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Review

Corrosion-Resisting Nanocarbon Nanocomposites for Aerospace Application: An Up-to-Date Account

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Abstract: The design and necessity of corrosion-resisting nanocarbon nanocomposites have been investigated for cutting-edge aerospace applications. In this regard, nanocarbon nanofillers, especially carbon nanotubes, graphene, nanodiamond, etc. have been used to fill in various polymeric matrices (thermosets, thermoplastics, and conducting polymers) to develop anti-rusting space-related nanocomposites. This review fundamentally emphases the design, anti-corrosion properties, and application of polymer/nanocarbon nanocomposites for the space sector. An electron-conducting network is created in the polymers with nanocarbon dispersion to assist in charge transportation, and thus in the polymers' corrosion resistance features. The corrosion resistance mechanism depends upon the formation of tortuous diffusion pathways due to nanofiller arrangement in the matrices. Moreover, matrix–nanofiller interactions and interface formation play an important role in enhancing the corrosion protection properties. The anticorrosion nanocomposites were tested for their adhesion, contact angle, and impedance properties, and NaCl tests and scratch tests were carried out. Among the polymers, epoxy was found to be superior corrosion-resisting polymer, relative to the thermoplastic polymers in these nanocomposites. Among the carbon nanotubes, graphene, and nanodiamond, the carbon nanotube with a loading of up to 7 wt.% in the epoxy matrix was desirable for corrosion resistance. On the other hand, graphene contents of up to 1 wt.% and nanodiamond contents of 0.2–0.4 wt.% were desirable to enhance the corrosion resistance of the epoxy matrix. The impedance, anticorrosion, and adhesion properties of epoxy nanocomposites were found to be better than those of the thermoplastic materials. Despite the success of nanocarbon nanocomposites in aerospace applications, thorough research efforts are still needed to design high-performance anti-rusting materials to completely replace the use of metal components in the aerospace industry.

Keywords: carbon nanotube; graphene; nanodiamond; corrosion-resisting; diffusion

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1. Introduction

In advanced technical applications, metal-based industries face corrosion problems [1]. To prevent these corrosion issues, protective coatings, additives, and other strategies have been exploited. In this regard, nanocarbon nanoparticles such as carbon nanotubes, graphene, nanodiamond, etc. have been considered for corrosion prevention [2–4]. Nanocarbon nanoparticles have been reinforced in polymers to form corrosion-resisting nanocomposites [5]. Thermoplastics, thermosets, and conjugated/non-conjugated polymers have been employed in anticorrosion nanocomposite coatings [6]. As compared with pristine polymers, polymer nanocomposites have revealed superior anticorrosion properties [7]. Incidentally, homogeneous nanoparticle dispersion and matrix–nanofiller interactions have been found to facilitate the electron conductivity and corrosion-resistant properties of polymers [8,9]. Moreover, nanofiller nanoparticles in anticorrosion coatings may form tortuous pathways to delay the diffusion of corrosive species towards metals [10]. Particularly, anticorrosion coatings based on the polymer/nanocarbon nanocomposites have been found to be effective in preventing the corrosive species from reaching the metal surface [11]. Numerous facile strategies have been adopted to form anticorrosion polymer/nanocarbon nanocomposite coatings on the metal surface, such as solution techniques, spin coating, spray coating, and other approaches [12]. Consequently, anticorrosion and barrier properties have been found to be dependent on uniform nanocarbon nanofiller dispersion and interface formation in the nanocomposites.

This state-of-the-art review describes the remarkable potential of polymer/nanocarbon nanocomposites in corrosion prevention. The potential of these nanocomposites has been explored particularly for the aerospace industry. Space-related polymer/nanocarbon nanomaterials have been scrutinized for their design, physical properties, and anticorrosion characteristics. The review proceeds as follows: Section 1, is the introduction, Section 2 covers polymeric nanocomposites for corrosion resistance, Section 3 covers anticorrosion polymer/nanocarbon nanocomposites, Section 4 is dedicated to corrosion-resisting polymer/nanocarbon nanomaterials for the aerospace industry, and finally, Section 5 provides future prospects and our conclusions. All the sections thoroughly and comprehensively describe the outlined contents. In this cutting-edge review, various notable future prospects of corrosion-resisting polymer/nanocarbon nanocomposites have been highlighted, particularly the design versatility, essential features, and significance of anti-corrosion polymer/nanocarbon nanocomposites for the aerospace industry. In this regard, the indispensable features of various anticorrosion systems prepared using polymers and carbon nanoparticles have been considered. To the best of our knowledge, such a specific and recent review on aerospace-related anti-corrosion polymer/nanocarbon nanocomposites is not currently present in the literature. Some previous literature reports on this particular review topic have been observed; however, the reported literature has not been sufficiently updated to portray the current state of anti-corrosion polymer/nanocarbon nanocomposites in the aerospace industry. Furthermore, future developments in the field of anti-corrosion polymer/nanocarbon nanocomposites are not possible for scientists/researchers before prior knowledge of the recently compiled literature has been attained. Therefore, this innovative review has been designed to assemble and discuss the significant recent literature, and the advancements of anti-corrosion polymer/nanocarbon nanocomposites for application in aerospace.

2. Polymeric Nanocomposites for Corrosion Resistance

Inclusion of nanoparticles in polymers has been found to enhance various physical properties of the matrices, such as heat stability, mechanical robustness, electron transportation, thermal conductivity, and corrosion resistance [13]. Anticorrosion polymer nanocomposites have been applied in a wide range of electronics, energy devices, automobiles/spacecraft, and construction applications [14–16]. In this context, numerous polymers and nanoparticle combinations have been used [17]. Most importantly, conducting polymers have fine electron transport properties, leading to superior corrosion-resisting properties [18]. Polyaniline [19], polypyrrole [20], polythiophene [21], and their derived polymers have been commonly applied for their anticorrosion properties. Non-conducting polymers such as epoxies have also been effectively used for corrosion prevention [22]. Furthermore, thermoplastic polymers have been utilized for the purpose of corrosion protection [23].

In anticorrosion nanocomposites, organic and inorganic nanoparticles (nanocarbons, metal oxides, metal nanoparticles, etc.) have been exploited [24,25]. Applying polymeric nanocomposite coatings to metal surfaces may reveal corrosion, scratch, and wear resistance features. The type of polymer as well as the nanofiller selection affect the anticorrosion and tribological characteristics of nanocomposites [26]. The amount of nanofiller also influenced the corrosion resistance of the nanomaterial coated on the metal substrate [27]. Guo et al. [28] produced epoxy resin, poly(dimethyl siloxane), and silica nanoparticle-based corrosion-resisting coatings. These anticorrosion nanomaterials possess fine superhydrophobic properties and a water contact angle of 163°. Guo et al. [29] also formed corrosion-resisting coatings based on epoxy and polypyrrole/Fe_3O_4 nanoparticles. Polypyrrole functional magnetite nanoparticles have the ability to develop interactions with the epoxy matrix. Inclusion of nanoparticles enhanced the volume resistivity of the nanocomposites up to 1.6×10^{13} Ωcm, therefore enhancing the anticorrosion properties. He et al. [30] developed polypyrrole- and zeolite nanoparticle-based nanocomposite coatings for preventing the corrosion of metals. The nanomaterial was tested in 3.5 wt.% NaCl solution, and revealed a high impedance modulus of 3.7×10^8 Ω cm^2. For corrosion prevention on metal surfaces, several mechanisms have been proposed in the literature (Figure 1) [31].

