Review Article
Polymer-Based Nanocomposite Coating Methods: A Review

S. Mathai*, P. S. Shaji
PG and Research Department of Chemistry, Mar Ivanios College (Autonomous), Thiruvananthapuram, India

Received 20 February 2022, accepted in final revised form 10 June 2022

Abstract
Coating technology is widely recognized as the most cost-effective and efficient method of preventing metal corrosion. Polymers have been regarded as a powerful coating material owing to their excellent barrier qualities, simplicity of modification, and large-scale production. Nanomaterials differ significantly from their physical and chemical properties, and have been hailed as highly promising functional materials in a wide range of applications, affecting nearly every aspect of science and technology. The addition of organic or inorganic nanofiller particles to polymer nanocomposite coatings may improve corrosion protection and lower the possibility of blistering or delamination. High hardness for polymer coatings, on the other hand, could be achieved by forming hard nanocrystalline phases inside the matrix. This article provides an overview of recent developments in polymer nanocomposite coatings in terms of their history, coating methods, properties, features, and drawbacks.

Keywords: Carbon black; Nanofiller; Roll-to-roll; Dip coating; Nano silica.

© 2022 JSR Publications. ISSN: 2070-0237 (Print); 2070-0245 (Online). All rights reserved.
doi: http://dx.doi.org/10.3329/jsr.v14i3.58338

1. Introduction

Nanotechnology is one of the most promising alternatives to addressing the technical challenges of the twenty-first century [1], particularly those in materials science and engineering. The genesis of nanotechnology can be traced back to the conception of science in the form of state-of-the-art techniques for dealing with materials of extremely small dimensions and varying colors. The ability to get a fundamental understanding of material processes that take place at the nanoscale and submicron scales has aided significant advancements in the fields of materials design and fabrication. It is also well known that shrinking materials to the nanoscale can dramatically improve their qualities. The term "nanomaterials" refers to materials with at least one dimension of less than 100 nm [2], where structural flaws are reduced and aspect ratio goes up exponentially. Nanomaterials (NMs) have emerged as fascinating materials for study, commercial construction, and cultural enhancement and growth. These materials were generated by

* Corresponding author: sujamathaikunnath@gmail.com
natural phenomena in the early meteorites shortly after the "supernova explosion," and nanostructures or nanoparticles were created by natural phenomena. The study of NMs has recently roused the curiosity of scientists and engineers all around the world. Mesopotamian sculptors utilized nanoparticles (in the form of silver-copper nanocomposites) to create a glossy effect on the surface of pots in the 9th century, which provided the early and particular knowledge about the employment of such materials [3]. Other archaeological examples for nanocomposites implementation include the Lycurgus cup, which was manufactured from Au-Ag-alloyed nanoparticles by Romans in AD 400 and is a glass that changes color from green to red when light shines on it [4]. The ability for nanotechnologists to produce new NMs with the potential to dramatically improve the quality of life will be aided by a better knowledge of the properties of these materials. The beneficial features of NMs make them more commercially viable, allowing them to emerge as consumables and be used in a variety of modern advancements, such as coatings, paints, and other consumer goods. Different chemical, physical, biological, and other behaviors are demonstrated by different types of NMs (inorganic, carbon, organic, and composite-based NMs), which might determine their implicational realm. However, when compared to their macro/micro counterparts, all nanoparticles have a vastly larger aspect ratio. These properties, together with the existence of a large number of active valence electrons on a particular surface area, increase the amount of interactions with other moieties such as polymer matrices. As a result, even a small number of NMs can take advantage of these materials greatly increased physical, chemical, and mechanical properties. As a result of their presence in polymers as nanofillers, more robust and impermeable polymer nanocomposite materials are formed [5,6].

Polymer nanocomposites are polymer matrices that incorporate organic or inorganic nanofillers that have a uniform nanoscale distribution typically 10 to 100 nm in at least one dimension, which are created through chemical polymerization or physical mixing processes [7]. The fillers may be particles, for example layered materials, fibers, or clusters embedded in a variety of natural or synthetic polymers. Their unique physical and chemical characteristics, which improve the composites performance, and generate a lot of attention even after decades of research. These polymers have a lot of promise for usage in aeronautics, the automotive sector, electronics, medical equipment, and consumer goods because of their exceptional qualities. Nanofilled materials come in a variety of shapes and sizes. Polymers, such as powders, bulk, and functional thin films, are widely used in a variety of applications (both industry and academia are involved). Coatings made of polymer nanocomposites are particularly important because they enhance the surface properties of substrates for certain applications. A polymer nanocomposite applied onto the surface of steel, for example, with an inorganic layered filler, can significantly slow corrosion. Due to the inorganic nature of the protective mechanism, it can also be employed to create a gas barrier layer [8,9]. The gas penetration pathway is lengthened by a multilayer filter covering for other surfaces self-cleaning, temperature resistance, and wear resistance are just a few of the unique features available. Many commercial items have used sophisticated optics and lasers. Electroactive coatings based on polymer
nanocomposites have recently been shown to have significantly lower resistivity than traditional coatings, paving the way for new applications such as electrochemical sensors [10], materials with a high dielectric constant [11], functional membranes [12], and electrochromic materials [13]. Aside from their inherent material properties, the ease and efficiency with which polymer nanocomposite coatings can be placed on substrates is a critical factor in determining their success.

