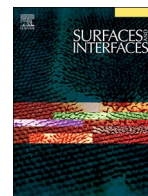




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Recently Emerging Nanotechnological Advancements in Polymer Nanocomposite Coatings for Anti-corrosion, Anti-fouling and Self-healing



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ABSTRACT

Recent nanotechnological advancements have enabled novel innovations in protective polymer nanocomposites (PNC) coatings for anti-corrosion, anti-fouling and self-healing services on material surfaces. Nanotechnology encompasses research, manufacturing, and application of nanoparticulate architectures, tubular structures, sheets or plates exhibiting sizes below 100 nanometers (nm) in at least a single dimension. Inclusions of nanoparticles into organic entities have demonstrated enhanced properties essential for attainment of aesthetics, anti-corrosion, thermal stability for high-temperature performances, mechanical strength essential for resisting coating deterioration in harsh environments, nano-architectural cross-linking capable of hindering penetration of corrosive, and biofouling entities. Unlike previously published literature, this paper elucidates very recently emerging important advancements in novel techniques utilized in developing PNC coatings for applications in aerospace, packaging, automotive, biomedicine, maritime, and oil and gas industries for attaining superior anti-fouling, anti-corrosion, and self-healing behaviors on critical material surfaces. Emerging market structures and novel applications are also presented.

1. Introduction

With the recent evolution in nanotechnology, nanomaterials have enabled modification of PNC nanocoatings for efficient suppression of corrosion, fouling, and scratching of metallic materials, in addition to attainment of nanocoating self-healing in varying ethereal and marine architectures with its attendant benefits. Nanomaterials are materials exhibiting at least a single morphological entity such as architectural dimension, granular size, particulate dimension, and so on, at the nanoscale, or below 100 nm [1]. These nanomaterials occur as nil dimensional entities such as nanoparticles, single dimensional entities such as nanorods, nanotubes, and nanowires or two-dimensional entities in form of nanolayers, nanofilms, nanosheets, and nanoplatelets. Nanomaterials demonstrate enhanced behaviors especially electronically, optically, mechanically, thermally, physically, chemically, and magnetically [2]. These behaviors are mainly ascribed to their very small dimensions which enables elevated surface volume unit, and broad surfaces for effective interaction [3]. Nanomaterials exhibit prospects of minimizing corrosion degree on metallic surfaces via surficial modification using nanocrystalline structural coatings. Fig. 1 schematically elucidates nanomaterial classification, while Fig. 2 schematically elucidates nanomaterial applications in varying vital

areas.

Nanocoatings have effectively been utilized in reducing negative effects of corrosion. A PNC coating is defined as a nanocoating exhibiting constituents either at the nanoscale level, or whose constitution is made up of sheets or layerings below 100 nm [4]. Nanomaterials dimension or sizes, in addition to their highly dense layering enhances good bonding, and highly appropriate physical covering of the coated surface. PNC coating is the most commonly available technique for inhibiting, hindering, reducing, or mitigation of the effects of corrosion because of the presence of varying types of coating entities and procedures for numerous environmental parameters and applications. PNCs coatings can be applied to the interior or exterior surfaces of a given material at varying temperature range thereby facilitating critical benefits including very smooth surfaces and interfacial flow efficiency on the surfaces [5]. Nanocoatings may seem expensive in the short term, but in the long run tend to be cheaper, especially in large-scale usages, because of high saving garnered from maximally reduced maintenance cost, safety, protection of equipment damages, natural resources, and so on [6]. Notably, successful utilization of PNCs coatings for hindering or mitigating fouling, corrosion, and scratching from self-healing capabilities is usually inhibited by inherent micro-architectural porosity which demonstrates deficiency at hindering the

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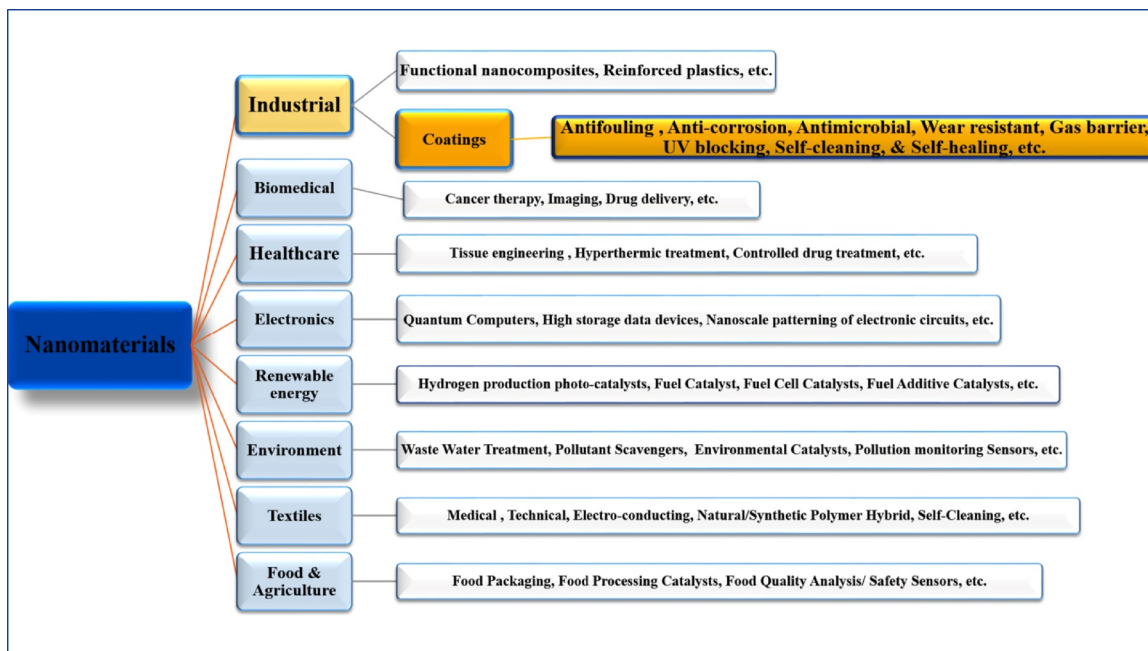


Fig 1. Classification of nanomaterials.

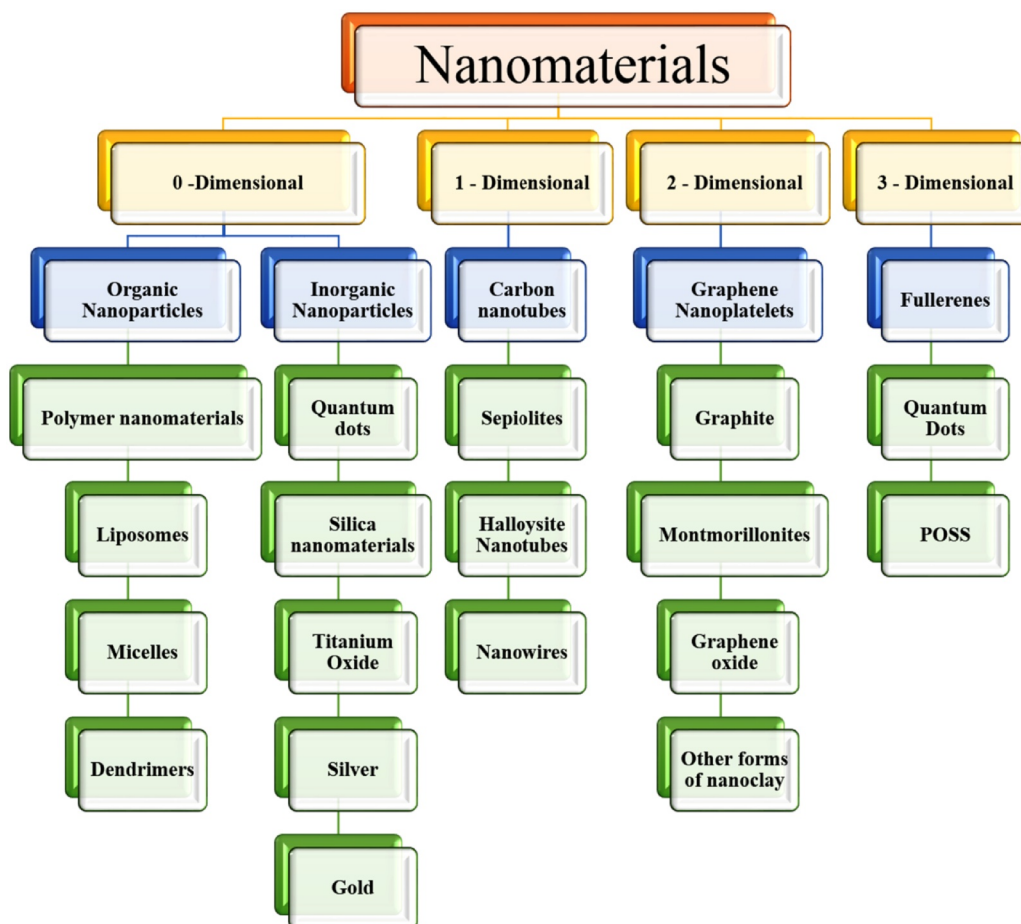


Fig. 2. Applications of nanomaterials.

penetration of extraneous entities detrimental to a given surface. Other parameters include damages induced by scratching, wearing or abrasion [7]. The inclusion of nanomaterials in PNC coatings highly improves their barrier protective performances.

Though, previous decades have witnessed numerous studies on PNC coatings, versatile insights into recently emerging functions of nanocoatings are not well documented. Unlike previously published literature on this subject, this paper presents very recently emerging

nanotechnological advancement in PNCs protective coatings, with broad insight into prospects of inorganic and organic hybrid substrates. Exposure is accorded to emerging novel trends in nanotechnological usage for enhancing anti-fouling, self-healing and anti-corrosion behaviors of PNC coatings. This is propelled by in depth elucidation of parameters affecting coating micro-architecture, along with cutting-edge insight into nanocoatings functionalization for effective covering power. Herein, effect of micro-architectures and nano-modification on coating behavior, as well as fabrication techniques relative to corrosion resistance, anti-fouling and self-healing are presented. Insight into past, present and future market structures of PNC coatings are also presented.

2. Emerging Market Structure of PNCs Nanocoatings

In a report released by Future Market Insights [8], within the spectrum of the global market for protection against corrosion, PNCs coatings are forecasted to witness a continual CAGR growth within 2017-2022. By ending of 2022, the [global market for polymeric based coatings for enhanced corrosion resistance](#) is anticipated to garner more than US\$ 19.5 billion in revenues. Furthermore, the global conductive PNCs market is expected to garner a CAGR of 9.2% during the forecast duration. The market is anticipated to accrue to about USD 10.57 billion towards the end of 2027 from USD 3.16 billion in 2016 [8]. The PNCs abrasion resistant coatings (PNCs-ARCs) market attained USD 8.0 billion in 2019. However, it is anticipated to garner USD 11.1 billion by 2024, at a CAGR growth of 6.5% between 2019 and 2024. Latin America occupied the largest chunk of the global abrasion resistant coatings market [8]. By 2024, Latin America is estimated to garner USD 2.3 billion, attaining a CAGR of 6.3% during duration of forecast. The use of PNCs-ARCs in power generation, oil and gas, mining, transportation, marine, and construction industries are anticipated to drive the highest growth in Latin America in nearest future. Though this forecast was done prior to covid-19 pandemic era along with its attendant severe economic downturn in 2020, it is still anticipated to maintain same value as the pandemic gradually subside. Escalating demand for semi-conducting products including optical devices, sensors, and so on are expected to boost the growth of global conductive polymer coating market. Industries expected to drive this growth include the smart textiles, solar, automotive, locomotive, and electrical and electronics industries. This growth is anticipated to be powered through use of conductive polymer coatings on sensors, fuel cells, cell phones, displays, touch panel, solid state lighting, displays, capacitors, batteries, photovoltaic cells, and so on [8].

3. PNC Coatings Properties and Classification

This section elucidates classification and properties of nanocoatings with special emphasis on varying approaches of applying coatings on surfaces. Generally, coatings are deposited as a multiple layering system composed of primer layering, and an uppercoat. For instance, in automotive coating system, this layering may vary between four to six layerings. Individual coating layerings undergo application to carry out specific functions. Additionally, interfacial interactions within various layering in the system play a key role in the total performance of the multiple-coating system [9]. Over the years, PNC nanocoatings have demonstrated efficiency as very effective approach for attaining anti-corrosion of metallic architectures. Water- and solvent-oriented PNC coatings are effective for protecting metallic architectures against corrosion. This protective propensity of PNCs coatings mainly depends on nanoparticle inclusion, and specialized additives included in the film-formulation, such as anti-corrosive entities, and corrosion inhibitors. Additives utilized as corrosion inhibiting entities in nanocoatings are generally divided into inorganic and organic materials. Inorganic inhibiting entities of the adsorption or oxidative types are majorly utilized in water-oriented PNC coatings [9], while organic inhibiting

entities are utilized for solvent based PNC nanocoatings [10]. The adhering behavior of PNC coatings is a critical parameter in achieving strong covering power [9-11].

PNC coatings are comprised of highly dense grain and interphasial boundaries, dislocations, and so on, where inter-layer spacing between them nearly attains inter-atomic distancing. Hence, PNCs coatings demonstrate varying properties based on highly-grained, traditional coatings enabling their ability to overcome the mechanical and anti-corrosive properties of their neighbours. This predisposes their classification into metallic and ceramic PNC coatings relying on their base materials. PNC coatings are composed of two or more entities in the nanoscale. As a result of inherently fine dimension of nanoparticles used in PNC coatings, void-filling and corrosive entities inhibition from penetrating surface of protected substrate enhances the coating efficiency [11-13].

Recently evolving nanocoating technology has impacted greatly on paints development with inclusion of properties like self-mending [14], self-cleaning [15], anti-scratching [16], and anti-wearing repression [17]. Furthermore, smart nanocoatings have proved advantageous in minimizing the effects of corrosion and biofouling on concerned materials. These nano-PNC coatings undergo development to enable responses to outside stimulus including electromagnetic radiation, stress, pH, heat, coating distortion, humidity, and so on, through the release of controlled quantities of inhibitors to enable the repairing and curing of voids and damages [18-21]. Conventional coatings of micro-sized particles or thicknesses usually present varying corrosion behaviour in comparison with PNC coatings [22]. Due to the superior properties exhibited by PNC, they are utilized in versatile applications including computers, cell phones, clothing, eye-glasses, and so on. In building and construction sectors, they are utilized in air filters, windows, tiles, walls, flooring, and so on. Application of coating nanolayering on the surfaces of these appliances enhances their flame-retardancy, anti-wearing and, anti-scratching, anti-graffiti, corrosion repression, self-cleaning, as well as electrical conductivity. Moreso, these materials exhibit improved adherence, anti-fogging, optical-clarity, and anti-fouling behavior, and additionally used as photo-voltaic substrates [23-25]. In the biomedical sector, metallic PNC coatings are used in modifying material surface disposition when essential. These materials are basically utilized in medicine for protection, surfacial covering, and corrosion suppression. Secondly, these materials are utilized in biocompatibility, drug delivery, and in other fields such as military, automobile, energy, environment, and so on [26].

PNC coatings are applied on surfaces via three main depositing techniques, vis-a-viz mechanically, physically, as well as chemical depositing techniques [27]. Mechanical depositing technique is relatively low cost, and attained via painting, spraying, dip-coating or spin-coating. Physical depositing technique can be conducted via sputtering, bonding, or condensation. During conduction of physically induced diffusing bonding, a mild pressure and temperature are utilized, in comparison to braze-bonding, where lubricants are included under elevated temperatures. Attaining adherence via surface-activated bonding (SAB) is feasible at lower temperatures and pressures for scrubbed atomic flattend, and polished surfaces. Moreso, selective laser sintering (SLS) is a novel additive manufacturing technique inferred as tri-dimensionally (3D) routed printing method where a material is structured in a layering order [27]. Another physical bonding technique is condensation, and conventionally conducted on a vacuum like in physical vapour deposition (PVD), which is conducted at normal pressure parameters, similar to liquid phase epitaxy (LPE). Chemical adhering techniques potend to be lower in cost, however, require expensive precursors, including atomically layered deposition (ALD), Langmuir, and sol-gel [27].