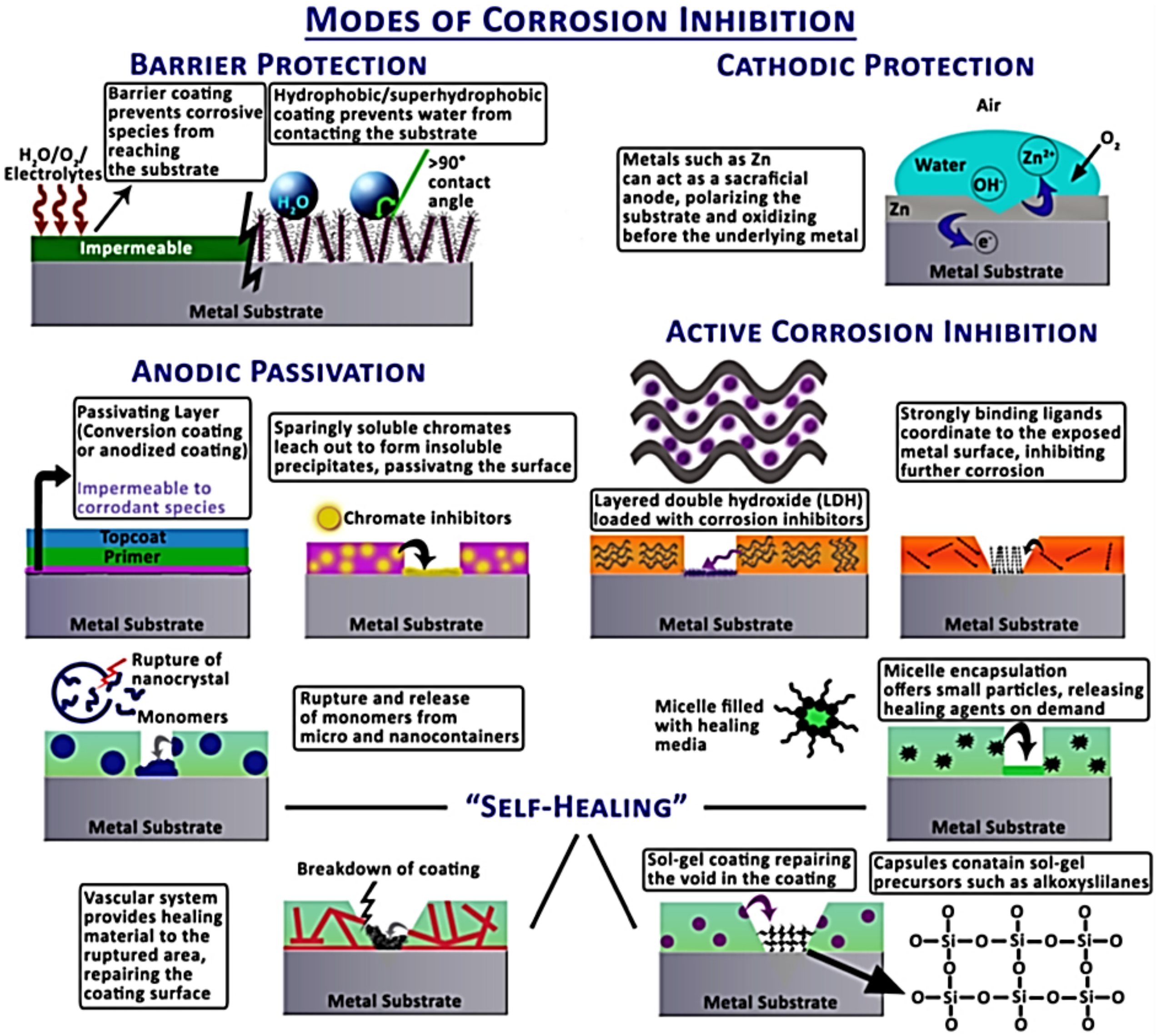

Figure 1. Schematic of various modes of corrosion inhibition such as barrier protection, cathodic protection, anodic passivation, active corrosion inhibition, and self-healing [31]. Reproduced with permission from IOP publishing.

The major phenomena involved are anodic passivation, cathodic protection, electrolytic prevention, and active corrosion inhibition. Previously, the cathodic protection of steel and aluminum alloys has been achieved using more electropositive metals such as zinc and magnesium. In anodic passivation, anodization has been used to inhibit ion transport to prevent the corrosion process. Electrolytic protection has also been used to prevent ionic transportation between the anode and cathode, therefore producing the diffusion barrier. Active corrosion protection has been achieved using coatings with additives, which can be released upon any damage to reform the protective layer on the metal surface. Similarly, the self-healing phenomenon comprises the use of monomers and catalysts in nanocomposites for corrosion-related damage recovery through reformation of coatings.

3. Anticorrosion Polymer/Nanocarbon Nanocomposites

Among thermosetting polymers, epoxy resins have been widely used in the engineering and aerospace industries [32–34]. Epoxies and epoxy-based nanocomposites have superior physical properties, including adhesion, electron conduction, heat stability, thermal conductivity, and flame resistance [35]. Epoxies and derived nanomaterials also exhibit a corrosion resistance phenomenon [36,37]. Subsequently, epoxy/nanocarbon nanocomposites have been effectively applied to improve the anticorrosion properties of metal substrates [38]. Nanocarbon nanoparticles such as carbon nanotubes [39], graphene [40], graphene oxide [41], nanodiamond [42], and other nanoparticles [43] have been utilized to fabricate corrosion-resisting epoxy nanocomposites. The resulting coatings demonstrated fine hydrophobicity, moisture resistance, and a high water contact angle for corrosion prevention [44]. The matrix–nanofiller interactions in polymer/nanocarbon nanoparticles may develop interconnecting pathways in polymers to prevent the corrosive species permeating the metal surface [45]. Consequently, the nanofiller contents, uniform dispersion, and less aggregation enhance the anticorrosion properties of polymers [46].

A carbon nanotube is a one-dimensional tube-like nanocarbon made up of sp^2 hybridized carbon atoms [47]. Carbon nanotubes have been considered rolled nanosheets of graphene. They are made up of sp^2 hybridized carbon atoms, i.e., a two-dimensional hexagonal lattice nanostructure. Depending upon their overlapping cylindrical structures, carbon nanotubes can be categorized as a single walled carbon nanotube, a double-walled carbon nanotube, or a multi-walled carbon nanotube. The rolled cylinders in carbon nanotubes are hollow. The length of these cylinders is several times the diameter. Carbon nanotubes have unique structural, electronic, magnetic, thermal, and mechanical properties. Technical applications of carbon nanotubes have been observed in the nanoelectronics, and energy devices, and in the biomedical and various nanocomposite-related fields [48]. Yang et al. [49] used tannic acid-modified carbon nanotubes to reinforce epoxy resin for corrosion prevention. The uniform distribution of nanotubes in the epoxy resin enhanced its corrosion resistance properties. In 3.5 wt.% NaCl solution, the nanocomposite coatings revealed a corrosion potential and corrosion current of −0.207 V and 5.281×10^{-11} Acm^{-2}, respectively. Lorwanishpaisarn et al. [50] prepared an epoxy vitrimer/carbon nanotube nanocomposite for corrosion protection. The inclusion of 5 wt.% nanofiller decreased the corrosion resistance to 3.12×10^{-5} MPY, in 3.5 wt.% NaCl solution. A corrosion protection efficiency of 99.99% was attained.

Nanodiamond is a type of nanocarbon with a size of ~4 to 5 nm [51]. Nanodiamonds have gained an important position among carbon nanoparticles. Nanodiamond has frequently been prepared through detonation techniques involving explosion or meteorite effects. It is a low-cost nanocarbon material that can be easily prepared using large-scale synthesis methods. Nanodiamond has also garnered attention due to its easy surface functionalization. Moreover, the superior structural, biocompatibility, strength, and thermal properties of nanodiamonds have been observed. Nanodiamonds have wide-ranging applications in the technical fields of electronics, engineering, and biomedicine. Nanodiamond nanoparticles possess fine surface functionalization, structural, and biocompatibility properties. Rahmani et al. [52] fabricated dodecylamine functional nanodiamond- and epoxy-based anticorrosion nanocomposites. A 1 wt.% nanodiamond-loaded epoxy coating was formed on the mild steel surface. The nanocomposite coating showed fine corrosion resistance and barrier properties in 3.5 wt.% NaCl solution. Mohammadkhani et al. [53] fabricated a polyaniline functional nanodiamond as a nanofiller for epoxy coatings. The synergistic effects of the polyaniline functional nanodiamond and the epoxy resin enhanced the anodic protection and barrier properties of the studied anticorrosion epoxy coatings.

