical applications has been witnessing a great deal of interest due to what these vital materials can provide in terms of replacing and renewing organs and tissues, especially with the increase in people life span and the rise in accidents worldwide. Despite the many advantages that these materials offer, biocompatibility and corrosion resistance limitations impose an urgent need to find approaches to improve their performance closely to what is found in human body. Therefore, abundant studies have been conducting to enhance these properties through a wide range of techniques, perhaps the most important of which is coating these materials with CPs such as PPy, PANI, PEDOT and their composites. This type of coating has been observed to greatly develop biocompatibility and corrosion resistance, especially by using CP-based composites that are reinforced with nanomaterials such as ZnO, ZnO₂, TiO₂, Nb₂O₅. The high surface area of nano-additives for the dopant release, and the promotion of barrier effect against diffusion are achievable with these composite biomaterials. It is expected that numerous further research will be conducted in the future to develop composite biomaterials based on CPs for the purpose of improving the performance of the devices currently used in implantation. Moreover, new alloys would be utilised in which coating them with such materials may be the reason for their future use in biomedical applications, mainly in orthopaedic and orthodontic implants.

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