Plasma-enhanced magneto optical chemical vapour deposition is another technique feasible at specific substrate pressure, temperature, and power [28]. Aforementioned methods of coating layering on a substrate surface influence the evenness and surface behavior such as

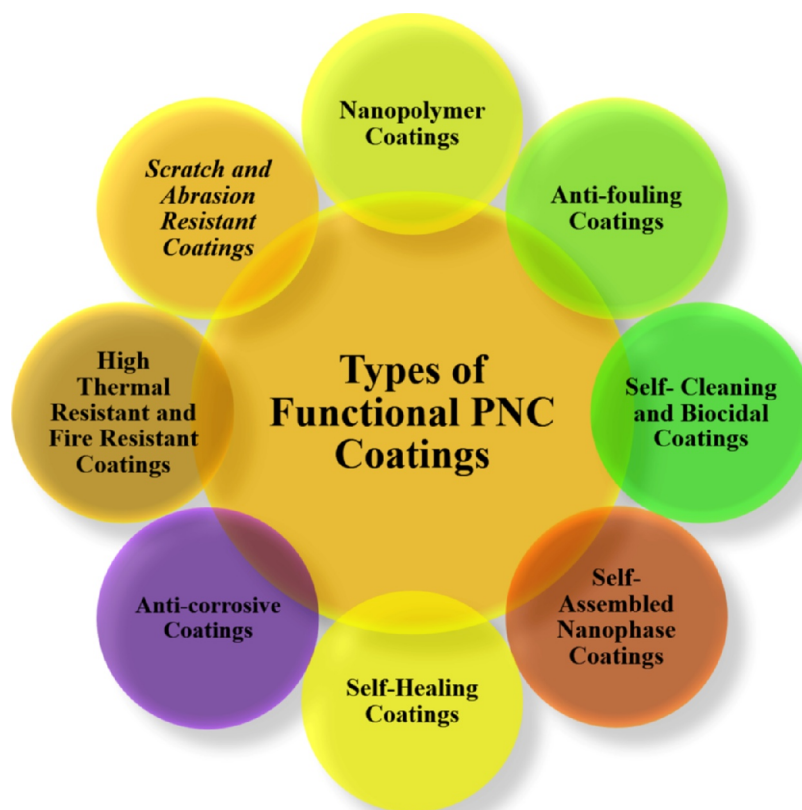


Fig. 3. Types of functional PNCs nanocoatings.

ductility, strength, and fracture toughness [28]. For any coating section, the proper coating technique should be carefully selected considering critical parameters. Regarding traditional coatings, selected methods should be applied using optimised parameters in order to attain excellent surfacial coverage relative to evenness, smoothness, adherence, void-free surfaces, and so on. Types of functional PNCs nanocoatings are schematically represented in Fig. 3.

3.1. Functional PNCs Nanocoatings

Fundamentally, coatings are majorly utilized on surfaces for functional, decorative, and protective purposes, and in most instances, a combination of these parameters. Functional coatings are referred to as systems demonstrating decorative and protective functions, in addition to other specific functionalities [29]. Depending on the appropriate use of a coated material, this additional functionality may be versatile. Furthermore, functional coatings are separated into ease of cleaning, self-cleaning, anti-fouling, soft feeling, antibacterial [30], and anti-viral [31]. Aside their unique behavior, PNC functional coatings must satisfy some expectations relative to their behavior, scratch and abrasion resistance. This is in addition to customized surfacial morphology, reproducibility, ease of application, cost effectiveness, and environmental compliancy. Hence, PNC functional nanocoatings are categorized based on their functional behavior. The performance of these coatings depends on their mechanical, chemical, physical, and thermal behavior [32-35].

Fundamentally, nanofillers undergo inclusion into polymeric matrices so as to improve the material conductivity, stiffness, strength, and thermal resistance, while also reducing permeability, fouling, thermal expansion, solvent attack, and flammability, while retaining processability, elongation, transparency, cost, density, and chemical inhibition. Polymeric materials are highly inhibiting to corrosion, scratching and wearing. The inclusion of ceramic nano-fillers into polymeric matrices

enhances self-healing, hydrophilic, and anti-wearing behavior, thereby resulting in enhanced corrosion inhibition. On inclusion of nanoparticles of ceramic-alumina, or silica in paints, anti-scratch behavior is enhanced. Moreover, nanoclay inclusion in polymeric matrices, result in decreased porosity and diffusion route of the fabricated PNC because of enhanced water barrier as well as gas permeability behaviors [35].

PNC processability is highly essential. Based on the procedure of synthesis, a uniform distribution or agglomeration of nanofillers in polymeric matrices is attained. Nanofillers uniform dispersion and distribution in polymeric matrices demonstrate optimal property enhancement in the PNCs. Varying chemical procedures are utilized in combining polymeric matrices with nanoparticles. These procedures include melt and solution intercalation, in situ and emulsion polymerization [36-39]. Relative to dispersion and distribution of nanoparticles' in PNCs, both solution intercalation and situ polymerisation are perceived excellent for PNCs fabrication. In some studies, enhancements in corrosion hinderance and mechanical strength have been attained. These enhancements in properties are demonstrated in incremental cohesive and adhesive behaviors of the nano-architecture attributed to appropriate dispersion of nanofillers in the matrix [40-43]. Additionally, both anti-scratch and anti-wear resistances are enhanced with increasing nanoparticle weight percent in polymeric matrices [44]. Moreover, hydrophobicity behavior is also enhanced through nanoparticles inclusion which in turn improves corrosion inhibition [44].

4. Anti-corrosion coatings

This section presents market structure, preparation, characterization and properties of anti-corrosion coatings. In recent years, organic coatings have increasingly become a highly common and cost-effective route to prolong the shelf life of metallic architectures exposed to weathering environment. The evolution of innovative and more efficient protective coatings are largely linked to rapid evaluation of anti-

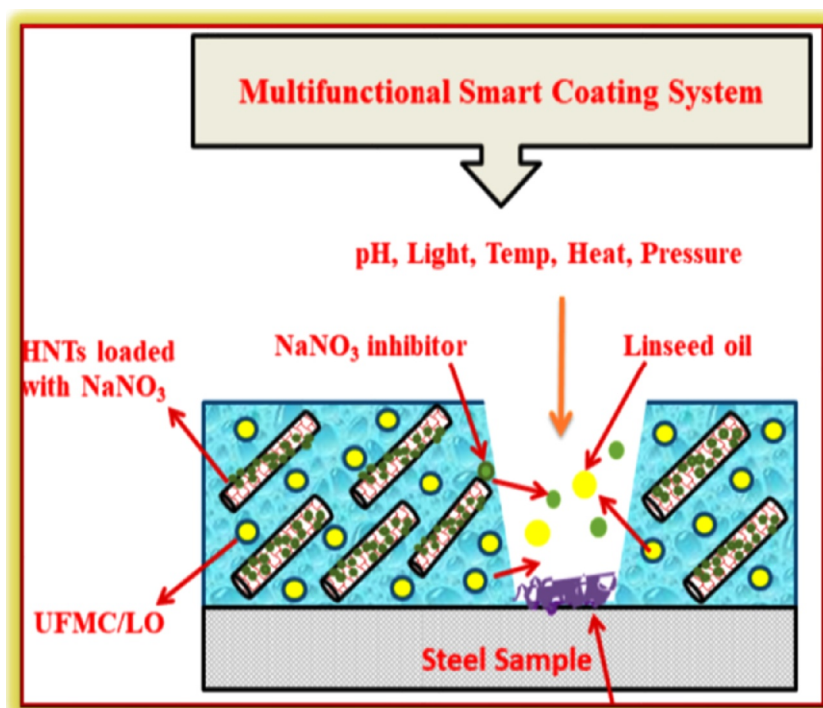


Fig. 4. Schematic elucidation of the multifunctional nanocomposite coating concept [62].

corrosive resistance prior industrialization. Corrosion is inferred as material deterioration due to chemically interacting with the immediate environment [45]. Metallic structural corrosion highly impact on the global economy. World Corrosion Organisation (WCO) has projected that the global cost of corrosion is presently greater than 1.3×10^{12} €, approximately equal to 3.8 % of the overall global Gross Domestic Product (GDP) [46]. As result of the economic effect of this protective system, there is a rapidly growing research involvement in the development of highly performing coatings, able to simultaneously satisfy safety, environmental, and health essentials [47]. An investigation conducted by National Association in Corrosion Engineers (NACE) approximate the cost implication of corrosion globally to about \$255 billion USD accounting for 3.4 % of world gross domestic product (GDP) [47]. The yearly corrosion costs on US economy directly and indirectly, is estimated equal to \$552 billion and constitute 6% of annual GDP [48]. Corrosion impacts directly on the cost of managing and instituting repairs on automobiles, household electronics, airplanes, highway-bridges, industrial plants like energy developing and channeling mechanisms, pharmaceutical, desalination, petrochemical, desalination, and so on. Indirect corrosion costs implication includes productivity losses as result of delayal, and outages, in addition to taxes and overhead costs incurred from corrosion, and so on [49].

In order to develop mitigation against the adverse effects of corrosion, protective PNC coatings have sufficed [50]. In accordance with dispersive media classification, anti-corrosion coatings are categorised into solvent, water, and powder-oriented, in addition to other notable formulations of coatings. Due to the enactment and concise implementation of policies and regulations guiding the release of volatile compounds (VOCs) emanating from solvent-oriented coatings, water-borne coatings have attained significant share of the market growth in previous decades [51]. Hence, mitigating routes such as organic/polymer coatings, anodic and cathodic protection, and corrosion inhibiting entities have been developed and versatily utilized in automobiles, pipelines, construction, and marine industries for corrosion alleviation and elimination. Nevertheless, highly effective protective systems aim to impact cost-effective techniques. Additionally, organic-inorganic synergistic coatings, PNC, and hydrophobic coatings, have

inculcated durability in shelf-life of varying materials in corrosion prone environments [51].

Corrosion implications are varied and versatile. The adversity of corrosion on safety, reliability, and optimal performances of equipments and/or structures are very critical compared with losing the metallic architecture. Various corrosion-controlling techniques have been innovated such as cathodic and anodic protection [52], use of inhibitors [53], alloying and coating [54]. Polymeric (or organic) coatings have for long been utilized in hindering metallic structures from corroding. The main use of polymeric coating is to act as physical barricade against corrosive entities such as O^{2-} and H^+ . Main causes of metallic corrosion are linked to atmospheric effects, which are triggered on metallic exposure to weathering parameters and highly affected by prevalent climatic entities such as duration of wetness, relative humidity, and salinity, activities of other pollutants, temperature, and acidity [55].

PNC coatings are complex formulations composed of a mixture of varing pigments, binders as well as functional nanoparticles [56]. Metallic architectural protection using PNC coatings are attained using multiplied-layered systems consisting of base primer, and an upper-coat [57]. The base primers in synergy with pigments hinder preliminary corrosion, whilst providing adherence. On the other hand, the upper-coat hinders adverse environmental effects such as microbial attack, UV, mechanical and water, while facilitating aesthetic, and functional essentials [57]. However, fundamental protective properties inhibiting ionic corrosion and moisture are proximally linked to the coating integrity which is commonly influenced by mechanical and environmental parameters [57].

Presently, coating/metallic substrate systems stability to corrosion is garnered through application of enhanced weathering tests [58]. Numerous testing techniques have evolved in the simulation of environmental factors, such as the neutral salt-spraying test (ISO 9227), which entail persistant exposure to salt-fogging, and cyclical corrosion tests, such as QUV® or Prohesion®, or the synergy of both - Prohesion®/QUV® (ASTM D 5894), simulating UV radiation and weathering environment [59-61].

In a recent study, a multifunctional PNC coating was synthesized

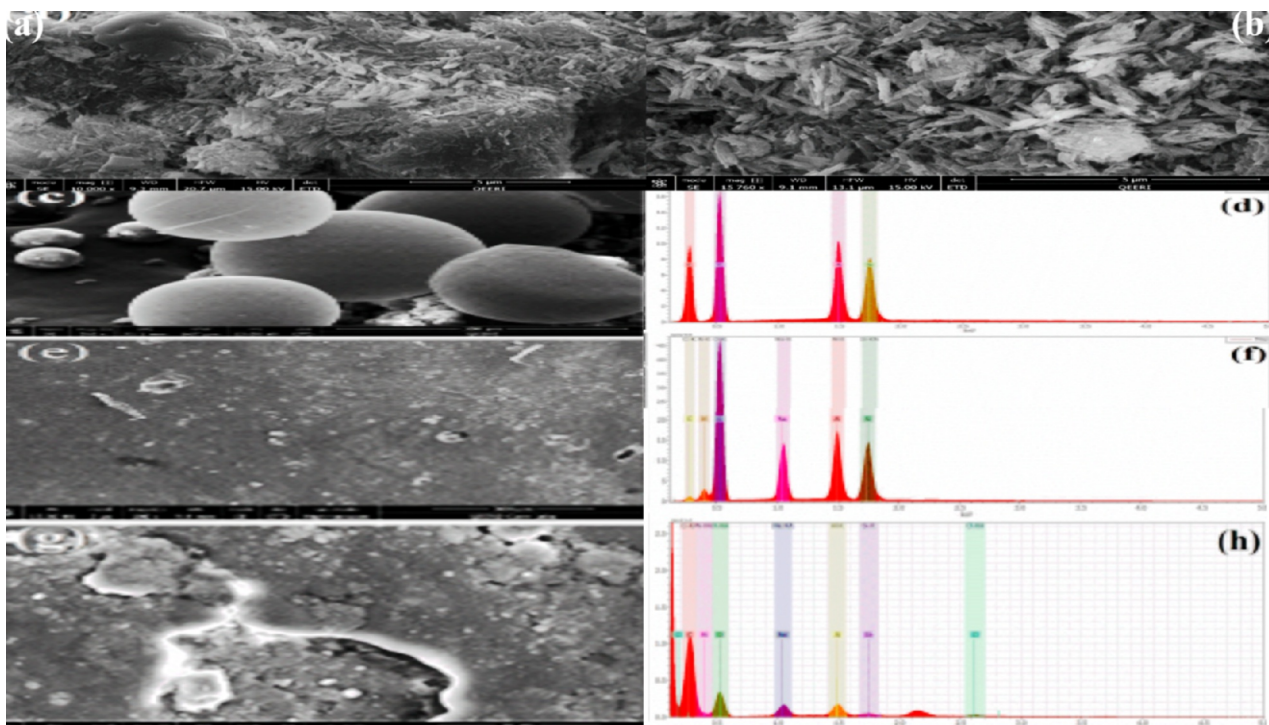


Fig. 5. FESEM analysis of: (a) HNTs (b) HNTs with inclusion of NaNO_3 , (c) urea formaldehyde microcapsules/linseed oil (UFMC/LO), and (e.g) PNC coatings; and EDX analysis of: (d) HNTs, (f) HNTs with NaNO_3 inclusion, and (h) PNC coatings [62].

through reinforcement of polymeric matrix with halloysite nanotubes (HNTs) included with the corrosion inhibiting entity (NaNO_3), and urea formaldehyde microcapsules (UFMCs) utilized for encapsulating the self-healing agent, linseed oil (LO). The PNC coatings developed were applied on a cleaned mild steel surface through use of the doctor's blade method. FTIR, and XPS used for structural analysis, and thermogravimetric (TGA) analyses demonstrate synergy of HNT/ NaNO_3 with UFMCs encapsulation of linseed oil. Fig. 4 is a schematic representation of the concept of PNC coating [62]. Fig. 5 represents FESEM analysis of samples.