Graphene is a one-atom-thick two-dimensional nanocarbon [54]. Graphene nanosheets are made up of sp^2 hybridized carbon atoms. They have a honeycomb lattice consisting of sp^2 hybridized carbon atoms [55]. Graphene can be considered a derivation of graphite, given it has stacking graphene layers [56]. Graphene has van der Waals interactions which may cause the wrinkling and restacking of the nanosheets [57]. Moreover, graphene has a high surface area, electron transport, thermal conductivity, Young's modulus, and strength properties [58]. Due to its unique structure and properties, graphene has attracted considerable research interest [59]. Graphene has been further applied to fabricate various nanomaterials [60]. Owing to its remarkable optical, electrical, mechanical, and thermal properties, graphene has applications in a wide range of technical fields such as energy, electronics, biomedical, aerospace, automotive, composites, etc. [61]. Chen et al. [62] fabricated epoxy/poly(2-butylaniline)/graphene-derived nanocomposites. Poly(2-butylaniline) was used to better disperse the graphene nanoparticles in the epoxy resin. Consequently, fine interactions were developed between the epoxy and graphene [63]. The epoxy/poly(2-butylaniline) nanocomposite with 0.5 wt.% graphene contents revealed improved anticorrosion properties. Yu et al. [64] fabricated a epoxy/reduced graphene oxide nanocomposite via in situ polymerization. The reduced graphene oxide was modified using diamino diphenyl methane to develop covalent interactions with the epoxy resin. Addition of 1 wt.% nanofiller enhanced the corrosion resistance of the coating. Table 1 demonstrates the corrosion potential and corrosion current density of the nanocomposites. The maximum corrosion resistance was observed at a 0.5 wt.% graphene content. At a higher nanofiller loading, the corrosion resistance was decreased due to nanoparticle aggregation [65].

Table 1. Potentiodynamic polarization of polymer/graphene-coated metal substrate [62]. P2BA = poly(2-butylaniline); E_{corr} = corrosion potential; I_{corr} = corrosion current. Reproduced with permission from Elsevier.

Sample	E_{corr} (V)	I_{corr} (Acm^{-2})
Neat epoxy	−0.75	1.6×10^{-7}
Epoxy/P2BA/Graphene 0.5%	−0.33	0×10^{-11}
Epoxy/P2BA/Graphene 1%	−0.69	5.5×10^{-10}

4. Corrosion-Resisting Polymer/Nanocarbon Nanomaterials for Aerospace

The use of metallic structures in industries faces corrosion as major challenge [66–68]. Corrosion is the chemical degradation of metal-based materials under the influence of environmental factors such as chemicals, moisture, etc. [69]. Figure 2 illustrates the metal-based structures and engineering properties of an aircraft structure. Space-related structures (outer body, stabilizers, wings, pressure cabins, fuselage, etc.) must have high durability, strength, toughness, fatigue, wear, and corrosion-resisting properties [70–72]. Figure 3 demonstrates metallic structures widely applied in aerospace manufacturing. Corrosion processes cause damage to metal parts, leading to poor aerospace performance [73].

Figure 2. Engineering property requirements for the main structural areas of a transport aircraft, i.e., corrosion, fatigue, fatigue crack growth, fracture toughness. CYS = compressive yield strength; E = elastic modulus; TS = tensile strength; DT = damage tolerance properties [66]. Reproduced with permission from Springer.

Advanced materials have been focused on for aerospace structures because they have enhanced engineering and anticorrosion properties [74]. Moreover, various corrosion protection coatings have been developed to shield aerospace-related metallic structures. Corrosion damage causes major economic expenses in the aerospace industry [75]. Conventional anticorrosion strategies have been found to be inefficient for corrosion prevention in aerospace parts [76–78]. Due to their high strength/weight ratio, ceramic-based anticorrosion materials have not been found useful for space structures [79]. Chromium-based coatings have also been used in aerospace to prevent the corrosion of parts [80]. Lately, metal nanoparticles [81] and carbon nanoparticles [82] have been studied for corrosion prevention in metals.

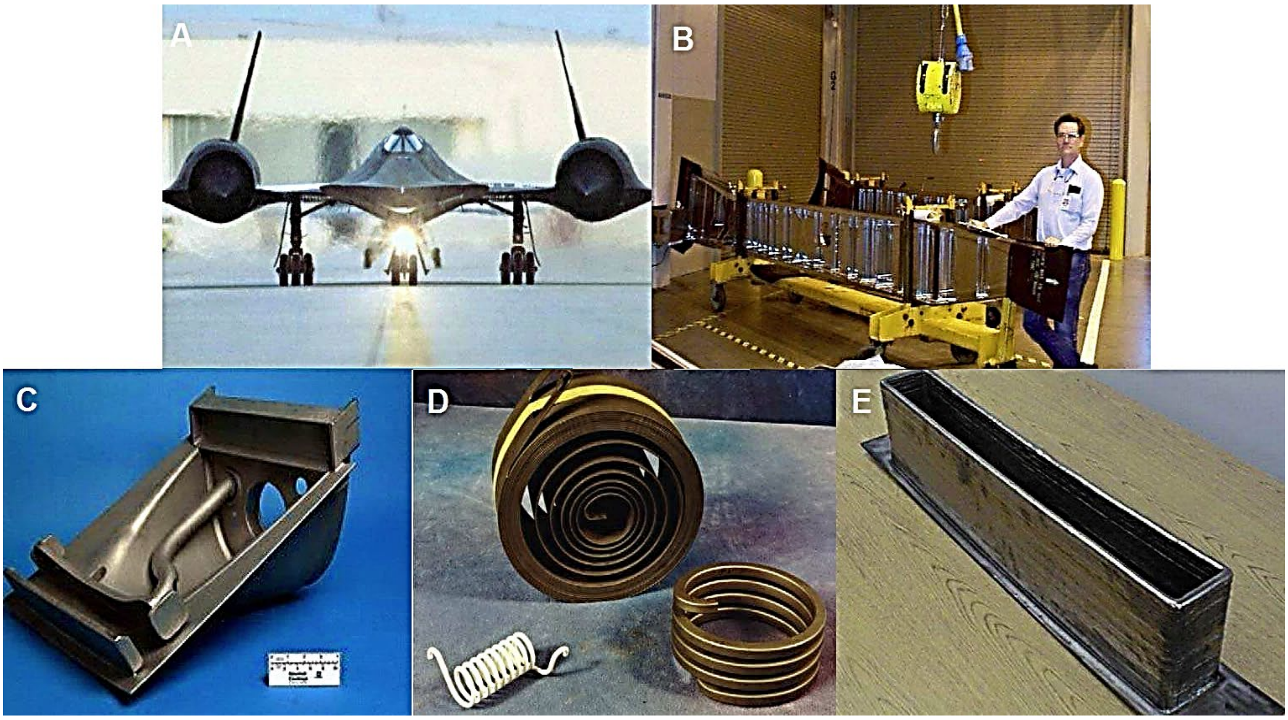

Figure 3. (**A**) Front view of the all-titanium SR-71 Blackbird; (**B**) Photo of the Ti alloy landing gear beam for the Boeing 747; (**C**) Ti alloy casting for large military transport aircraft; (**D**) alloy springs used in the Boeing aircraft; and (**E**) Ti alloy shape with a deep pocket formed by laser additive manufacturing [83]. Reproduced with permission from Elsevier.