This paper gives a comprehensive review of some basic aspects including processing, characterization and properties of various polymer nanocomposites. It starts with introducing history of polymer-based nanocomposite coatings (PNCs). Then, processing of PNCs using different methods, types of polymer nanocomposites coating systems, and importance of nano fillers used are systematically described and discussed.

1.1. History of polymer-based nanocomposites coatings (PNCs)

Polymer-based nanocomposites, with their unique design, properties, and uses, are the materials of the twenty-first century. These qualities set them apart from traditional composites. Despite the fact that they were first postulated in 1992, their features and mechanisms are still unknown [14,15]. It is widely known that the characteristics of nanofillers are greatly influenced by their size, with the maximum value being obtained at "its critical size" [16]. As a result, for the preparation of nanocomposites, their surface area to volume ratio is a significant and crucial component that aids in the understanding of their structural-property correlations. For example, the discovery of carbon nanotubes (1991) and their use in nanocomposite manufacturing infused the fillers unique properties (mechanical, electrical, and thermal) into the matrix [17], which gave the final product a new dimension [18,19]. Furthermore, these improvements opened new options for the application [Fig. 1] of ecofriendly PNCs in sophisticated technology [20].

Polymer-based coatings have been widely utilized to protect metals from corrosion and ageing during the last few decades because they are easy to produce and tailor and can have great chemical resistance, adhesion (to metallic surfaces), and mechanical, thermal, and other properties [21,22]. Polymer coverings primarily served as a physical barrier for underlying metallic substrates, preventing aggressive (corrosive) species from accessing the substrates surface and therefore reducing corrosion [23]. Normal polymers are frequently problematic in their application as anticorrosive coatings due to the following factors: (1) their intrinsic porosity microstructure fails to prevent the passage of corrosive ions, and (2) they are susceptible to wear, surface abrasion, and scratches [20].

Anticorrosive polymer coatings must have inbuilt durability, strong adherence to the underlying substrate (metals), high toughness, and flexibility to resist cracking and deformation when exposed to stress, high temperatures, various chemical conditions, and harsh environments [21-23]. Scientists and engineers have tried a variety of methods to accomplish these perfections, including the creation of copolymers, structural modification of polymers, and hybrid and nanocomposite formation, all of which have altered the microstructure of polymer coatings [24]. In terms of adhesion, flexibility, and
mechanical properties, strategies such as structural modification and hybrid polymers have shown some improvement [25,26].

![Fig. 1. Applications of polymer-based nanocomposite coatings (PNCs).](image)

2. PNC Coating Methods

Coating success necessitates not only the intrinsic features of the polymer nanocomposite, but also viable methodologies for depositing the material on various substrates. In this context, 'workable' means meeting a number of criteria to assure good coating quality attributes such as surface uniformity, interphase adhesion, thickness control, and material non-toxicity. For large-scale manufacturing, production capacity is another important factor to consider. In both research and production, a wide range of coating technologies has been used. However, not all of them are suitable for use with nanofluid polymers. Vaporizing operations, which are often carried out at very high temperatures or energies, can readily destroy polymer chains. As a result, for polymer nanocomposites, a low deposition temperature is frequently a need. In general, there are mainly four types of coating processes for polymer nanocomposites: (1) physical vapor deposition (PVD) [27,28], (2) chemical vapor deposition (CVD) [29-32], (3) chemical and electrochemical deposition [33–35], and (4) roll-to-roll (R2R) casting deposition [36-38]. In this chapter, we give a quick overview of each deposition method [Fig. 2].