Results demonstrate that the inhibiting agent self-release from HNTs while responding to variation in pH was a time dependent procedure. The PNC coatings exhibited efficient self-mending while responding to externally influenced mechanical deterioration. Studies using electrochemical impedance spectroscopy (EIS) demonstrate PNC coatings potential anti-corrosive effect. The corrosion inhibition demonstrated by the developed PNC smart coatings may be attributed to effective release of inhibiting entity and self-mending agent while responding to external stimulation. Therefore, PNC coatings treated with multi-functional entity is a potential steel corrosion inhibitor for the oil and gas industry [62].

When water contact angle (WCA) on a surface is 150° or higher, the surface is said to be a super-hydrophobic (or ultra-hydrophobic) surface (SHS). A good example of a naturally occurring SHS is the lotus leaf, whose WCA is above 150° [63]. This super-hydrophobic impact is caused by both lower surface energy substrates and hierarchical or nano-/macro- architectures characterized by very low water roll-off angle or very low WCA hysteresis [64]. Former study has demonstrated that droplets of water on textured surfaces easily balance on top of nano-architectures because bubbles of air cover the entire contours in the architectures beneath the droplets. Water-droplets on these surfaces are hindered from penetrating into micro- or nano-architectures, wetting the surfaces and causing very high contact-angles. Hence, these leaves demonstrate high super-hydrophobicity. Various techniques such as chemical deposition [65], casting, and chemical etching [66], sol-gel procedure [67], photo-lithography [68], plasma modification [69],

templating [70], and chemical vapor deposition (CVD) [71], have undergone utilization in fabricating super-hydrophobic surfaces. Numerous investigations have demonstrated application of polymeric matrices, and PNCs in fabricating hydrophobic/superhydrophobic surfaces [72–75]. Hence, the evolution of hydrophobic/super-hydrophobic polymeric matrices and PNCs has attracted great interests in the field of materials science, and engineering. Recently, very negligible amount of researches have been conducted on use of polymeric matrices and PNC coatings in investigating anti-corrosive behavior of hydrophobic/super-hydrophobic surfaces [72–75]. Moreover, studies involving organic polymeric inorganic silica composite anti-corrosion coatings exhibiting bio-inspired super-hydrophobic surfaces have never been reported.

Thus, a recent research demonstrated the feasibility of developing advanced PMMA/silica composite (PSC) coatings for anti-corrosive activity [76]. Here, the combination of nano-casting and UV-curing techniques was used in designing and duplicating fresh plant leaf surfaces such as *Xanthosoma sagittifolium* leaves (XSL). Derived exact imprint of super-hydrophobic XSL was imposed on the composite surface such that the produced material displayed exact super-hydrophobicity required for hindering corrosive activity. An eco-benign procedure was utilized in preparing the PNC anti-corrosion coatings devoid of any solvent usage [76].

Hence, the PNC anti-corrosive coatings fabricated enabled versatile effects in protecting metallic substrate from corrosive activity. Conventionally, some polymeric resins utilized in attainment of anti-corrosive behavior require usage of organic solvents presenting a degree of adversity to human health. However, as a result of introduction of new regulative policies guiding release of volatile organic compounds (VOCs), increasing demands for ecobenign coating systems has necessitated replacement of hazardous compounds in these coatings. These replacements have resulted in availability of solvent-free and water-borne coatings. Thus, bio-inspired architecture exhibiting super-hydrophobicity replicating that garnered from *Xanthosoma sagittifolium* leaf with the capability of repelling moisture, and with improved reduction of the water/corrosive adsorption media on the PMMA surfaces hindering underlying metallic corrosive propensity and derivation

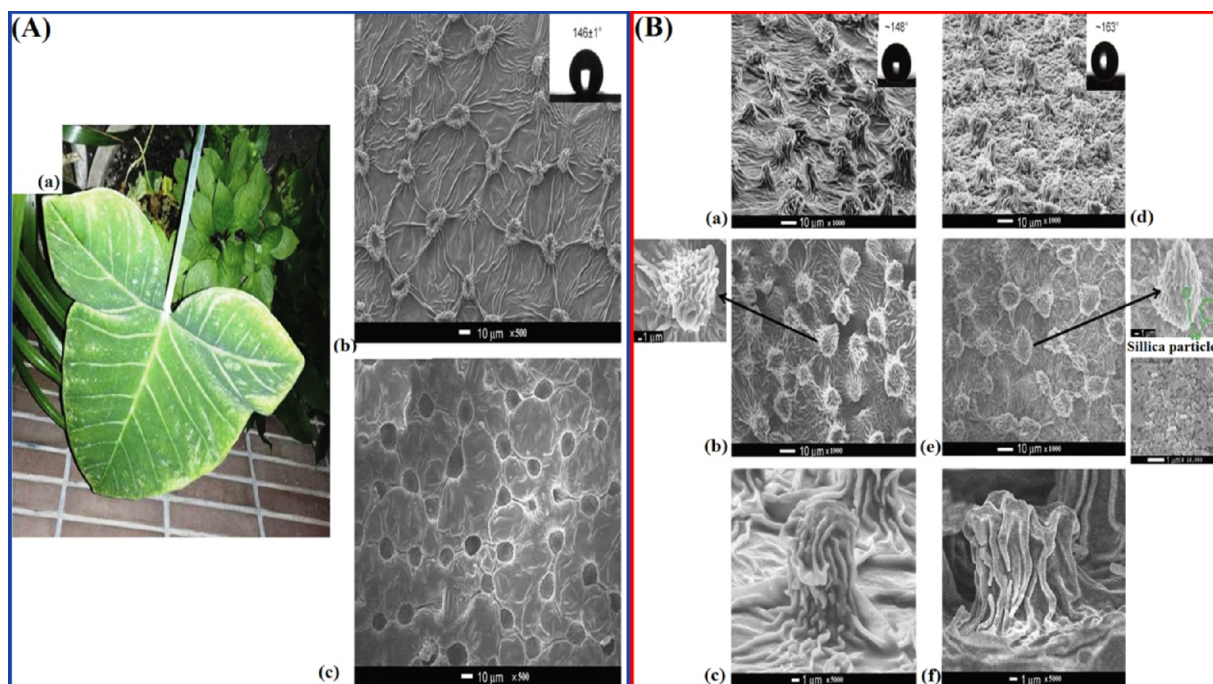


Fig. 6. A. (a). Photograph of *Xanthosoma sagittifolium* leaves. (b) SEM image of a freshly removed natural leaf. Elucidation reveals *Xanthosoma sagittifolium* leaf water contact angle. (c) PDMS negative template; B: SEM images for (a, d) the *Xanthosoma sagittifolium* leaf-like PMMA hydrophobic surface and the superhydrophobic surface of the nanocomposite. Inserted image reveals the surface contact angle (b, e) Top views of PMMA surface and nanocomposite. Inserted images show (e) silica nanoparticles. (c, f) Sectional views of PMMA surfaces and the nanocomposite [76].

of silica nanoparticle improving surface hydrophobicity to a superhydrophobicity were attained. Fig. 6 (A, B) further elucidates results from this study [76].

A mixture of organic/inorganic, photocatalytic and hydrophobic nanocomposite coatings including Ce/TiO₂ nanoparticles (c-TiO₂/NPs) have been developed using the sol-gel technique. The incorporation of c-TiO₂ NPs in the hydrophobic coating demonstrated good self-cleaning ability [77]. Moreso, nanoparticles were assembled in a dried film constituting of bio-oriented polymeric matrices. Varying nanoparticles underwent distribution along with hydroxyethyl starch (HES) and hydroxyethyl cellulose (HEC). Results revealed that morphology of the polymeric substrate exhibited profound impact on the assembly architecture of the nanocomposite. Premised on attained results, a bio-oriented water-based coating system was developed to efficiently repress UV radiation while controlling transparency utilizing ZnO NP. This investigation offer opportunities for usage of sustainable bio-oriented substrates for effective smart coating usages [78].

A PNC coating has been prepared exhibiting effective corrosion resisting and encapsulating attributes, and capacity to control delivery of benzotriazole (BTA) for simultaneous transfer of both active and passive corrosion repressive attributes to the coating layerings. Subsequently, metallic organic frameworks (MOFs) underwent synthesis and utilized as nano-containing conveyors for BTA loading. Based on this premise, tetraethyl orthosilicate (TEOS) underwent inclusion thereby forming a film for wrapping the MOFs. The incorporation of TEOS conferred pH-responsiveness and active suppressing abilities to the coatings ascribed to the film susceptibility to degrade under acidic, or alkaline environment. Results revealed that the BTA-MOF-TEOS-GO included in the epoxy coatings demonstrated elevated impedance values of about $8.6 \times 10^8 \Omega \text{ cm}^2$, implying very effective and durable corrosion repressive behaviors [79].

Aniline tetramer (AT) in conjunction with electro-activated imide oligomeric (EIO) anti-corrosive entity has been synthesized successfully in a recent research. The advanced anti-corrosive performance of PI coating behavior on CRS electrodes was ascribed to the redox catalytic affinity of AT entities available in EIO [80]. Figs. 7 and 8 depicts mass,

ATR-FTIR spectroscopy, and SEM images of samples.

Fig. 7 depicts the mass and ATR-FTIR spectra of AT. AT characterization reveal ion trap-MS m/z: $[M + H]^+$ calculated for C₂₄H₂₀N₄ = 365.4. [80]

Fig. 8 (a) shows SEM image of ground CRS surface while Fig. 8 (b) depicts the grinded CRS surface post 30 days duration of immersion in 3.5 wt.% NaCl solution, exhibiting a densely, irregularly projected particles. Moreover, Fig. 8 (c–d) depicts CRS surface with elimination of PI, AT, and EIO coatings post saline modification on immersion. Insight from Fig. 8c reveals CRS surface to be covered by sparsely granulated entities. This implies that the coating was not able to exhaustively repress entry of the harsh corrosive medium constituting of dissolved oxygen ions and chlorine into the material during long-term modification immersion. As depicted from Fig. 8 (d, e) AT and EIO coatings were somewhat purer. This implies that a passive metallic-oxide layering was formed on surface of CRS [80].

The evolution of efficient corrosion suppressive pre-modifications for metallic surfaces is challenging in attaining prolonged shelf-life of metallic architectures, and components. Thus, a recent study enhanced anti-corrosion protection behavior of sol-gel hybrid coatings garnered from synergy of [2-mercaptobenzothiazole (MBT) and 2-mercaptobenzimidazole (MBI)] in the presence of β -cyclodextrin (β -CD). Synergy of MBI or MBT with β -CD resulted in encapsulative anti-corrosion attainment ascribed to active corrosive electrolytes capable of gradual diffusion from the host material to maintain continual transfer of inhibiting entities to the corrosion locations and ensure durable anti-corrosion activity [81].

Inferior mechanical behavior hinder artificial superhydrophobic coatings from extended application despite availability of these coatings decades earlier, and attraction of broad research awareness. Previous researches from epoxy/nanoparticle delivered a weak nano-architecture and inferior surfacial energy devoid of appropriate and strong micro-architecture to enable protection and strength resulting in poor mechanical adherence, and weak wearing behavior. Hence, an inversely infusive procedure referred as (IIP) was used in constructing hierarchical architectures through novel synthesis of epoxy resin with

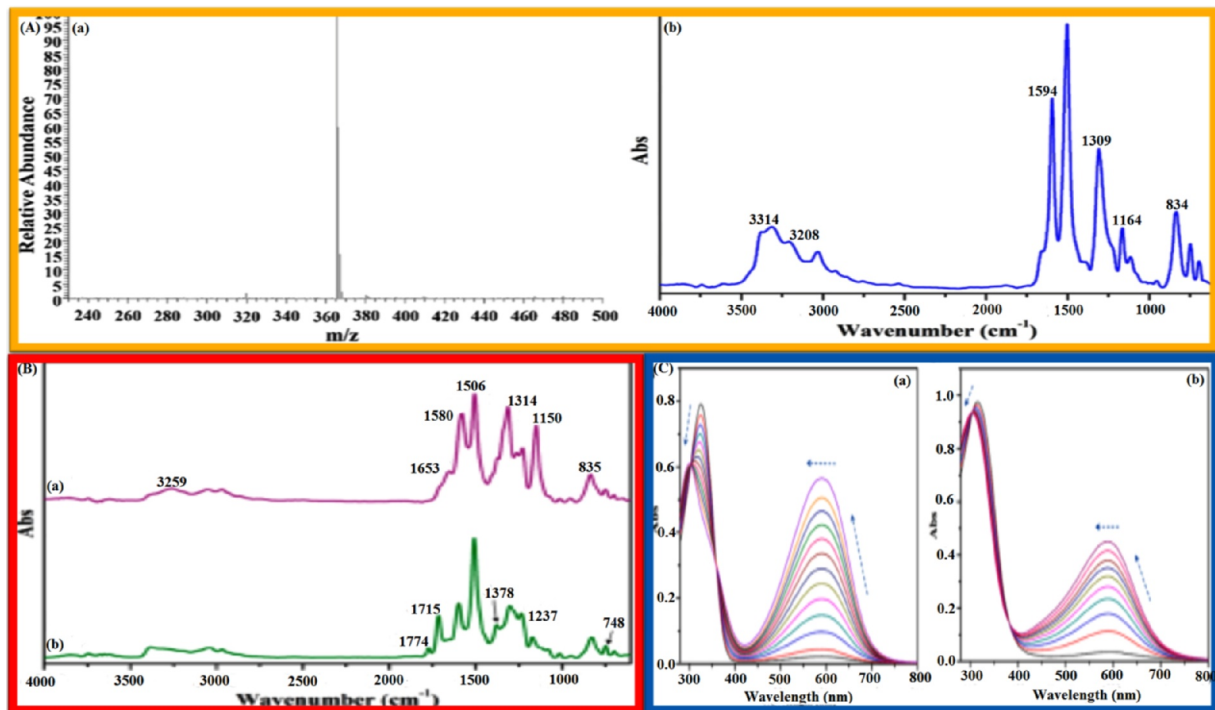


Fig. 7. A. Characterization of aniline tetramer by (a) Mass and (b) ATR-FTIR spectroscopies, B; ATR-FTIR spectroscopies of (a) EAAO and (b) EIO, C; UV-Vis spectra monitoring chemical of (a) AT and (b) EAAO [80].

alumina nanoparticles (NPs). Results revealed that this coating resisted highly corrosive environment, containing sodium hydroxide and hydrochloric acid solutions with high potentials for use as anti-fouling, self-cleaning, and anti-icing coating system [82].

Epoxy-TiO₂ nanocomposite coatings were prepared via solution intercalation technique. Varying concentration of TiO₂ nanoparticles ranging from 0.1, 0.2, and 0.3 wt. % respectively were used in preparing three types of epoxy nanocomposite coating systems designated

as ET1, ET2, and ET3, respectively [83]. Amongst other tests conducted to ascertain anti-corrosion efficiency was atomic force microscopy (AFM) which investigated the topological behavior of the prepared coating systems, in addition to variations in their surface roughness. Fig. 9 depicts 3-D topography of pristine epoxy-TiO₂ and nanocomposite coating systems [83].

A notable decrease in surface roughness was attained post TiO₂ nanoparticles inclusion in epoxy matrix especially within 0.1 to 0.2 wt.