Due to their ability to withstand high temperatures, shocks, and corrosion, epoxy-based materials have been employed in the space sector [84]. Consequently, epoxy and other polymer-based nanocomposites have been considered for aerospace [85,86]. Epoxy nanocomposites depicted better corrosion resistance compared with neat epoxy coatings [87]. Ebrahimzad et al. [88] developed carbon nanotube-based coatings for improving the mechanical stability and corrosion resistance of aluminum for aerospace structures. Such coatings have been applied to enhance the life span of space-related metal alloys [89]. Asmatulu et al. [90] developed epoxy/multi-walled carbon nanotube nanocomposite coatings. The nanocomposite (1 mm thick) was coated on the aluminum surface for corrosion prevention. Epoxy/multi-walled carbon nanotube nanocomposites were tested in UV and salt fog chambers for moisture and chemical resistance. The contact angles of the nanocomposites with 0.25–2 wt.% nanofiller were investigated. A contact angle of 84–91° was observed for the coatings, indicating the hydrophobicity and anticorrosion properties of the nanocomposite material made for aerospace [91]. Jakubinek et al. [92] fabricated aerospace-grade epoxy and single-walled carbon nanotube-derived nanocomposites. Nanofiller contents up to ~1 wt.% were reinforced in the matrix. Figure 4 shows the fabrication of aerospace-grade epoxy/single-walled carbon nanotube nanocomposite adhesives. The nanomaterial was de-gassed prior to spreading on the panels. Lap shear and peel tests were performed on the nanocomposite adhesive samples. Figure 5 depicts the performance of adhesive joints with 0.5 wt.% nanofiller contents. With the reinforcement of 1 wt.% nanotube contents in the adhesive, the peel strength was found to be 30% higher than the neat polymer. The fine lap shear performance of the nanocomposites with 0.5–1 wt.% nanofiller loading was observed. The properties the revealed excellent application potential of this nanocomposite adhesive for the aerospace sector.

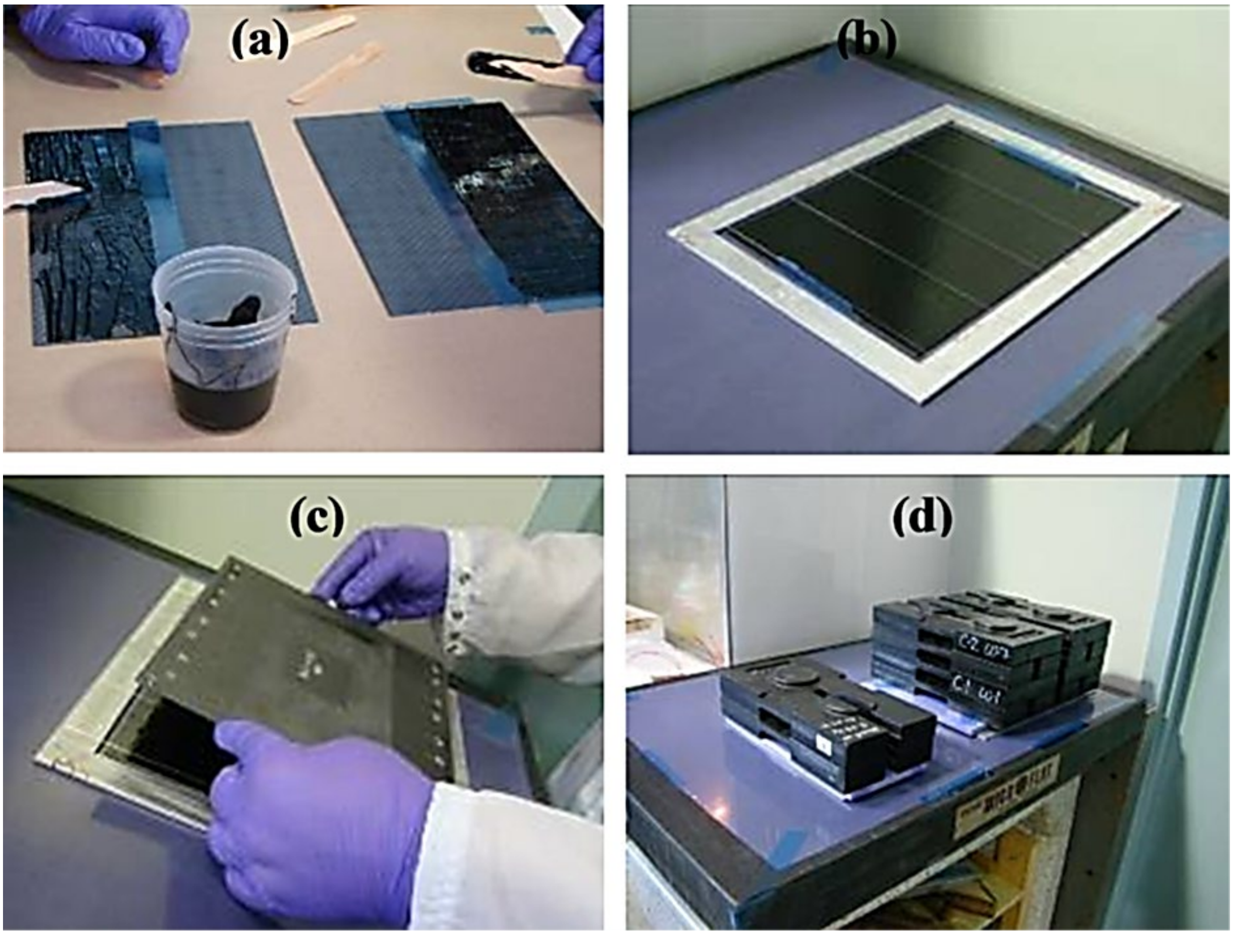

Figure 4. Formation of adhesive bonded panels using an adhesive composite with single-walled nanotubes, showing (**a**) spreading of adhesive onto peel test panels (covering half a panel), and (**b**–**d**) assembly of lap-shear test panels [92]. Reproduced with permission from Elsevier.

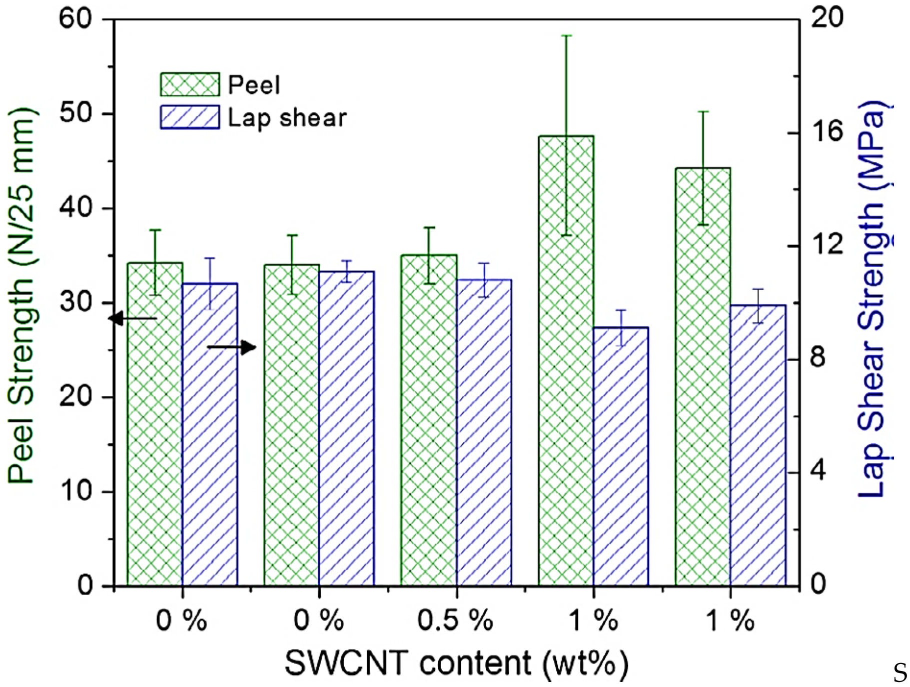

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Figure 5. Joint performance in peel and lap-shear tests with composite adherends [92]. Reproduced with permission from Elsevier.