2.1. Physical vapor deposition (PVD) method

Physical vapor deposition (PVD) method is commonly used to make inorganic matrices and inorganic nanoparticles for inorganic/inorganic polymer nanocomposite coatings [39-43,44–49]. Laser ablation [50], thermal evaporation [51], ion beam deposition [52], ion implantation [53,54], laser-assisted deposition [55], and atom beam cosputtering technology are some of the PVD methods used for these coatings. Schild [56] used
aerosol-assisted plasma deposition to produce organic/inorganic polymer nanocomposite coatings. PVD is a term used to describe thin film deposition procedures that require the condensation of vaporized solid material on the solid materials surface in a partial vacuum environment [57]. PVD is an atomistic deposition method in which atoms or molecules are physically discharged and then condensed and nucleated onto a substrate in a vacuum, low-pressure gaseous, or plasma environment. The vapor phase is typically made up of plasma or ions. It is possible to add a reactive gas into the vapor during the deposition process, which is known as reactive deposition. The atoms or molecules are transported to the substrates surface in the form of a vapor via a vacuum or a low-pressure gaseous or plasma environment. PVD methods are commonly used to deposit thin films ranging in thickness from a few nanometers to a thousandth of a nanometer.

Fig. 2. Types of PNC methods.

2.2. Chemical vapor deposition (CVD) method

Chemical vapor deposition (CVD) is based on a heating method that produces a vapor from a solid target material, followed by chemical reactions in the vapor phase. As a result, this deposition involves either a homogenous gas phase or heterogeneous chemical processes that occur on or near the heated surface, resulting in powders or filaments, respectively [58]. CVD is usually carried out at extremely high temperatures, up to 1000 °C, to stimulate chemical processes in the vapor phase. These extremely high temperatures cause the chemical structure of the solid targets to break down, resulting in qualities that differ from the original material. As a result, inorganic and metallo-organic precursors were used in a low-temperature CVD process at 350–700 °C. The use of a plasma has allowed for much lower activation temperatures of 200–400 °C. Because of their inexpensive cost compared to other coating processes, hot-wall CVD (HWCVD) and hot-fi lament CVD (HFCVD) reactors are the most extensively utilized CVD devices for delivering a high-temperature stage. HWCVD, on the other hand, is better suited to the
deposition of polymer nanocomposites than HFCVD because it does not necessitate the high temperatures required by HFCVD. Nonetheless, these coating processes are rarely applied for polymer nanocomposites, with the exception of highly specific circumstances such as the deposition of nanodiamonds.

CVD with plasma-assisted cooling is a cost-effective approach to lower the temperature. It activates chemical reactions by using a microwave plasma at a low pressure (10–100 Pa) rather than a high temperature. The technique uses a 2.45-GHz microwave plasma stimulating source and simply requires a low ambient temperature. Silicon dioxide (SiO₂), carbon nitride (C₃N₄), and cubic boron nitride (c-BN) have all been deposited with this technique. Polymers containing fluorine, such as polyfluorohydrocarbon and polyperfluorocarbon [59,60], have been coated on certain surfaces as well [61].

2.3. Chemical and electrochemical deposition

Chemical and electrochemical depositions are of great interest, both theoretically and practically; both methods can be implemented for electroplating and solution analysis. The low ionization temperature should have no effect on the coating objectives. Chemical and electrochemical depositions main goal is to convert precursors into active species using reducing agents or an input voltage given to the polyelectrolyte matrix. Conductive polymers such as polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT) have been the most often utilized conductive polymer matrix in nanocomposites attributable to this requirement. The electrochemical approach, on the other hand, necessitates the use of an external current, the anodic and cathodic reaction sites are separated. Reduction is caused by a reducing agent in chemical deposition, and the anodic and cathodic reactions occur simultaneously on the workpiece [62]. Furthermore, these reactions can only take place on catalytically active surfaces, which means that newly coated metallic surfaces must be catalytically active enough to stimulate redox reactions. Electrochemical deposition has been frequently employed with conductive polymer nanocomposites to immobilize nanofillers within the conducting polymer matrix, such as heavy metal colloids or specific enzymes. Furthermore, bioactive thin films may be used as biotransistors, converting analogue biosignals into electrical signals.

2.4. Roll-to-roll (R2R) processing deposition

Roll-to-roll processing deposition (R2R) is a low-cost industrial coating technology that has been used to make flat electronics like organic light-emitting diodes (OLEDs), photovoltaics (PV), and electrophoresis displays (EPDs). Coyle et al. define a simple roll coating as follows: fluid flows into the area between two revolving rollers, which control the thickness and homogeneity of the coated film. Some versions of this definition have
been utilised in industry for specific reasons, such as reverse-roll coating [63], and gravure coating [64].