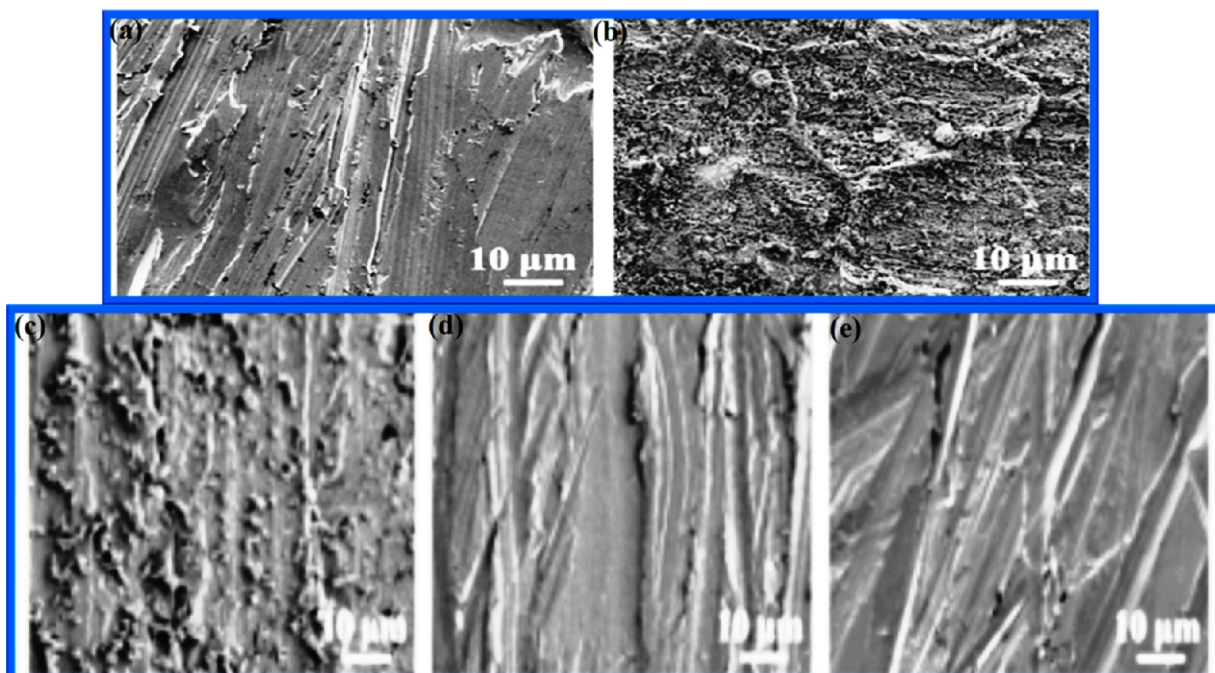


Fig. 8. depicts SEM images of (a) grinded CRS, with coating on CRS surface with (b) pristine, (c) PI, (d) AT and (e) EIO immersion in 3.5 wt. % NaCl solution time-frames for 30 days [80].

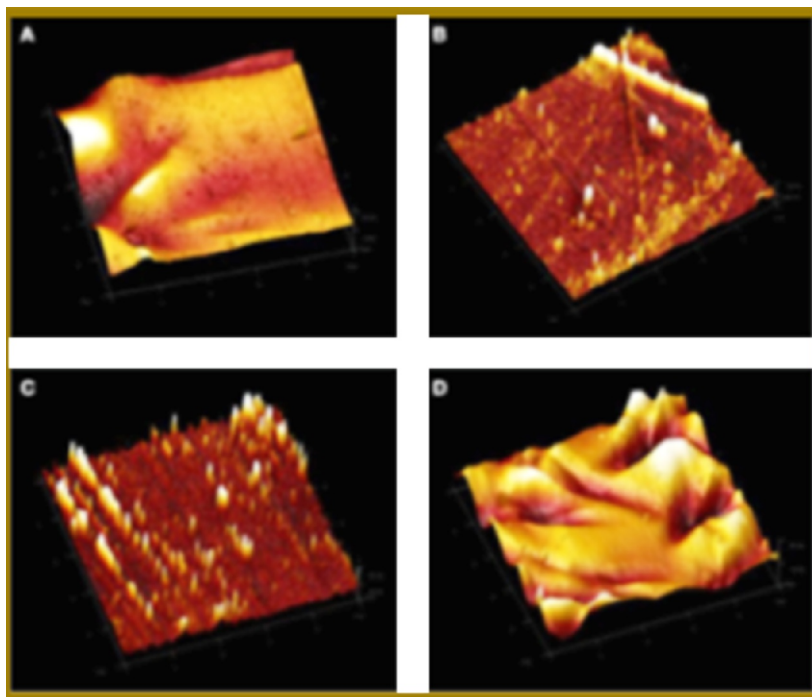


Fig. 9. 3D AFM images of (A) neat epoxy, E, coating system and (B) ET1, (C) ET2, and (D) ET3 epoxy-TiO₂ nanocomposite coating systems [83].

% concentration revealing efficient distribution state of TiO₂. On the other hand, a higher surface roughness was observed on application of ET3 coating system ascribed to the affinity to agglomeration of TiO₂ nanoparticles at higher inclusion, through escalation of nanoparticles clustering. Results exposed capacity of TiO₂ nanoparticles at improving the anti-corrosion performance of these coating systems.

5. Anti-fouling coatings

This section provides insight into novel preparation approaches, characterization, properties, and coating techniques of anti-fouling coatings. Marine architectures such as underwater pipelines, oil well-heads, platforms, ship-hulls, barges, jetties and so on are prone to severe and deteriorative biofouling. Notably, most anti-fouling systems are fundamentally based on use of protective coatings. Biofouling adversely and severely impacts on the hydrodynamics of ships hull through escalation of the basic propulsive power, which in turn affect the degree of fuel consumption thereby increasing cost of maintenance [84]. The 2001 prohibition of tributyltin (TBT), a self-polishing copolymeric coating by the International Maritime Organization (IMO), as a result of environmental challenges, and its subsequent replacement with eco-benign anti-fouling coatings, impacted progressively on anti-fouling coatings [85,86].

Marine engineered architectures including oceanographic-sensors, ships, platforms, heat-exchangers, offshore rigs, jetties and so on, are under consistent attack from marine organisms. For instance, it has been demonstrated that high biofouling agglomerates exhibited by a ship hull is capable of causing 86% penalties at moderate cruising speed [86]. Also, low fouling caused by diatom 'slimes' can incur a 10–16% penalty. Hence, speed maintenance becomes difficult with high fuel consumption and greenhouse gas emission, where there is lack of appropriate anti-fouling (AF) regulations [86]. Biofouling development on architectural structures submerged in aquatic environment is an intricate procedure as schematically elucidated in Fig. 10, comprising mostly of initial formation of biofilm, containing microbes and micro-algae, and subsequent agglomeration of algal-spores and invertebrate-larvae [84–86]. Biofouling agglomeration on marine based architectures is composed of millions of marine organisms including algae, phyto-

plankton, bacteria, ascidians, fungi, barnacles, polychaetes, and molluscs as represented in Fig. 11.

These flaws result in increased managerial and monitoring costs, aquacultural productivity losses, and increased shipping fuel costs. Thus, due to the economical repercussions of these marine challenges, varying mitigating strategies are utilized in marine environment as schematically elucidated in Fig. 12.

Copper paints, despite their elevated toxicity in marine environment were utilized as replacement for TBT containing anti-foulants [87]. Additionally, numerous other compounds have also been used as anti-fouling biocides. These compounds included zinc, dichloroflumid, irgarol-1051-diuron, pyridine, chlorothalonil, and pyriothione [88–89]. As a result of high toxicity and negative impact on the marine environment or ecosystem, most of these anti-fouling agents are presently placed under strict surveillance and regulation in various countries [90].

5.1. Anti-fouling techniques

Anti-fouling systems include paints, and defined as aesthetic covering composed of materials including stoppers, varnishes, sealers, enamels, lacquers, primers, undercoats, surfacers, fillers, and so on [91]. Anti-foulants are amongst numerous additives included in the formulation of marine protective coating systems. Anti-fouling paints are composed of organic primers forming surface-coatings with anti-corrosive attribute. Antifouling techniques are categorized into three namely chemical, physical, and biological techniques [91].

5.1.1. Chemical anti-fouling techniques

Marine biofouling is a naturally occurring process originating via adsorption of organic and mineral molecules, followed by adhering of micro-fouling such as bacteria and micro-algae, and macro-fouling in form of macro-algae and invertebrates [92]. Varying strategies have been developed in combating fouling based on self-polish-coatings (SPC), and controlled-depletion-paint (CDP) [92]. Many of these strategies are hinged on application of PNC coatings such as polyacrylic resins in blend with metallics including copper and/or toxic organic compounds [93].

A research based on the application of a hemibastadin analog

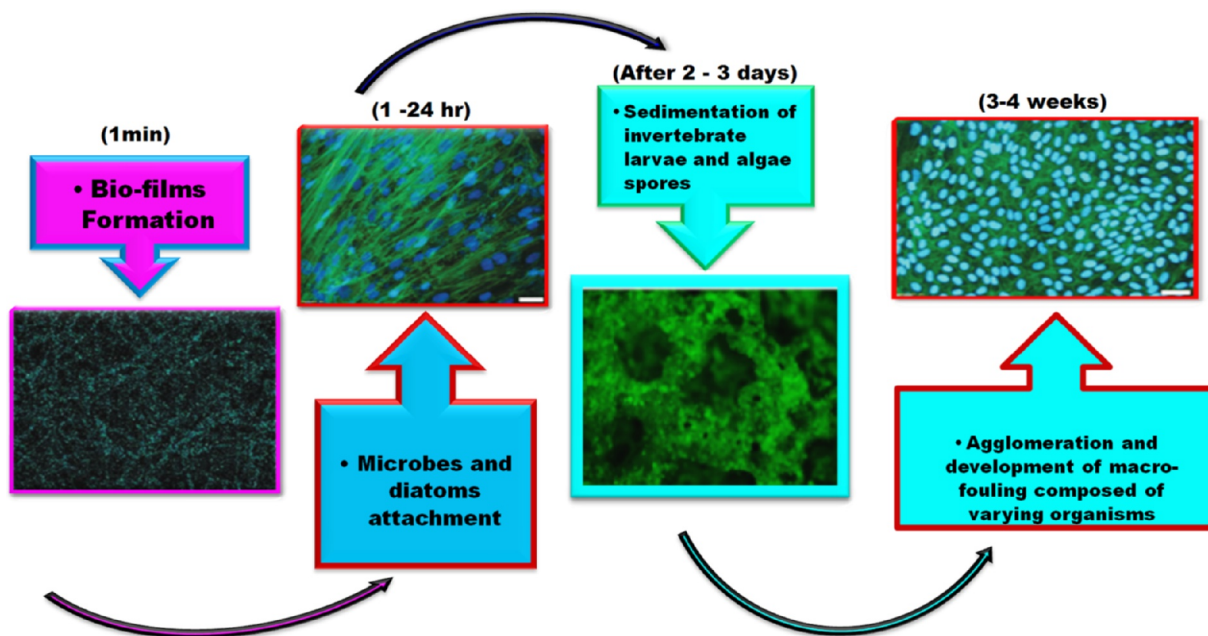


Fig. 10. Schematic elucidation of the stages of biofouling development on structural architectures submerged in marine environment.

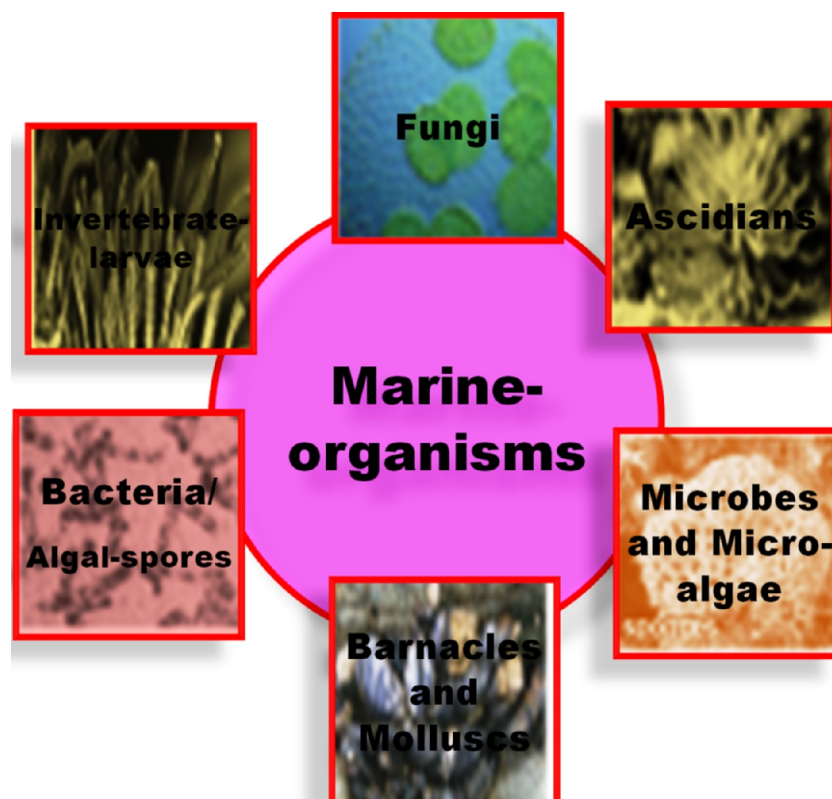


Fig. 11. Representation of marine organisms.

referred as dibromohemibastadin-1 (DBHB), a non-toxic anti-fouling compound suppressing the stability of cyprid larvae of barnacle improvises and byssus which form mytilus edulis on nauplii of *Artemia salina* has been developed [94]. Results revealed nil effect of DBHB relative to the Minimal Inhibition Concentration (MIC) which was greater than 80 M. With regards to adhesion and biofilm formation, observations were carried out using CLSM in the presence of 16 M DBHB. Bacteria gumming on glass slide was not minimized by the presence of DBHB: nil inhibition was observed as shown in Fig. 13 [94].

However, as revealed in Fig. 14, a notable inhibition of biofilm formation (39.6%) was demonstrated for *Paracoccus* sp. 4M6 [94]. However, nil effect of DBHB on *Pseudolateromonas* sp. 5M6 and *Bacillus* sp. 4J6 biofilm formation was recorded. Also, DBHB inclusion resulted in zero mortality in varying biofilms as observed by Syto 9/Sytox red staining. The mortality percent was lower than 1% for the three strains [94].

In another antifouling research, it was revealed that inclusion of polydimethylsiloxane (PDMS) into coatings improved the antifouling

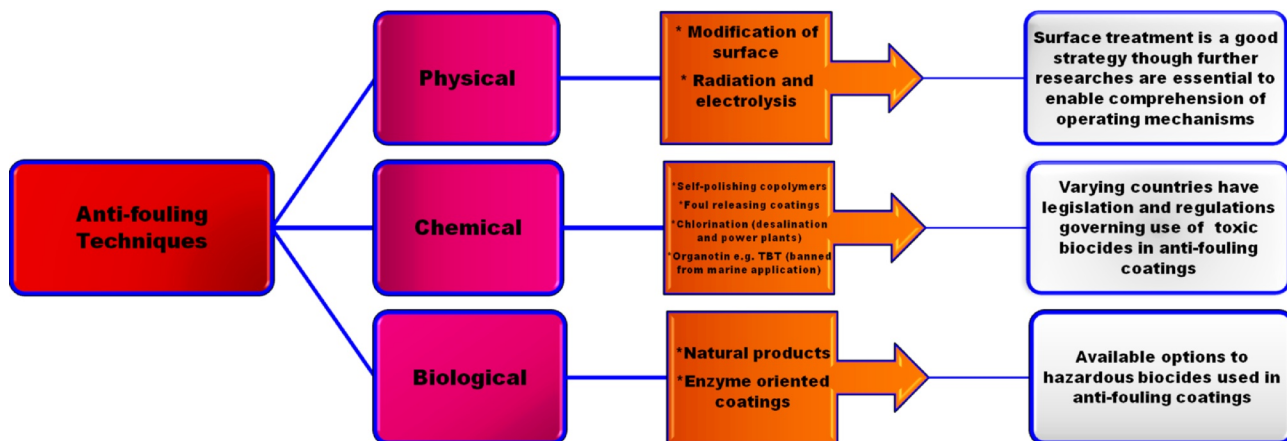


Fig. 12. Various anti-fouling used by different sectors in the marine environment.