For the aerospace industry, nickel-carbon nanotube-based anticorrosion coatings have been designed [93]. Jyotheender and co-researchers [94] fabricated nickel–carbon nanotube-filled epoxy nanocomposite coatings for the corrosion resistance of space parts. Nyquist plots indicated the impedance measurements of the nanocomposite coatings (Figure 6). Semicircle capacitive loops were observed in the impedance curves. Inclusion of 7 wt.% nanofiller contents revealed a larger capacitive loop and impedance value, indicating effective corrosion prevention. It was suggested that the uniform nickel–carbon nanotube dispersion and matrix–nanofiller interface formation led to enhanced anticorrosion properties.

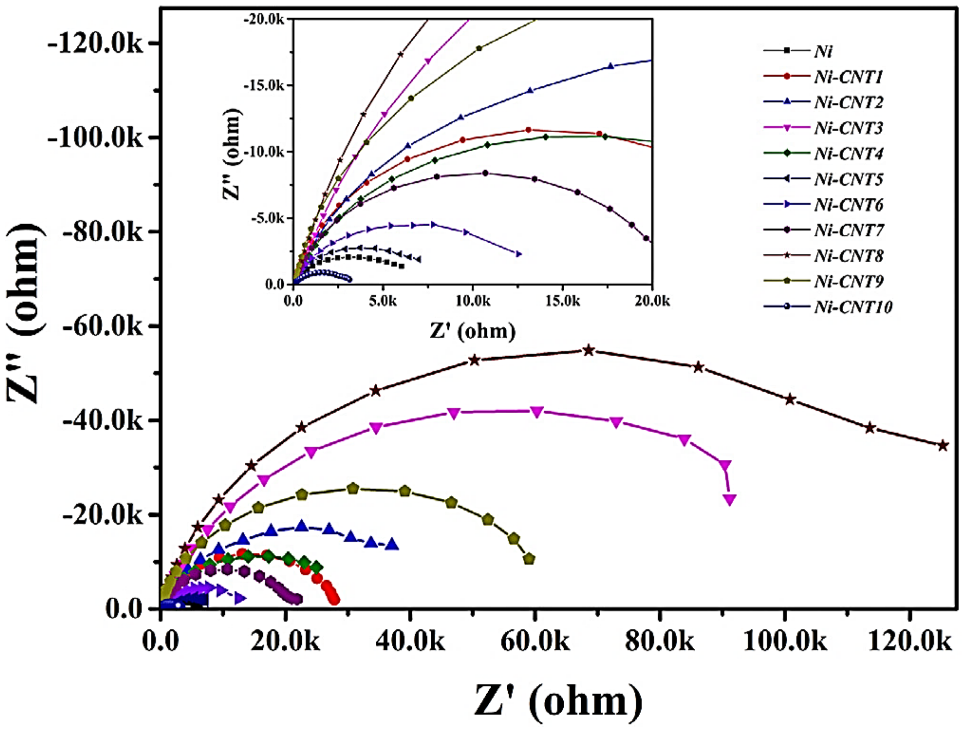

Figure 6. Nyquist plots of Ni and Ni-CNT composite coatings [94]. Ni = nickle; Ni-CNT = nickle–carbon nanotube. Reproduced with permission from Elsevier.

Zheng et al. [95] designed and investigated neat polyamides, polyamide/purified multi-walled carbon nanotubes, and polyamide/modified multi-walled carbon nanotube nanocomposites for aerospace. Table 2 shows the tensile strength, Young's modulus, and elongation at break of the materials. The inclusion of modified multi-walled carbon nanotubes enhanced the tensile strength and Young's modulus of the nanocomposites by 82% and 119%, respectively, relative to the neat polymer. This enhancement was observed due to better nanofiller dispersion and interface formation with the inclusion of modified nanofiller. Figure 7 illustrates the results of the nanoindentation test. Due to the presence of the interlinked modified multi-walled carbon nanotubes, high elastic modulus areas alternating with low elastic modulus areas were observed. Consequently, a higher interfacial transition area of 4.6 GPa was observed for the polyamide/modified multi-walled carbon nanotube nanocomposite, compared with the neat polyamide (1.46 GPa). The results demonstrated the better load transfer properties of the matrix and the modified nanofiller. The nanocomposite depicted 16% improvement in the electrical conductivity of the nanocomposites, indicating superior corrosion prevention.

Table 2. Tensile properties of neat polyamide and nanocomposites [95]. Reproduced with permission from ACS.

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at Break (%)
Neat polyamide	54.6 ± 3.8	2410.2 ± 60.2	258.14 ± 14.84
Polyamide/purified multi-walled carbon nanotube	77.0 ± 5.3	3675.6 ± 125.3	4.56 ± 0.24
Polyamide/modified multi-walled carbon nanotube	99.4 ± 8.1	5278.8 ± 112.9	2.96 ± 0.17