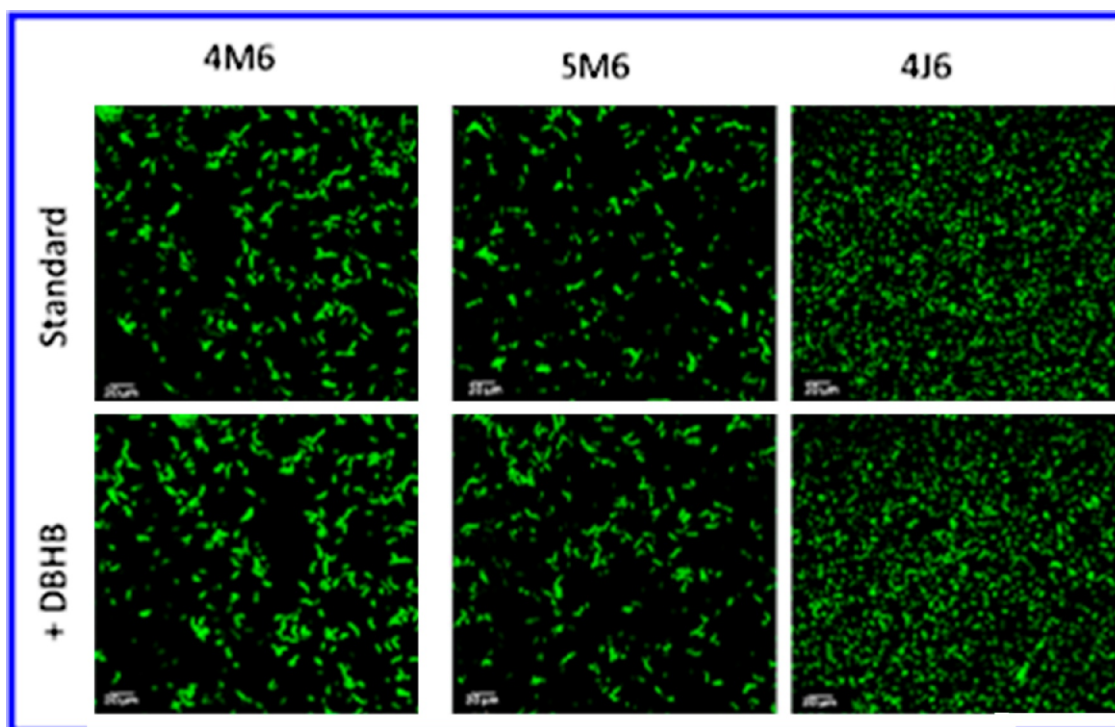


Fig. 13. DBHB impact on the bacterial adhesion on glass surface at 20 C devoid of DBHB (Standard) inclusion and composed of DBHB at 16 M (+DBHB). Adherence of *Paracoccus* sp. (4M6), *Pseudolateromonas* sp. (5M6) and *Bacillus* sp. (4J6) was observed by DBHB and detected via cells staining using Syto 9. DBHB: Dibromohemibastadin. Sale bar: 20 m [94].

performance through enhancement of coating hydrophobicity and reduction in elastic modulus, while PDMS leaching from the coatings enhanced degree of coating fouling elimination. This implies a twin improvement effect on the antifouling propensity of fouling release coatings oriented on PDMS inclusion [95]. Fig. 15 shows the morphologies of varying amounts of PDMS leached on the specimens [95].

Anti-fouling release coatings made from siloxane are presently the most viable non-toxic commercially available replacement for toxic biocide anti-fouling coatings [96]. Having the objective of improving the degree of bacterial inhibition of siloxane coatings when treated with non-ionic surfactant (NIS), anti-oxidant (AO) or both NIS/AO, the prospects of PEG-silane co-cross-linkage was studied to minimize *Cobetia marina* adherence and multispecies biofilm formation from naturally occurring sea-water. PEG-silane co-cross-linkage, in combination with NIS and AO can efficiently reduce bio-adherence of Gram-

negative marine bacteria and multi-species bio-film formation on siloxane anti-fouling coatings [96].

Microbial clustering on solid surfaces is function of varying surface factors such as topography, hydrophilic/hydrophobic equality, roughness, and surface-tension [97], in addition to other factors including surface mechanical parameters. Placing the expectation of being influenced by the used treatment agents (PEG-silane, NIS and AO), the surface examination of each test surface was conducted prior to examination of the bacterial adhesion and biofilm formation. The results are shown in Fig. 16 [97].

Results revealed enhanced antifouling resistance of the coatings.

Fluorescent microscopy with SYTO-9 staining was utilized in visualizing bacterial biofilms formed after 1 h incubation of *C. marina*. Images of these biofilms revealing a single layering of cells with some 3-D agglomerates are displayed in Fig. 17 (on glass; 1 on control coating without PEG-silane; 2 and 3 on coatings, composed of 2 wt. % PEG-

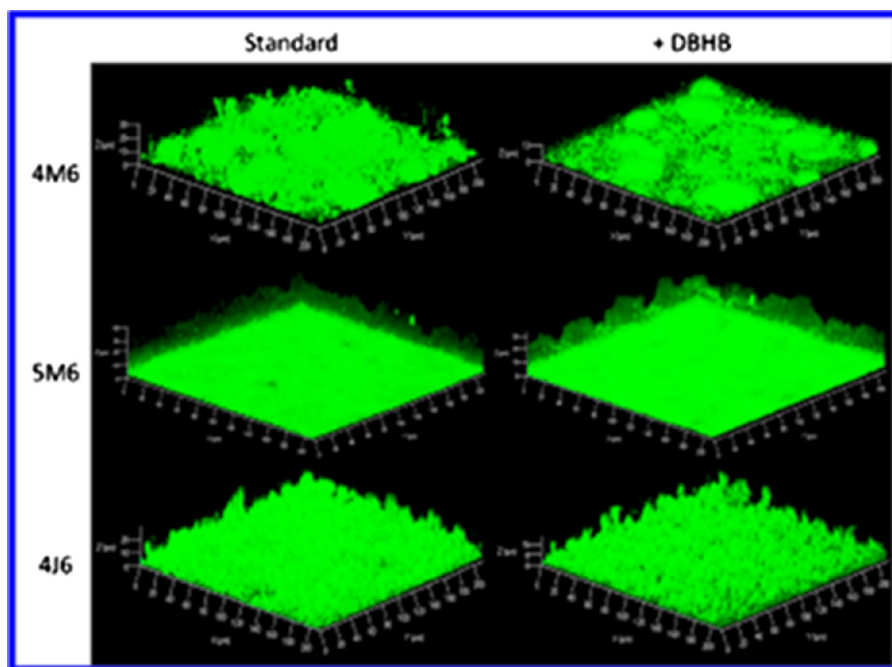


Fig. 14. DBHB effect on bacterial biofilm formation. CLSM observations of the bacterial biofilm developed on glass surface at 20 C under mild flow in absence of DBHB (Standard) and composed of DBHB at 16 M (+DBHB). Biofilms of *Paracoccus* sp. (4M6), *Pseudoalteromonas* sp. (5M6) and *Bacillus* sp. (4J6) were observed through cell staining using Syto 9 [94].

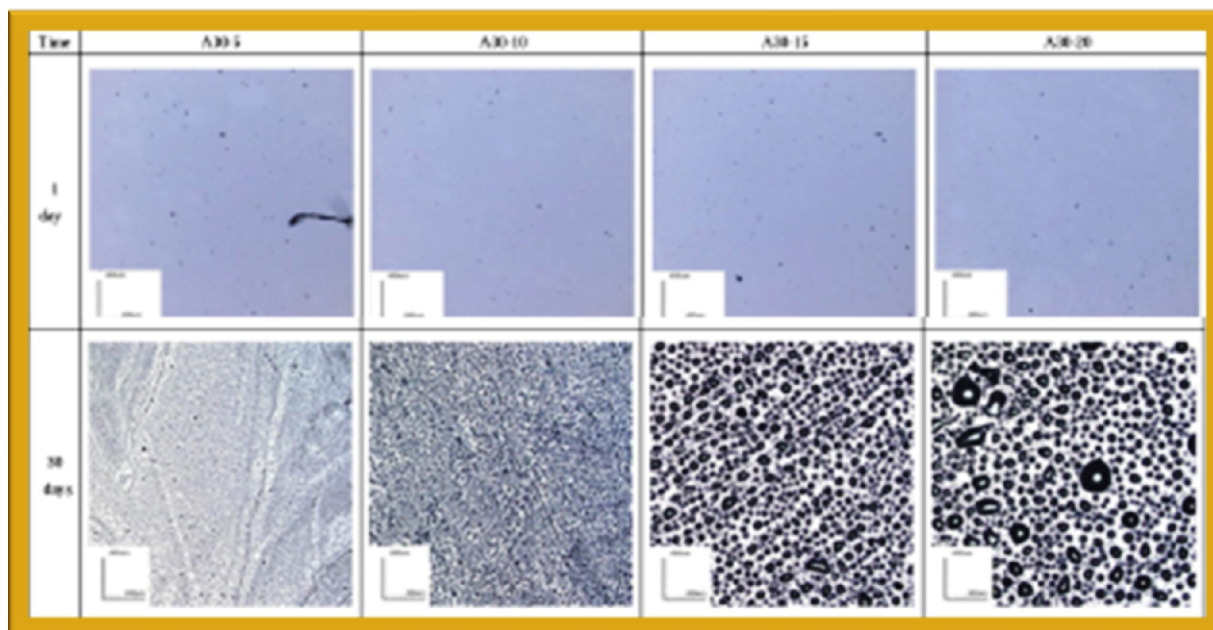


Fig. 15. Morphologies of varying amounts of PDMS leached on specimen [95].

silane) and Fig. 18 (coatings composed of 2 wt. % PEG-silane and 4–NIS; 5–NAO and 6–NIS/NAO) [98].

Fluorescent microscopic pictures of SYTO 9 stained *C. marina* biofilms formed after 1 h incubation on (NC) negative control, glass slide with staining procedure and without bacteria; and on glass samples with PEG-silane co-cross-linked coatings composed of (1) 6.0 wt % conventional cross-linkage, ES 40 (control, bacteria and staining); (2) 4.0 wt % ES40 + 2.0 wt % PEG-silane; (bacteria and staining); (3) 6.0 wt % ES40 + 2.0 wt % PEG-silane, (bacteria and staining). The yellow arrows reveal areas containing stained bacteria. Oil looking blemishes are seen on the pictures of coatings 5 and 6 (Fig. 18), both composed NAO in the corresponding siloxane composition. Most probably, they are formed by NAO migrating to the surface and do not succeed in completely wetting the surface because of relatively low surface energy of the cross-linked siloxane-coating. Fine fibril elements (the longest of

about 2–3 μ m) are observed in all PEG-silane containing coatings (Fig. 17, samples 2, and 3; Fig. 18 [98]).

Previously, biofouling was perceived as a challenge and varying forms of anti-fouling techniques have been studied. Organotin substrates such as tributyltin-oxide (TBTO) and tributyltin-fluoride have been applied as anti-foulants. Organotin and its other forms have also been versatily applied as anti-fouling coatings due to their efficiency in repressing a wide range of fouling agglomerates. Those antifouling organotin compounds are powerful fungicides, and will completely inhibit growth of most fouling organisms at a very low concentration [98,99].

5.1.2. Biological antifouling

Numerous organisms are capable of secreting enzymes or metabolites to hinder development of their competitors [100]. These secretions

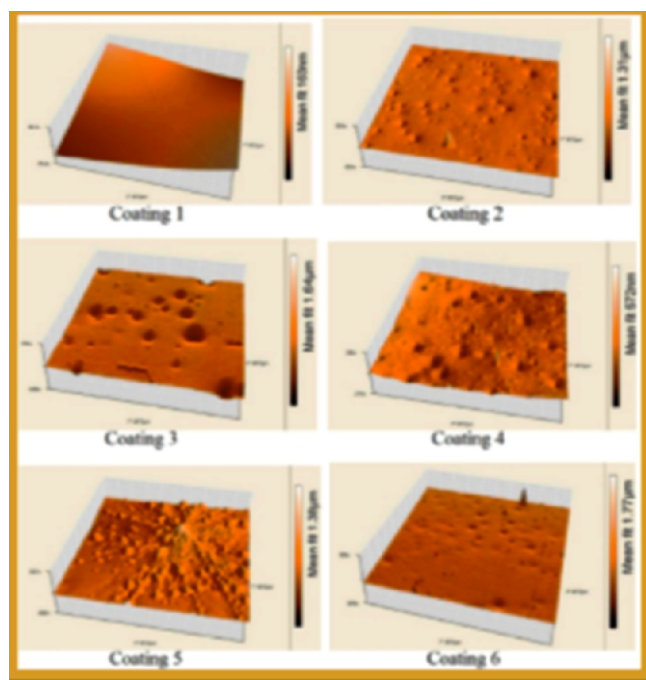


Fig. 16. Nano-topography (49 m × 49 m surface area) of the studied coatings, containing: (1) 6 wt % conventional cross-linker, ES 40 (control); (2) 4 wt % ES40 + 2 wt % PEG-silane; (3) 6 wt % ES40 + 2 wt % PEG-silane; (4) 4 wt % ES40 + 2 wt % PEG-silane + 0.5 wt % NIS; (5) 4 wt % ES40 + 2 wt % PEG-silane + 2.0 wt % AO; (6) 4 wt % ES40 + 2 wt % PEG-silane + 0.5 wt % NIS + 1.5 wt % AO [97].

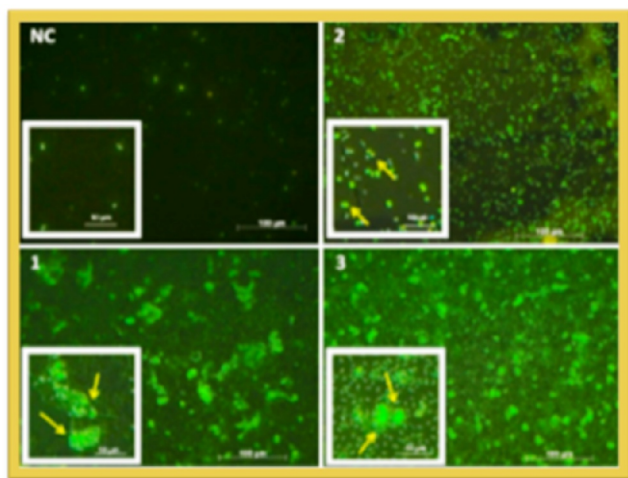


Fig. 17. Fluorescent microscopic pictures of SYTO 9 stained *C. marina* biofilms formed post 1 h incubating process on (NC) negative control, glass-slide containing stained and unstained bacteria; and on glass specimens with PEG-silane co-cross-linked coatings composed: (1) 6.0 wt. % conventional cross-linker, ES 40 (control, bacteria and staining); (2) 4.0 wt % ES40 + 2.0 wt % PEG-silane; (bacteria and staining); (3) 6.0 wt % ES40 + 2.0 wt % PEG-silane, (bacteria and staining). The yellow arrows imply regions with stained bacteria [98].

exhibit minimal-toxicity which are biodegradable, and have garnered much interest recently. Investigators have tried in extracting high concentrations of these secretions for application in biological anti-fouling [100–102]. The anti-fouling behavior of bioactive compounds separated from marine microbes can be examined in the laboratory against biofilm-forming bacteria, diatoms and barnacle-larvae as instances of organisms under investigation. A naturally occurring anti-fouling agent will influence these organisms in various ways as

schematically elucidated in Fig. 19. Generally, the agent must hinder biofilms development, perceived as lead for further agglomeration of invertebrate larvae in marine environment.

5.1.3. Physical antifouling techniques

5.1.3.1. Antifouling by electrolysis and radiation. Many techniques for physically inhibiting biofouling have been studied. Anti-fouling can also be attained via micro-cosmic electro-chemical techniques, relying on direct electron exchange between an electrode and the microbial-cells [103]. This results in electro-chemically induced oxidation of inter-cellular substrates, though this is costly and the effectiveness has not been confirmed. Acoustic technology as a form of anti-fouling vibrational technique has been established. Hydroids, mussels and barnacles can also be resisted to a great extent by either exterior vibrational sources or piezo-electric coatings. However, the large power consumption tendencies of these techniques have posed challenges to deal with. However, due to high surface voltage reduction across the surface, some of these mechanisms are not highly effective and this will escalate corrosion issues on the steel substrate. Thus, titanium-enhanced anodic layering has been effectively used due to accruable benefits such as reduced decomposition tension, elevated current effectiveness, and reduced energy consumption although the development has been limited [103].

5.1.3.2. Antifouling via surface topographical and hydrophobic behavior modification. Recently, varying surface behaviors, such as surface roughness, topography, hydrophobic behavior, and lubricity, have been investigated for use in antifouling [104]. Biofilm is mainly formed by micro-organisms such as bacteria and micro-algae, with dimensions of approximately 1–100 µm. At this level, it is feasible to accurately modify the surface micro-structure. An investigation has revealed that fouling diatoms bond strongly to hydrophobic surface of polydimethylsiloxane (PDMSE) than adhering to glass [104]. Additionally, hydrophilic surfaces exhibit antifouling affinity [104–106].

5.1.3.3. Biomimetics strategy. Biomimetics refer to bio-inspired design instead of direct duplication of natural biological behavior. It presents natural existence as model for engineering development, or as a ‘bottom-up’ route for hierarchical architectures [107]. Usages of biomimetics technique for coatings involve control of inorganic deposition such as silica and silver by biomolecules. The main chemical antifouling systems for marine organisms occur via production of secondary metabolites which hinder fouling. Naturally occurring systems may be applied as focus for biomimetic or bio-inspirational coatings, and significant interests has been alligned for its designing based on topographical behavior.

5.1.4. Physico-chemical antifouling strategies

Interfacial chemistry is a notable parameter determining the formation, gumming release, and stability of fouling organisms on surfaces. A route of varying surface energy lacking bulk material manipulation is via self-arranged monolayering (SAMs). In a study, the potential of different varieties of SAM chemistries to inhibit protein adsorption was undertaken. This research demonstrated that though SAMs, are hydrophilic, with electrical neutrality, and composed of hydrogen bond receivers, they are also very efficient at hindering protein adherence [108–111].

6. Amphiphilic nanostructured coatings

It has been have proposed that the commonly observed protein resistance of some nano-architected, amphiphilic di-block copolymers is as a result of the inherently high density of interfacial surface differentials. An instance of amphiphilic coating for use in marine AF is focused on the hyperbranching of fluoropolymers and linear poly

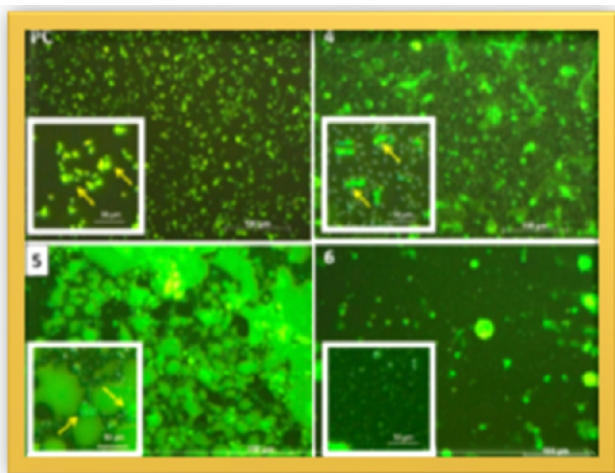


Fig. 18. Fluorescent microscopic pictures of SYTO 9 stained *C. marina* biofilms formed after a 1 h incubation on (PC) positive control, glass-slide composed of stained and unstained bacteria and glass samples with PEG-silane co-cross-linked coatings containing modifying agent: (4) 4.0 wt % ES40 + 2.0 wt % PEG-silane + 0.5 wt % NIS; (bacteria and staining); (5) 4.0 wt % ES40 + 2.0 wt % PEG-silane + 2.0 wt % AO; (bacteria and staining); (6) 4.0 wt % ES40 + 2.0 wt % PEG-silane + 0.5 wt % NIS + 1.5 wt %AO, (bacteria and staining). The yellow arrows show regions stained with bacteria [98].

(ethylene glycols) (PEG), which self-align on cross-linking thereby forming intricate interfacial topographies and chemical regions of both nanoscopic and microscopic zones [112-114].

7. Flame and thermal retardant coatings

This section elucidates flame retardant coatings (FRCs), with emphasis on preparation, characterization, properties, and coating techniques of FRCs. In recent years, it has become highly imperative to develop FRCs. The use of FRCs enhance feasibility of delaying fire

spread or maintaining material architecture against devastating effect of fire, thereby facilitating enough time for implementation of safety measures, although hindering fire through use of coatings for prolonged duration is not feasible. Presently, varying types of fire additives such as phosphorus based, halogen-oriented, and intumescent fire-repressing systems, operating on varying principles have been established. Phosphorus based additives operate through formation of a barricading protective layering in form of a glass-like surfacial protective covering. Antimony and halogen oriented fire repressants exhibit toxicity and are environmentally unfriendly. Intumescent coatings exhibit capability of forming a broad carbon-oriented matter acting as a protective barricading layering against heat transport thereby hindering diffusive penetration of combustion prone gases and polymeric melt to the combustion site. Three entities constituting these coatings include: (i) inorganic acid referred as a dehydrating entity; (ii) a carbon-oriented charring material; and (iii) a blowing entity. The output of intumescent entities is function of the disposition of the ingredients, in addition to their synergistic effect [115].

Recent fire technologies have inculcated expandable graphites as fire retarding entities; composed of chemical matter, such an acid, engulfed within the carbon layering. When exposed to elevated temperatures, graphite exfoliation occurs providing an insulative layering to the given material. Synergy of polyurethane (PU)/phosphate (PT) has demonstrated a fire-suppressing intumescent system [116]. Presently, fire retardant coatings based on silicon/inorganic hydroxide are broadly utilized over a wide range of industrial applications [117]. Recently, polymer clay nanocomposites (PCN) coatings have been developed as FR coatings [118]. Here, PCN coatings were prepared via uniform dispersion of organically treated montmorillonite clay (Cloisite 20A and 30B) in differing concentrations. FR results revealed effective fire repression [118].

A comparative flame retardant and thermal stability analysis of epoxy-EG and epoxy/halloysite nanotubes (HNTs) nanocomposite coatings have been conducted [119]. Results revealed that the synergy attained between HNTs/EG decreased peak of Heat Release Rate (pHRR), and Total Heat Release (THR), while simultaneously increasing Time-To-Ignition (TTI) of the materials [119]. Also, intumescent

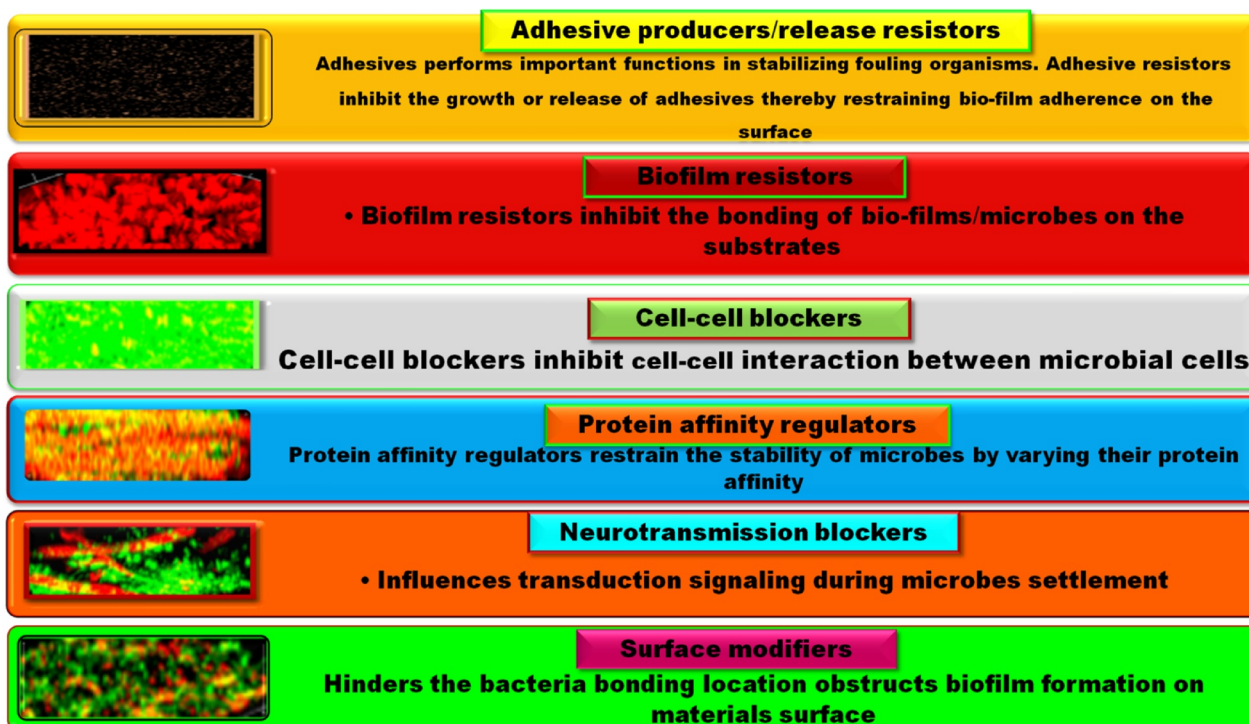


Fig. 19. Operational strategies of antifouling agents on fouling organisms.

coatings composed acrylic/nanoclay nanocomposites coatings have been prepared to enable fire protection of metallic surfaces [120]. Results demonstrated that FR efficiency of the intumescent nanocomposite coating was enhanced by 1.5 % via evenly dispersed nanoclay.

FR acrylic nanocomposite coatings with varying acrylic polymers have been prepared [121]. Influence of molecular architecture, and molecular weight of acrylic nanocomposite in combination with nano-SiO₂ on char formation and interaction of ammonium polyphosphate-dipentaerythritol-melamine (APP-DPER-MEL) coating were analysed via TG, DTA, Limiting Oxygen Index (LOI), SEM, XPS, and fire protection test. Results revealed that interaction of APP, DPER, MEL and 3F-1 acrylic resin resulted in creation of a compact intumescent char at 300–450°C which enhanced the material FR. Notably, nano-coating fire hindering behavior of acrylic nanocomposites demonstrated superiority to those of FRCs with traditional acrylic resins [122].

Epoxy/HA nanocomposites intumescent FR has been fabricated [123]. The fabricated PNC coatings resisted a direct flame originating at 1700°C with capacity of self extinguishing. HA nanoplatelets availed a gas phase effect as a result of the emission of active fire scavengers. Moreso HA caused a condensed phase effect by forming a protective char layer on the surface of the material. Generally, intumescent thermosetting nanocomposite coatings reduce heat while forming thick cohesive insulative barrier fire protection on steel surface.

Extremely flammable polyurethane foam (PUF) has posed a highly risky parameter relative to bedding and upholstery furniture, contributing to annual destruction of lives and properties [124]. In a bid to solve this challenge, and evolve a more environmentally benign FR for PUF, a mica oriented nanocomposite was formed via layer-by-layer architecture [125]. Chitosan (CH)/poly (acrylic acid) (PAA) was utilized in stabilizing high-aspect-ratio mica. Modified foam composed of eight bilayers of CH- and PAA-stabilized mica protected void-filled foam architecture through melt-dripping hindering, and self-extinguishing during a 10s torch testing, while uncoated foam completely burnt. On exposure to 35 kW/m² heat flux during CCT, the pHRR was minimized by 54% and less-volatile molecules emitted during burning, resulting in a 76% minimization of TSR. This multiple coating barrier offer ecobenign formulation for FR PUF and other 3-D entities.

This is similar to FR coatings preparation using chitosan (CS) and phosphorylated chitosan (PCS) in combination with poly-acrylate sodium (PAS) deposition on surface of polyamide 66 (PA66) fabrics through layer by layer (LbL) assembly technique [126]. Results exposed that only LbL formed fabric exhibited FR in vertical burning test after 5 cycles of washing. LbL fabrics exhibited superior uniformity in the coating architecture. PA66-10BL-UV LbL treated fabric sample with increased weight % gain demonstrated superior FR in LOI test with 23%, and a minimized pHRR of 25%.

A similar study for enhancing FR of PUF using synergy of water-soluble phenolic resin (WSPR) and 0.5 wt% zeolitic imidazolate framework-67 (ZIF-67) was undertaken [127]. Combustion results revealed that inclusion of WSPR/ZIF-67 FR coating minimized PHRR, THR and smoke release of FPUF and hindered foam melt-drops from occurring during the combustion.

Influence of particulate sized flaky graphite (FG) on FR of intumescent flame retardant (IFR) coatings (polyester resin-ammonium polyphosphate-urea-pentaerythrite) was investigated via CCT, XRD, and SEM, in order to determine best FG for the preparation of FG-IFR coatings [128]. CCT results revealed that doped FG₁₅₀₀ possessing average particulate dimension of 1500 mesh exhibited superior FR efficiency, demonstrated by the lowest peak heat release rate (p-HRR) of 23.5 kW m⁻² at 409 s and fire growth index (FGI) of 0.06 kW m⁻² s⁻¹, attributed to creation of expanded laminar char residue. This study revealed that FG with proper nanoparticulate dimension is best at enhancing flame suppression behavior of IFR coating.

8. Self-healing PNC coatings

Generally, Self-healing materials (SHM) are synthetic materials capable of self-repairing after subjected to damages. Nowadays, SHM have garnered great interests because of their capability to prolong materials shelf-life, minimize costs of maintenance, and improve safety of the citizenry [129]. SHM are categorised into two groups vis-a-vis intrinsic (ISHM) and extrinsic (ESHM) [129]. ISHM possess a latent self-repairing ability initiated by damages. It can also be triggered by external factors, so they can propagate self-mending. In ESHM, damages are recovered through releasing of healing entities from micro-containers engulfed in matrices. ESHM are generally classified into two major groups: capsular SHM (CSHM) and vascular SHM (VSHM). As regards CSHM, on rupturing of capsules by infliction, the healing entity is propagated from ruptured capsules, filling damaged areas thereby triggering healing activities. VSHM repairing activities is quite similar to CSHM however; the capsules here are substituted by a vascular pipeline network occurring in 1D, 2D or 3D. In comparison with ISHM, the ESHM posit advantages in healing a broad zone of the damaged volume [130].

Self-healing coatings (SHC) are potential technique of solving aforementioned challenges, as result of autonomously mending damages without external interferences [131]. Initially, dicyclopentadiene (DCPD) was encased in the interiors of urea-formaldehyde (UF) shells through in situ polymerization to fabricate microcapsules, and discovered that epoxy matrix and Grubbs catalyst demonstrated self-mending after damage infliction [132]. Hence, microcapsules loading with healing entities in order to form SH coating has garnered much attention [133]. Additionally, numerous healing entities have undergone microencapsulation for propagation of self-mending, including epoxy [134-136], polydimethylsiloxane [137], and others.