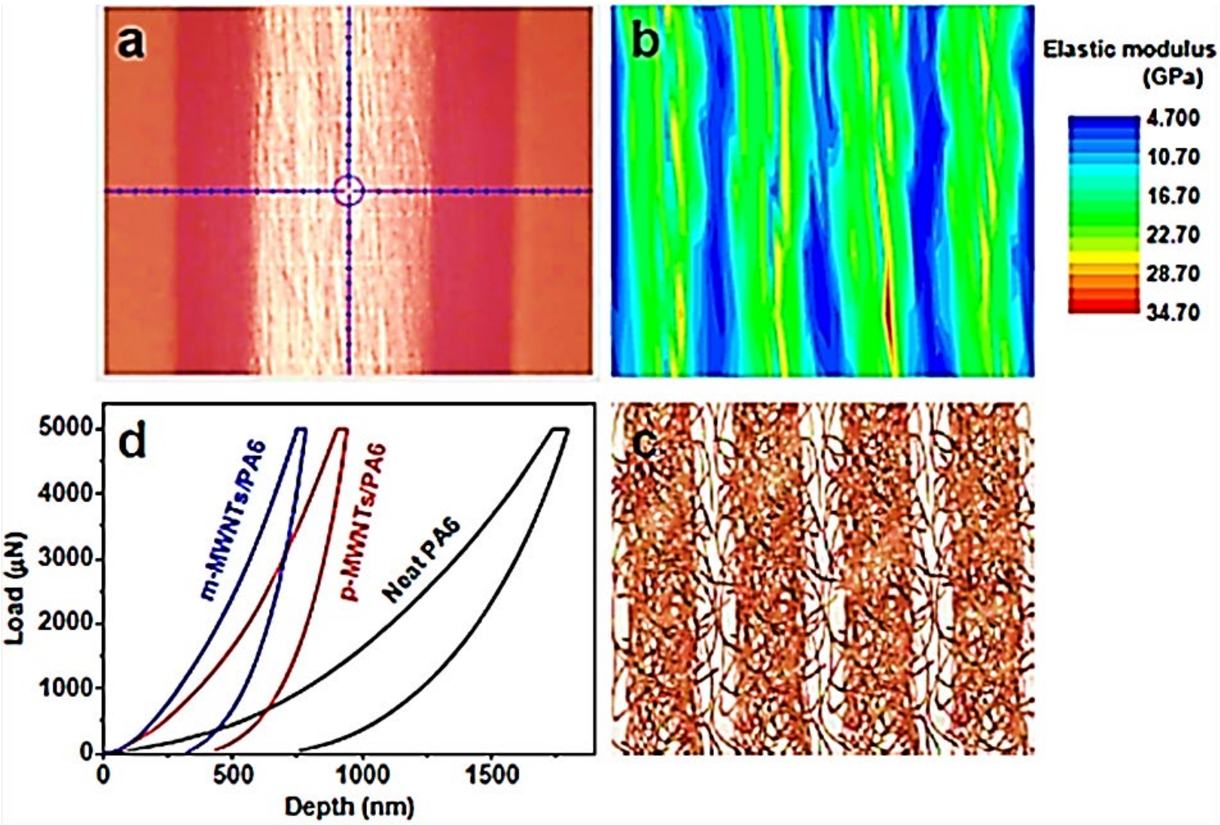

Figure 7. (**a**) The image of the sample after nanoindentation test; (**b**) elastic modulus contour map of cross section of polyamide/modified multi-walled carbon nanotube nanocomposite; (**c**) internal sandwich structure sketch of polyamide/modified multi-walled carbon nanotube; (**d**) loading–unloading curves of neat polyamide 6 (PA6), polyamide/purified multi-walled carbon nanotubes (p-MWNTs/PA6), and polyamide/modified multi-walled carbon nanotubes (m-MWNTs/PA6) [95]. Reproduced with permission from ACS.

Verma et al. [96] developed nanocomposite coatings based on poly(vinyl alcohol) and multi-walled carbon nanotubes. The anticorrosion coatings were prepared using a dip-coating technique on aerospace-grade anodized alloys of magnesium, aluminum, and titanium [97]. The nanocomposite layers were heat-treated (200 °C) after the dip-coating process. A hatch tape test was performed to study the adhesion properties of the coatings, and these were found to be significant. Inclusion of 0.5 wt.% nanofiller loading also enhanced the anticorrosion properties of the alloys. The poly(vinyl alcohol)/multi-walled carbon nanotube coatings were found to be effective for spacecraft structural parts. Other research groups have also investigated the effectiveness of poly(vinyl alcohol)/multi-walled carbon nanotube nanocomposites for the corrosion resistance of aerospace structural components [98,99].

Epoxy/nanodiamond nanocomposite coatings have also been used for aerospace structures [100,101], and epoxy and nanodiamond nanomaterials have been applied in aerospace structures [102]. Particularly, functional nanodiamonds have been used to reinforce epoxy matrices to enhance their mechanical and anticorrosion characteristics. Carbon fiber modified with nanodiamond has also been used to reinforce epoxy nanocomposites for aerospace structures [103]. Recently, inclusion of 0.2–0.4 wt.% nanofiller loading has been found to enhance the corrosion resistance of epoxy/carbon fiber composites by 12.6%, relative to unfilled epoxy/carbon fiber materials [104]. Singh et al. [105] investigated the increase in the mechanical and anticorrosion properties of epoxy/glass fiber/carbon fiber composites with nanodiamond loading. However, relatively few studies on aerospace-related polymer/nanodiamond nanocomposites have been found, and more comprehensive efforts are needed in this field.

Additionally, carbon nanotubes, nanodiamond and graphene have been applied as corrosion-resisting materials [106]. Monetta and co-workers [107] considered epoxy/graphene nanocomposites for the corrosion protection of aerospace assemblages. Both a pristine epoxy coating and epoxy/graphene nanocomposite layers have been applied to aluminum alloy using a bar applicator [108–110]. The addition of 1 wt.% graphene nanofiller enhanced the adhesion and coating thickness on the metal surface. The water contact angle values were measured to analyze the moisture resistance of the epoxy/graphene nanocomposite (Table 3). As compared to pristine polymers, epoxy/graphene nanocomposites revealed higher contact angles. Consequently, the properties of hydrophobicity and corrosion resistance were attained.

Table 3. Water contact angle values of neat epoxy and graphene-filled epoxy resin [107]. Reproduced with permission from MDPI.

Sample	Contact Angle (Degree)
Unfilled epoxy resin	60.4 ± 1
Epoxy/graphene	75.3 ± 1

Accordingly, epoxy resin has been filled with few-layer graphene for enhanced anticorrosion performance in aerospace [111]. Daradmare and co-workers [112] reinforced the epoxy matrix with few-layer graphene for use in aerospace. The few-layer graphene was synthesized using the electro-exfoliation technique [113]. Here, 0.1–1 wt.% graphene nanofiller was included in the epoxy matrix. The coatings were applied to the mild steel substrate. Relative to the neat epoxy coating, the corrosion resistance of the few-layer graphene dispersed polymer was improved by >20 times. The reason was suggested to be the uniform graphene dispersion and formation of twisting paths for restricted diffusion of the corrosion molecules [114]. Electrochemical impedance spectroscopy was used to obtain the Nyquist and Bode plots of the epoxy/few-layer graphene nanocomposite coating (Figure 8). The impedance of the nanocomposite was found to be higher (~47 kΩ cm^2), relative to the neat polymer (5.9 kΩ cm^2), revealing superior corrosion resistance. Improvement in the anticorrosion properties was also depicted through an increase in the polarization resistance and protection efficiency of the nanocomposite coating. The nanocomposite coating corrosion efficiency was found to be up to 90%, i.e., that required for aerospace applications.

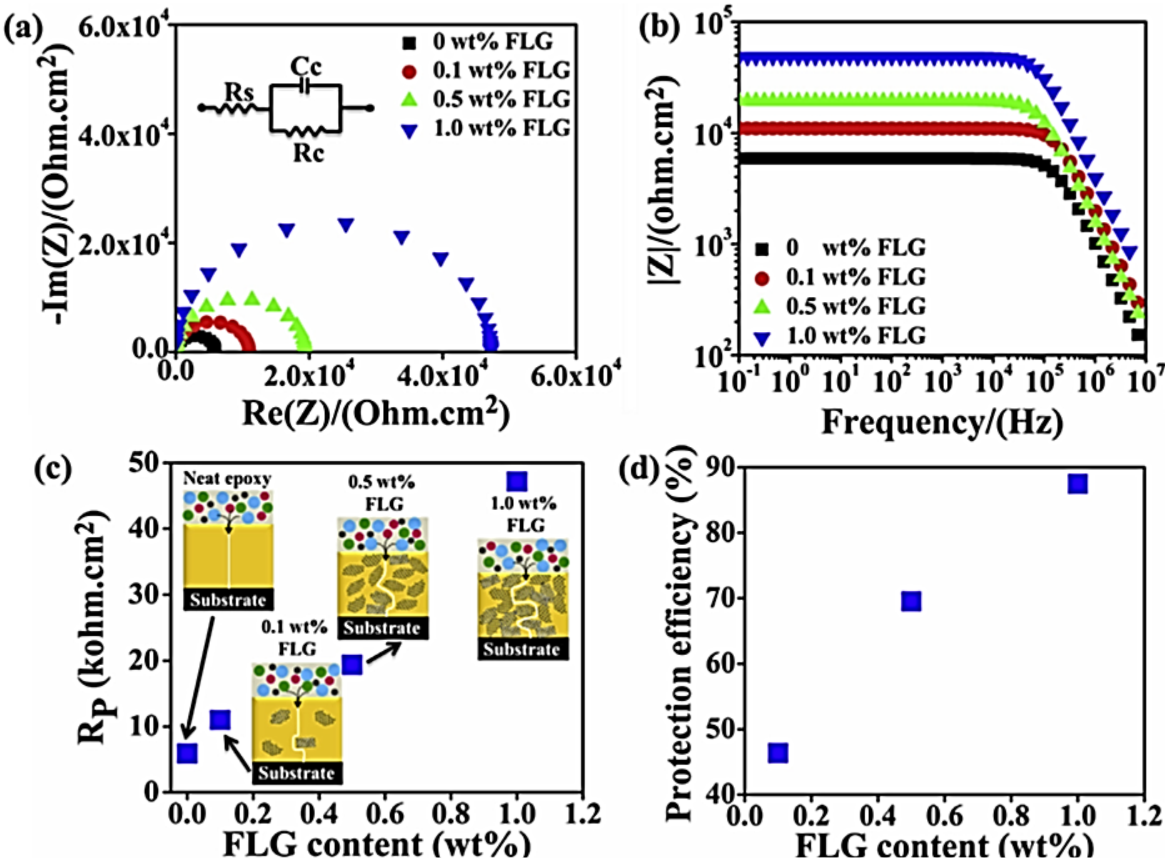

Figure 8. (**a**) Nyquist plot; (**b**) Bode plot; (**c**) change in polarization resistance (R_P); and (**d**) variation in protection efficiency of FLG-based nanocomposite coatings of different nanofiller contents [112]. FLG = few-layer graphene. Reproduced with permission from Elsevier.