In a study, linseed oil (LO) went through an oxidative drying procedure on exposure to air, forming a soft film [138]. After 48 h, the reaction conversion attained 88 % and 59 % at ambient temperature and 20 °C, respectively. LO-included microcapsules were formed via urea-formaldehyde polymeric material as shell-wall material. The microcapsules were then incorporated into a protecting coating formulation in order to enable preparation of SH coating samples of varying levels of capsular inclusion. Self repair was successfully demonstrated for both scratched and cracked damages in the coatings. Architectural micrographs of the microcapsules were analyzed using SEM as shown in Fig. 20 (a). Optical microscopy was used in analyzing the microcapsular size distribution as depicted in Fig. 20 (b). The microcapsular average diameter was 53 μm. The self-mending coating underwent scratching using a 30 μm-thick cutter and abandoned for 48 h at ambient temperature to induce self-repair. Another scratched control coating was also fabricated in a likewise manner in absence of microcapsules. SEM images of the scratched zone of LO SH coating demonstrated that the healing entity filled the scratched area, thereby facilitating effective scratch mending as depicted in Fig. 20 (b), while Fig. 20 (a) reveals the scratch was unfilled in the control coating.

Polyurea is a potential coating material for effective protection. This is ascribed to its compressive/tensile attributes and capacity to absorb elevated level of energy [139]. Thus, in a recent study, spherical microcapsules with inclusion of isophorone-diisocyanate (IPDI) as core substrates were fabricated using interfacial polymerization included in an oil-in-water emulsion, utilizing sodium lignosulfonate (NaLS) as an emulsifying agent, and polydiphenylmethane diisocyanate (PMDI) capsule shell reinforcement. Morphological images of the capsules fabricated under varying NaLS composition are shown in Fig. 21 (a, b). Morphological images of the capsules fabricated under varying O/W ratios are shown in Fig. 21 (c). As depicted in Fig. 22, results exposes spherical capsules as having a mean diameter of 47.8 μm and a shell thickness almost equal to 1.9 μm. The ease of polyurea coating flow, and dispersion is enhanced by the smooth surface of the capsules [139] (Fig. 23).

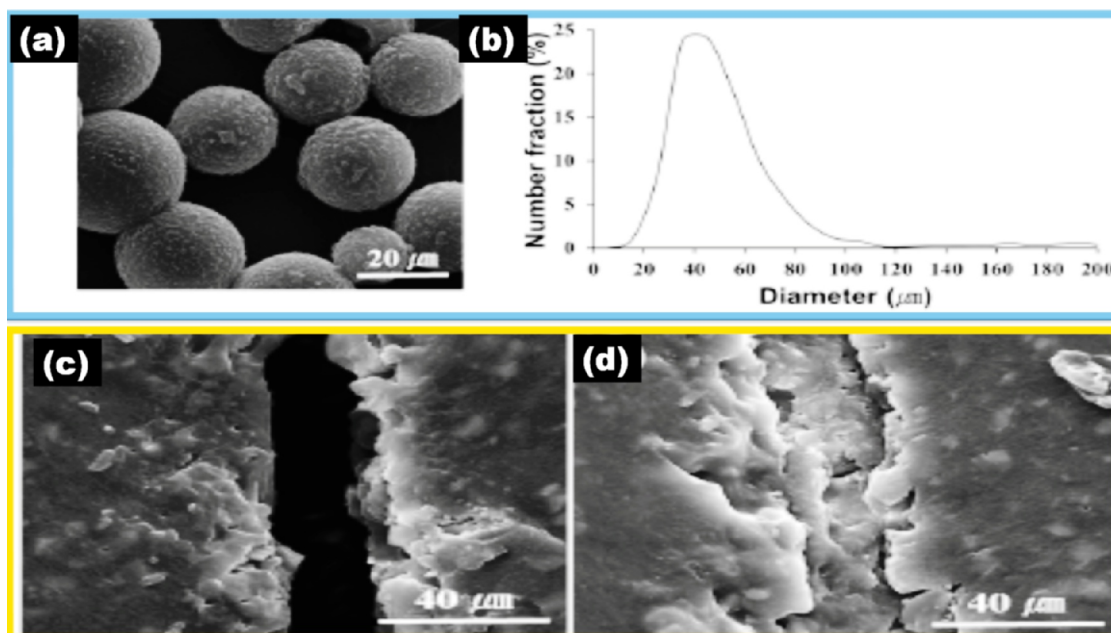


Fig. 20. (a). SEM image of LO microcapsules; (b) LO size distribution; SEM images of the scratched (c) control and (d) self-healing coatings [138].

The future of smart coating is dependent on the multi-operational attributes attained in coating matrices. The development of smart coatings on SH and self-lubricating attributes is highly challenging. Generally, the concept of hindering corrosion via SH facilitates autonomous repairs of cracks and damages in absence of any external intrusion [140]. SH entities encapsulation potending sensitivity to external stimuli such as pH, moisture, light, or crack propagation is critical for inculcating functionalities capable of damage repair. Numerous coating systems included SH agents have been investigated [135-141]. A commonly studied smart coating system is urea formaldehyde microcapsules (UFMC) with encapsulation of varying inhibitors and SH agents incorporated into polymeric matrix [142].

Varying nanoconveyors have been inculcated for polymeric matrices. They include; halloysite [143], ion exchanging organically based resins [144], nanocontaining materials from polyelectrolyte based shell [145], layered double hydroxide (LDH) conductive polymeric matrix [146], montmorillonite [147], and mesoporous inorganically focused materials [148]. Varying routes of attaining SH behavior have been exposed, relative to encapsulation [149], reversibility chemistry [150], micro-vascular complexes [151], nanoparticulate phasial separation [152], polymeric ionomers [153], hollow fibres [154], and monomeric separation [155].

PNC coatings exhibit satisfactory SH effects while responding to externally controlled mechanically based deterioration.

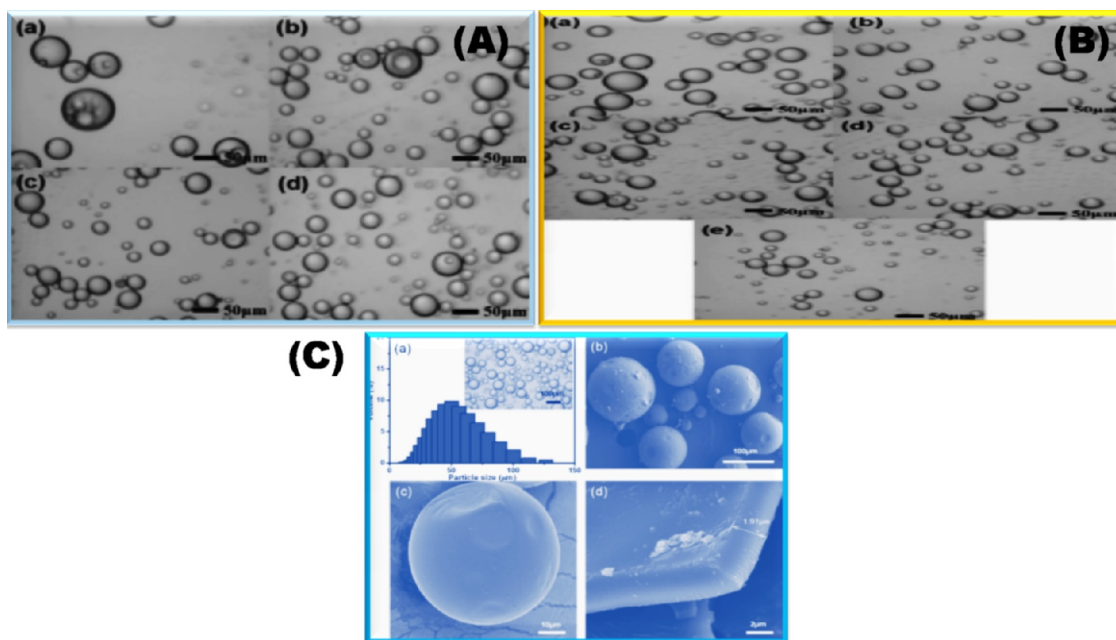


Fig. 21. A. Optical microscopic images of IPDI-included O/W emulsions stabilized by varying composition of NaLS at a O/W ratio of 1:1. (a) 0.1%, (b) 0.5%, (c) 1%, (d) 2%. B. Optical microscopic images of IPDI-included O/W emulsions stabilized by 1 wt. % NaLS under varying O/W ratios. (a) 2:1, (b) 1.6:1, (c) 1.2:1, (d) 0.8:1, (e) 0.4:1 [139].

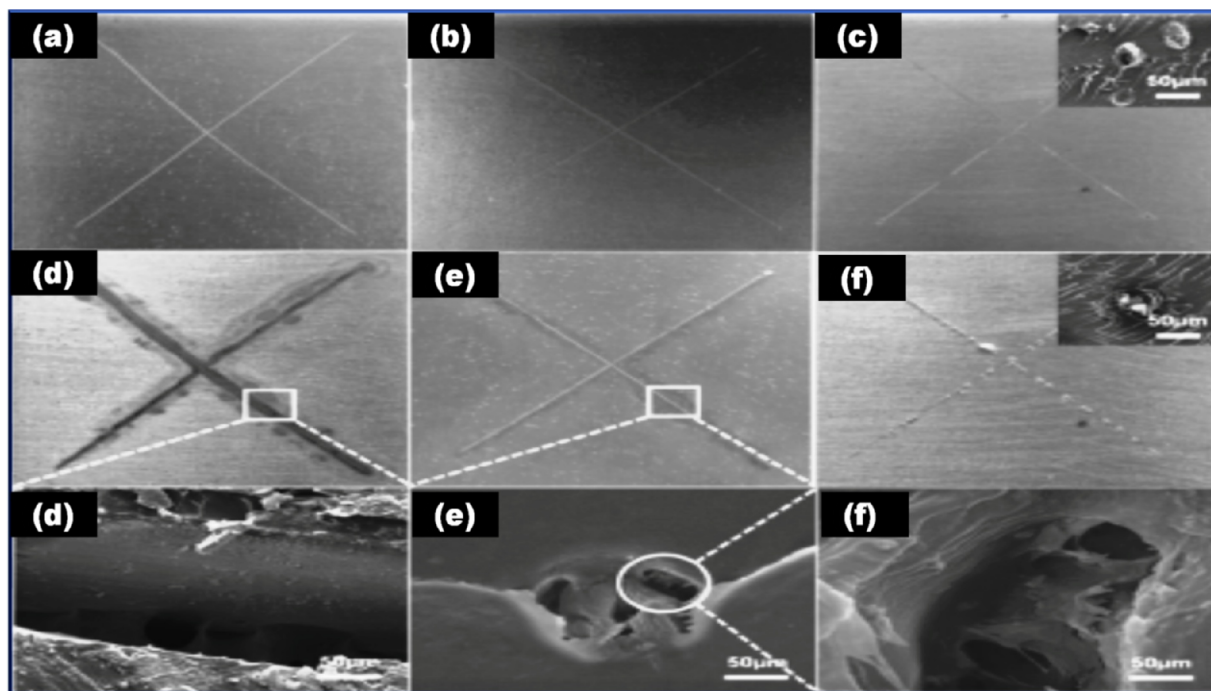


Fig. 22. Corrosion rating of steel sheets coated with pure and SH polyureas (SHPU) in 10% NaCl aqueous solution for 48 h. (a, b) Optical images of pure and SHPU coatings; (c) Optical image of SHPU coating with twice NaLS microcapsules; Insert: SEM image of NaLS microcapsules in SHPU; (d, e) Optical images of scratched pure and SHPU; (f) Optical image of SHPU coating with twice NaLS microcapsules post scratching; Insert: SEM image of broken NaLS microcapsules in SHPU; (g) SEM image of crevice in pure polyurea coating; (h, i) Influence of crevice SH in SHPU coating post scratching [139].

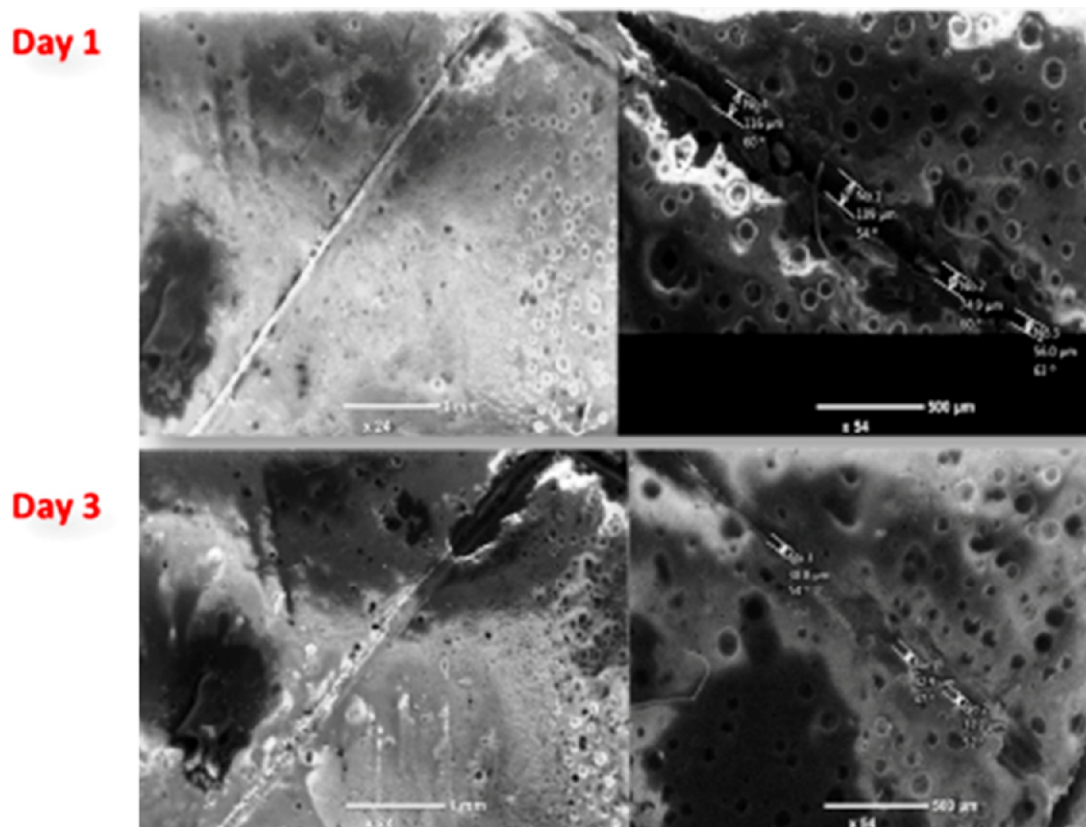


Fig. 23. SEM images of the scratched samples after different time intervals [62].