Nazir and co-researchers [115] designed epoxy and nickel-graphene based nanocomposite coatings on steel substrate. Their corrosion resistance features were studied using a molecular dynamics simulation. The anticorrosion properties were found to be adequate for aerospace applications. Chang and co-workers [116] designed a diglycidyl ether of bisphenol A epoxy resin and graphene-based nanocomposites. Hydrophobic epoxy and hydrophobic epoxy/graphene nanocomposites have been tested for their corrosion resistance performance. Cold-rolled steel and poly(dimethyl siloxane) was used as a substrate. A nanocasting technique was employed to develop the hydrophobic epoxy and epoxy/graphene nanocomposite coatings (Figure 9). Figure 10 illustrates the Nyquist plots of bare metal, epoxy, and nanocomposite coatings. The high impedance of the epoxy/graphene nanocomposite was attained from the large semicircle arc, relative to the neat epoxy and metal substrate. Figure 11 demonstrates the mechanism of the diffusion of O_2 and corrosive molecules through the neat epoxy and the epoxy/graphene nanocomposite coating deposited on metal substrate. Fine graphene distribution in polymer matrix formed tortuous pathways for the permeation of corrosion molecules, and so the corrosion phenomenon was hindered [117]. In this way, several polymer/carbon nanotubes, polymer/nanodiamonds, and polymer/graphene-based anticorrosion coatings have been effectively developed for the aerospace sector.

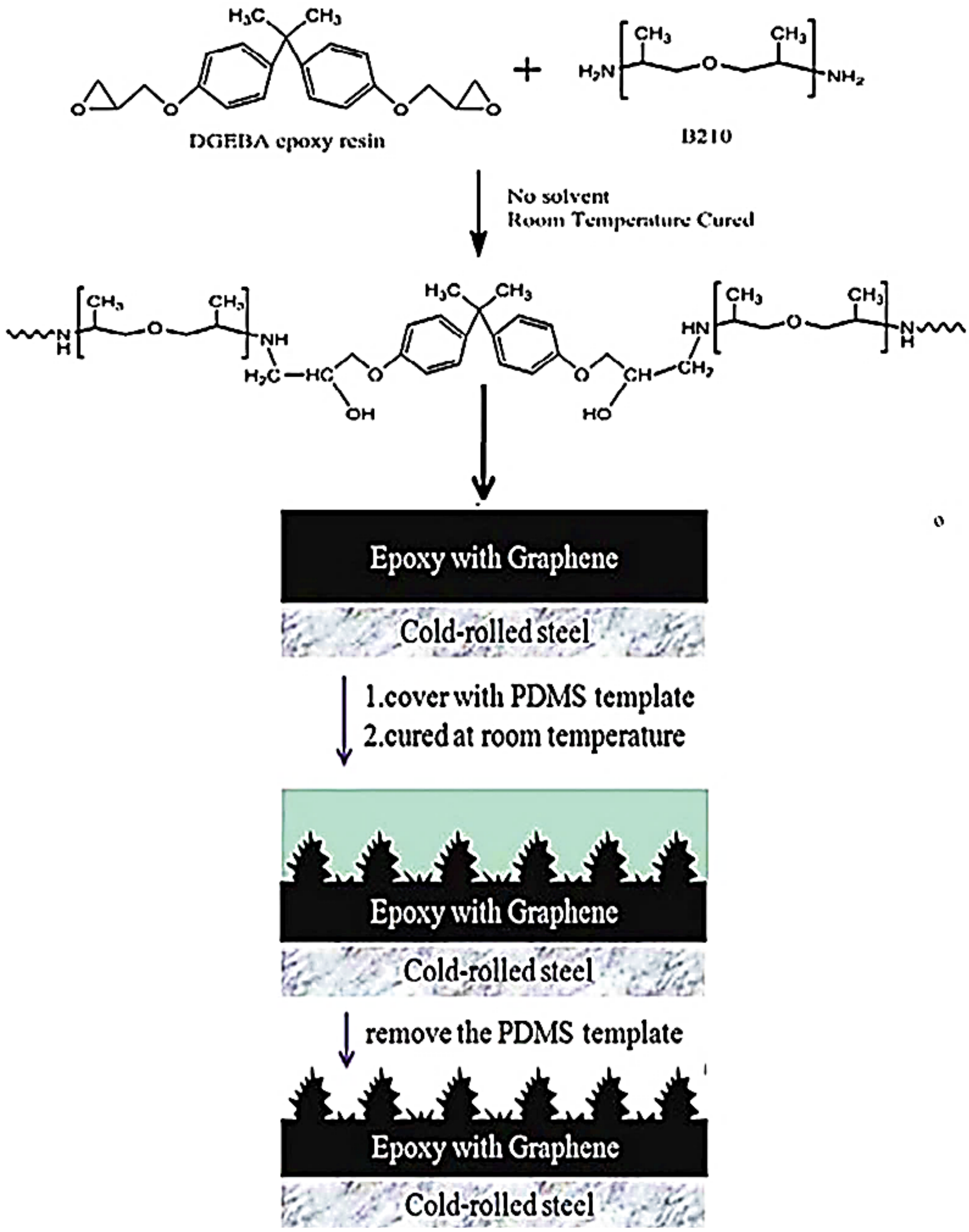

Figure 9. Fabrication of hydrophobic nanocomposite surfaces through the nanocasting technique [116]. DGEBA = diglycidyl ether of bisphenol A; PDMS = poly(dimethyl siloxane). Reproduced with permission from Elsevier.

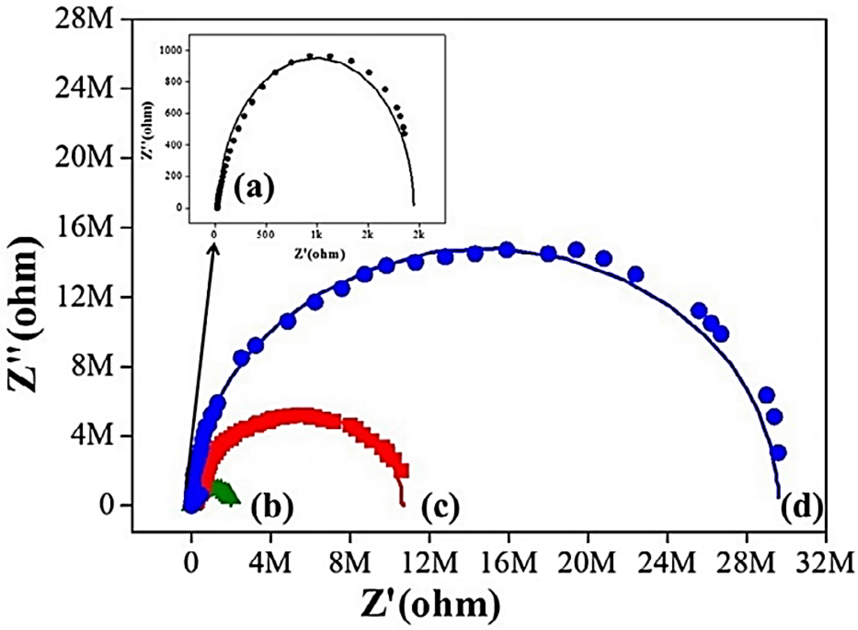

Figure 10. Nyquist plots for (**a**) bare metal; (**b**) epoxy-coated; (**c**) hydrophobic epoxy-coated; and (**d**) hydrophobic epoxy/graphene nanocomposite-coated cold-rolled steel [116]. Reproduced with permission from Elsevier.

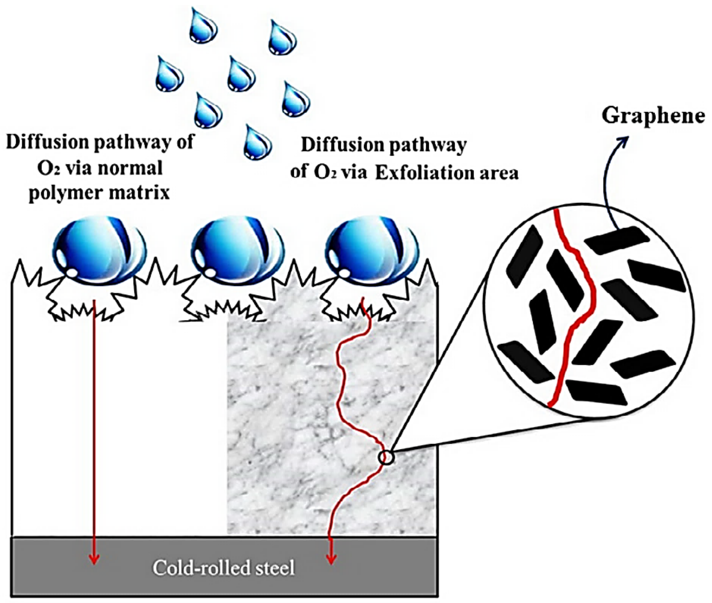

Figure 11. Schematic of hydrophobic surface and oxygen following a tortuous path through neat epoxy and hydrophobic epoxy/graphene nanocomposite [116]. Reproduced with permission from Elsevier.

In this regard, our research group has reported novel nanocomposite systems for aerospace applications. We have reported on diglycidyl ether of bisphenol-A/tetrabromobisphenol-A/multi-walled carbon nanotube nanocomposites [118]. The electromagnetic interference shielding effectiveness of diglycidyl ether of bisphenol-A/tetrabromobisphenol-A/multi-walled carbon nanotube nanocomposites was found to be ~12.1 dB for aerospace application. The materials had a high thermal stability of 369–569 °C. Moreover, the nonflammability and anticorrosion properties of the nanomaterials were observed. In another attempt, we prepared a diglycidyl ether of bisphenol-A/polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene nanocomposite with a purified and acid-functional graphene nanoplatelet [119]. The ultimate tensile strength and toughness of the nanomaterials were in the range of 60.4–64.5 MPa and 422.6–725.5 MPa, respectively. Thermal stability was observed within ~547–568 °C, and the glass transition temperature was ~229–258 °C. The EMI shielding effectiveness of nanocomposite was sufficiently high, in the range of ~17.9–20.07 dB, for aerospace applications. In another attempt [120], we fabricated diglycidyl ether of bisphenol-A/polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene nanocomposites, with amine-functional graphene nanoplatelets, for aerospace. A high maximum decomposition temperature was observed around 545 °C. The glass transition temperature of the nanocomposite was also observed to be high, at ~230 °C. The EMI shielding effectiveness of the nanocomposite was ~18.87–20.15 dB. Moreover, the nanocomposite had fine anticorrosion properties for space application. The novel epoxy blend and nanocarbon-based systems have fine potential for space application. Moreover, we have developed polyimide/polybenzimidazole and carbon nano-onion-based system for corrosion protection [121]. The electrical conductivity of the nanocomposites was observed to be in the range of 1.6–3.3 S cm^{-1}, with varying nanofiller loading. Inclusion of 5 wt.% nanofiller enhanced the corrosion protection effect up to 70%.

5. Prospects of Corrosion-Resisting Coatings

Corrosion-resisting polymer/nanocarbon nanomaterials have been successfully designed and investigated in the literature [122–124]. These nanocomposites possess light weight, high electrical conductivity, and impendence features supporting the corrosion protection characteristics [125]. Anticorrosion polymer/nanocarbon nanocomposites have been found to be effective in protecting metals and metallic alloy substrates [126]. Their corrosion inhibition mechanism was developed through the cathodic behavior of the nanocomposite and the anodic action of the metallic substrates. The anode–cathode behavior in turn prevented the corrosion process. Carbon nanotubes, graphene, and nanodiamonds have been widely used as nanocarbon nanofillers in anticorrosion polymer coatings [127]. The derived nanocomposite coatings restricted the passage of corrosive molecules to the metal surface. In the space sector, thermoplastics as well as thermosetting matrices have been used to develop corrosion-resisting coatings [128]. Epoxy resins and conducting polymer-based nanocomposite coatings have been widely employed for preventing the corrosion of aerospace structures [129]. Polymer/nanocarbon nanomaterials have been found to hinder corrosion-causing factors such as chemicals/moisture, and to prevent gases reaching the metal surface [130]. Several mechanisms have been proposed for the corrosion prevention phenomenon of polymer/nanocarbon nanocomposites [131]. Despite their superior design and properties, these materials face the limitations of porosity, defects, and fragility. Therefore, 100% corrosion resistance cannot be achieved for the aerospace sector. In this regard, future research attempts must focus on the functionalization of carbon nanotubes, graphene, and nanodiamonds, and on polymer modification to enhance the structural stability, coating durability, and corrosion resistance properties of aerospace materials. Moreover, several nanocarbon nanofillers have yet not been explored for corrosion-resisting aerospace materials. Thus, new polymer/nanocarbon designs must be produced to fulfil the demands of future aerospace structures.

6. Conclusions

In a nutshell, this review has portrayed the design and properties of corrosion-resisting polymer/nanocarbon nanocomposites, especially focusing on the aerospace industry. Combinations of various polymers and carbon nanoparticles have been explored for the development and use of anticorrosion nanomaterials in the space industry. Moreover, the factors and mechanisms behind the anticorrosion of these materials have been investigated. Nanocarbon-based corrosion-resisting nanomaterials have been found effective for advanced aerospace applications. Carbon nanotube coatings were tested with carbon nanotube contents in the range of 0.25–2 wt.%. Higher nanotube loadings were found effective for corrosion prevention. Further, higher loading of 7 wt.% nickel–carbon nanotubes in epoxy coatings was needed for anticorrosion properties. Contrarily, graphene loading of below 1 wt.% was needed to enhance the corrosion resistance of the epoxy coatings. Epoxy/carbon nanotube nanocomposites have been tested for their contact angle, which was found to be high, at ~91°. On the other hand, the contact angle of epoxy/graphene nanocomposites was found to be lower, i.e., ~75.3°. Polyamide/carbon nanotube and poly(vinyl alcohol)/carbon nanotube coatings revealed lower corrosion-resisting efficiency than the epoxy/carbon nanotubes. The results revealed that epoxy is a better matrix for the corrosion protection and adhesion properties of aerospace structures, relative to thermoplastic matrices. Moreover, low nanodiamond contents of 0.2–0.4 wt.% were needed for the corrosion protection of the epoxy matrices.

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