Electrochemical impedance spectroscopic analysis (EIS) exposes potential corrosion restraining effects of PNC coatings. PNC treated with multifunctional entities may demonstrate effective corrosion

repression of steel in the oil and gas sector [156]. In a bid to enhance coatings performance to keep up with industrial standards, coating systems referred to as smart coatings have evolved to interesting

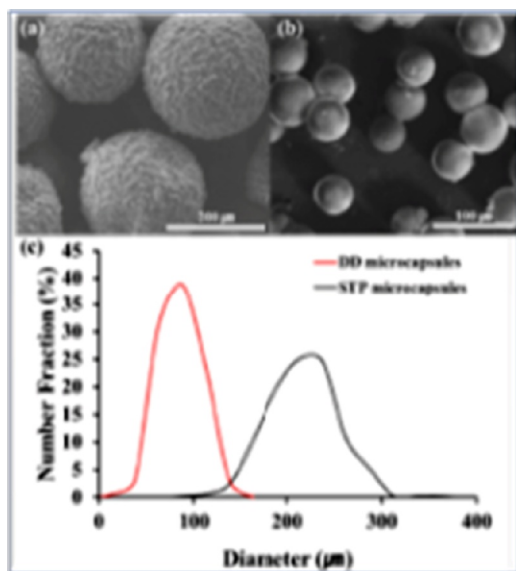


Fig. 24. SEM images of (a) the STP-based microcapsules and (b) the DD-oriented microcapsules; (c) STP and DD size distribution of microcapsules prepared at 1000 rpm [158].

multifunctional levels such as SH and self-hinderances [156]. External stimuli including variations in pH, metallic ions, and/or electrochemically based interactions results in propagation of multifunctional effects [157]. The aim of inculcating SH behavior is to attract satisfactory healing of crevices or scratches on the surface of coatings. As regards attainment of this aim, SH behaviors of developed PNC coatings are analysed. In line with this procedure, the coatings were exposed to

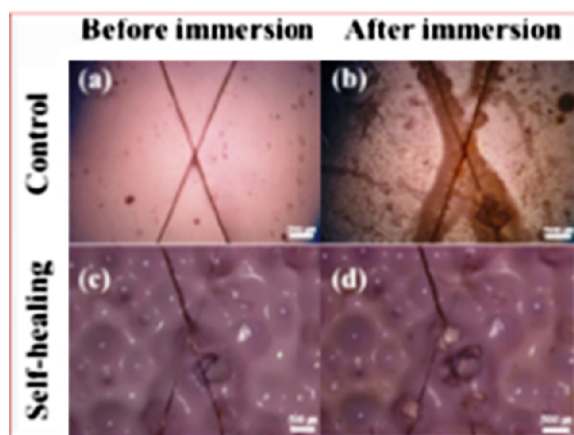


Fig. 26. Optical microscopic images of scratched-control and SH coating specimens prior to- and post immersion for 48 h at 20 C in 25 wt. % NaCl aqueous solution. (a) Control coating prior to immersion; (b) control coating post immersion; (c) SH coating prior to immersion; (d) SH coating post immersion [158].

controlled damages. To study the SH performances of developed PNC coatings, SEM images of the deteriorated PNC coatings were derived at varying durations, as elucidated in Fig. 22 [62].

Results revealed significant SH of PNC coatings with increasing time duration. The potential SH mechanism is such that while responding to mechanical damage, the SH entity as linseed oil (LO) is transported to the crevice from the submerged and encapsulated UFMCs which flows into the crevice, facilitating SH effect [62]. Emitted LO assists in SH of scratched coating while enabling mild layering to hinder direct contact of metallic surface from the adverse environment.

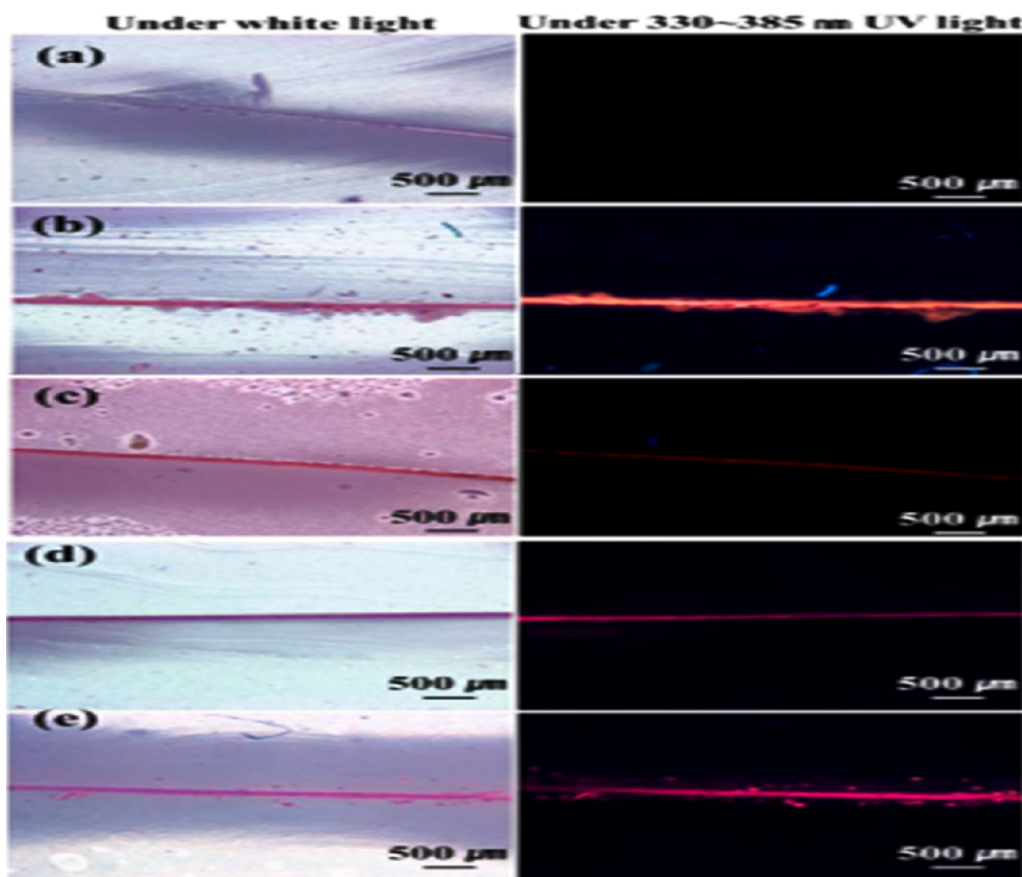


Fig. 25. Optical micrographic images of scratched areas in comparative coatings and SH coatings beneath white and UV light (a) n-Hexadecane-oriented compared coating analysed at 20 to 17 C; (b) n-hexadecane-focused comparative coating at ambient temperature (23 C); (c) STP-oriented coating at 20 to 17 C; (d) DD-oriented coating at 20 to 17 C; and (e) STP and DD-oriented SH coating at 20 to 17 C [158].

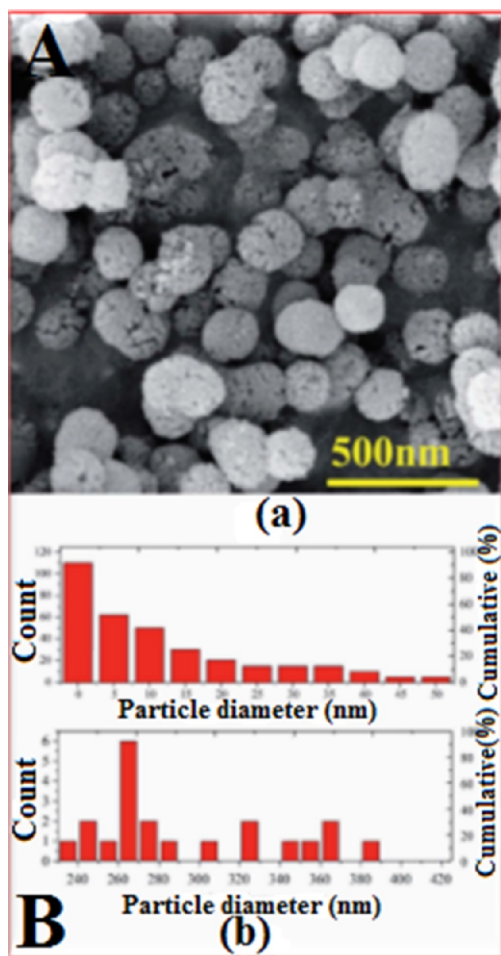


Fig. 27. (A). SEM micrographic images of synthesized MCM-41 nanoparticles functionalized using Mo, B; (a) corresponding mesopore size (upper panel) and (b) particle size (lower panel) distribution histograms [159].

Low-temperature SH abilities are important for SH materials subjected to cold weather. In a recent research, low-temperature SH of a microcapsular protective coating was revealed [158]. Here, silanol-terminated polydimethylsiloxane (STP) was used as a healing entity and dibutyltin dilaurate (DD) was used as catalyst. On damage of SH coatings at low temperature of 20 C, STP/DD were emitted from damaged microcapsules and subsequently filled the damaged crevices. This procedure underwent efficient visualization via fluorescent dye. Results garnered from subsection of SH coatings to scratches, corrosion, electrochemical, and saline solution permeability tests revealed high performances in these areas. The dimension and shape of the microcapsules underwent observation using SEM as shown in (Fig. 24 a, b), and by optical microscopy as revealed in (Fig. 24 c). Spherical microcapsules were formed at an agitation rate of 1000 rpm. The average diameters of STP- and DD-inculcated microcapsules were 240 and 90 nm respectively.

However, on scratching at room temperature, n-hexadecane rapidly flowed from the microcapsules and occupied the damaged area as depicted in Fig. 25 (b). On observation of STP- or DD-oriented coatings at 20 to 17 C, the scratched region was occupied as shown in Fig. 25 (c, d). The STP/DD-oriented coating demonstrated same results as depicted in Fig. 25 (e). The implication of these results is that STP and DD were easily emitted from broken microcapsules and occupied the damaged zone of the SH coating at low temperatures of 20 C [158].

SH STP/DD-oriented coating low-temperature SH mechanism was evaluated using steel corrosion analysis as depicted in Fig. 26. The SH coating formulation was utilized on steel boards, while the control

coating sample was fabricated without microcapsules. On post storage of the coating specimen at 20 C, scratch inculcated damages on the coatings were observed at 20 C within the low-temperature confinement as shown in Fig. 26 (a, c). The scratched STP/DD-oriented SH coatings were maintained at 20 C for 12 h in order to propagate reaction of the emitted healing entity. Results demonstrated that all control specimens underwent corrosion as shown in Fig. 26 (b), but STP/DD-oriented SH coatings revealed nil visual proof of corrosion as shown in Fig. 26 (d). Continual corrosion analysis revealed good reproducibility [158].

The SH mechanism and performances of Zn-MCM-41-Mo have been studied via OCP, EIS, and polarization curves [159]. Nanoparticles of mesoporous silica (MCM-41) underwent impregnation with molybdate, a corrosion inhibitor, and used in forming a SH entity to minimize corrosion rate. Results exposed that the protective entities were formed post molybdate release from MCM-41, thereby facilitating enhanced corrosion suppression [159]. Fig. 27 depict FESEM images of MCM-41 nanoparticles functionalized by molybdate. As depicted in the Fig., MCM-41-Mo nanoparticles exhibit spherical mesoporous architecture. Fig. 27 (b) reveals measured SEM image dimensional distribution histograms elucidating the size distribution of meso-porosity in a range below 50 nm expressing an average pore diameter below 5 nm. Size ranges depicted are: MCM-41-Mo nanoparticle size and (ii) mesoporous sizes as shown at the upper panel of Fig. 27 b [159].

Results revealed that Zn-MCM-41 electrodeposited coating exhibited even distribution and continual adherence to zinc metallic matrix. SEM images picked from cross section of MCM-41-SH-Mo depicted in Fig. 28 shows there was neither aggregation nor damages. However, it is feasible that some routes were attained due to molybdate functionalization with MCM-41-SH [159].

9. Conclusions

Recent advancements in nanotechnology have engineered novel innovations in conventional techniques of suppressing corrosion at the metallic and/or electrolyte interfacial region. Nanomaterials inclusion in PNC coatings have greatly enhanced their barricading, and protective performances through reduction of porosity and irregularities occurring at diffusion routes of corrosive entities. Nanomaterials expressing varieties of shapes and dimensions have been utilized in fabricating PNC coatings, and other PNC reinforced with natural fibers for versatile applications where flame retardancy, and thermal conductivity are essential through varying approaches including in-situ polymerization, solution exfoliation, and melt intercalation [160–183]. PNC micro-architectures are classified in accordance to the interaction occurring between polymeric matrices and incorporated nanomaterials relative to phase separation, hybridization phases, intercalation and exfoliative PNC nanocoatings. Nanomaterials cost-efficiency at improving anti-corrosive performances of PNC coatings are based on efficiency of their distribution in the host polymeric matrices. The inclusion of nanomaterials in polymeric matrices presents ecobenevolent routes of improving durability, and integrity of PNC coating systems. Generally, PNC coatings with inclusion of small quantities of nanomaterials enable enhanced barrier, and protective behavior towards corrosion resistance and minimization of coating propensity towards delamination and blistering. These materials have demonstrated critical efficiency at repairing unseen micro-deterioration occurring in protective coatings. However, effective, ecobenevolent and simple techniques for fabricating PNC coatings with highly enhanced wettability, hydrophilicity, anti-fouling, and anti-corrosion performances are envisaged in the nearest future. In addition, aside enhanced corrosion hinderances, prolonged durability in severe media is imperative to applicability of these PNC coatings. Hence, in attainment of prolonged durability during service relative to improved self-life, further enhancements in architectural properties and synthesis parameters are essential in developing highly performing PNC protective coatings applicable in varying corrosive,

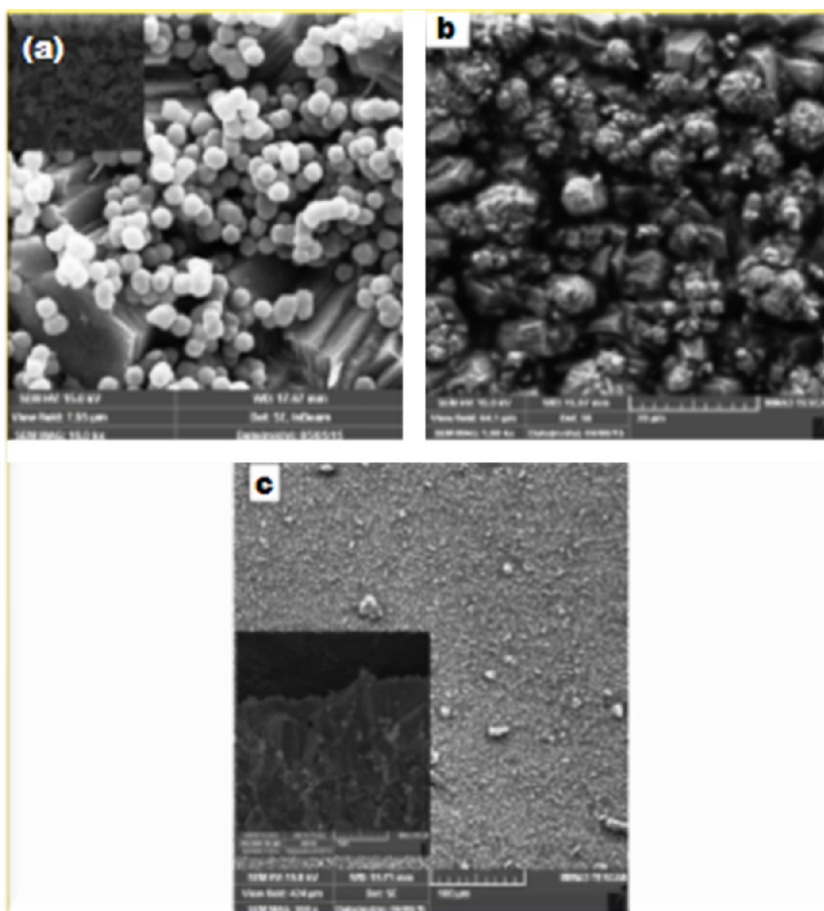


Fig. 28. SEM images of (a) Zn-MCM-41, (b) Zn-MCM-41-Mo functionalized and (c) Zn-MCM-41-Mo-SH composite coatings electrodeposited at 17.5 A cm^{-2} with nanoparticulate concentration of 1 g L^{-1} [159].

fouly, and abrasive environments.

Declaration of Competing Interest

No conflict of interests is availed.

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Supplementary materials

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