2.5. Other coating methods

2.5.1. Sol-gel method

The sol-gel method is a complement to physical deposition ways of obtaining high-quality coatings up to micron thickness. However, when it comes to covering metallic substrates with sol-gel, there are several limitations. This process has a number of flaws, including crackability and thickness constraints. In the case of inorganic nanofillers, such as inorganic/inorganic coatings, the second phase can be added to the sol-gel for inorganic nanofillers [65-68]. In the creation of nanocomposite coatings, inorganic sol-gel precursors such as silicon (Si), titanium (Ti), aluminium (Al), and zirconium (Zr) metal alkoxides are used. Organic phase preparations have been documented to include a wide range of oligomers as well as low molecular weight organic molecules. Silanes and organic compounds can combine to produce coatings containing silica nanoparticles or nanophases under certain conditions. A system combining tetraethyl orthosilicate (TEOS), methacryloxypropyltrimethoxysilane (MAPTMS), a urethane acrylate resin, and an acrylated phenyl phosphate oxide oligomer (APPO) was reported to generate silica nanocomposites [69]. Facio and Mosquera [70] also succeeded in generating nanocomposite coatings combining monomeric and oligomeric ethoxysilanes, hydroxyl-terminated polydimethylsiloxane (PDMS), colloidal silica particles, and a surfactant (n-octylamine). Furthermore, the sol-gel approach could be integrated with electrodeposition to include inorganic nanofillers into the polymeric organic matrix [71] or inorganic matrix [72].

2.5.2. In situ polymerization method

Organic matrices, such as conducting polymer [73,74] or other monomers with initiators, were employed to manufacture PNCs using this approach. Metals or metal oxides were used as nanofillers. Electrodeposition [75], oxidizing agents [73,74,76], or photo-polymerized) [77,78] are all used to polymerize. For organic matrices, emulsion polymerization [79,80] or latex emulsions [81] are related approaches. Guo et al. used in situ polymerization to make graphene (GN), and functionalized graphen oxide (GO)-epoxy nanocomposites [82]. The filler was first ultrasonically dispersed in acetone before the synthesis began. The dispersion was then added to the epoxy matrix before being placed in a vacuum oven at 50 °C. When 80 % of the solvent had evaporated, the m-phenylenediamine (MDP) was added, along with vigorous stirring. To make the composites, the liquid was put into a stainless-steel mould, dried at 60 °C for 5 h to remove the remaining solvent, precured in an oven at 80 °C for 2 h, then postcured at 120 °C for 2 h. PMMA/GO [82] and polypyrrole (PPy)/GO [83] are two more GO composites
that have been reported. Liquid–liquid interfacial polymerization was used to make PPy/GO composites. The authors chose this method over the more traditional in situ polymerization method because it is slower and more controlled. This procedure can also be used to prepare large quantities.

2.5.3. Solution dispersion

Solution dispersion is mostly used to synthesize PNCs that are reinforced with nanofillers such as metal oxides, nanoclays, and carbon nanotubes (CNTs) [84–87]. In this method, ultrasound-assisted (sonication) stirring [84,85,87] was implemented in addition to traditional magnetic/mechanical stirring methods for superior dispersion of nanofillers into polymer matrices. Bian et al. used solution dispersion to create poly(propylene carbonate) (PPC)/modified GO (MGO) nanocomposites [88]. MGO was disseminated for 30 min in 25 mL dimethylformamide (DMF) before being mechanically agitated for 10 min. After that, PPC was added to the dispersion and agitated for 24 h at 40 °C. The solvent was evaporated in a Petri plate at room temperature under vacuum. The incompatibility of hydrophobic PPC with hydrophilic GO necessitated the modification of GO. In order to improve interfacial adhesion and promote nanocomposite formation, hydroxyl groups were grafted onto the GO surface.

Gu et al. [89] described the solution intercalation synthesis of an elastomer/organo-MMT nanocomposite. Before introducing the organo-modified MMT to the cis-1,4-polybutadiene rubber (BR) solution, it was first dispersed in a solvent oil. The solvent was evaporated after 30 min of stirring at 60 °C. For specimen preparation, the nanocomposite powder was synthesized and cured.

2.5.4. Spray coating and spin coating methods

PNCs are usually encountered using spray coating and spin coating processes. In the instance of spray coating, using an atomizer improved the characteristics of nanocomposite coatings [90,91]. The atomizer could also be utilized for atomized spray plasma deposition [92], which is a thermal spray technique. It delivers homogenous thin films to flat substrates in the case of spin coatings [93]. The coating materials are dispersed by centrifugal force on the substrate, which is rotated at a high speed. This technique can be used to make thin-film nanocomposite coatings.

2.5.5. Dip Coating

Dip coating is a widely used process that involves soaking a substrate in a polymer nanocomposite solution and pulling it up at a consistent and regulated speed. As the substrates are taken from the solution, they are covered with nanocomposite. The amount of polymer nanocomposite on the substrate surface is likewise controlled by the enforced pulled up rate. This process has the advantage of being able to prepare a flat
surface for any type of coated substrate. The fact that the solution can be reused until the solute is depleted or evaporated makes this procedure extremely useful for industrial applications.

3. Different Types of PNC Systems

Different types of PNCs formed by using nanofillers as follows: (i) polymer-inorganic nanocomposite coatings, (ii) polymer-metal oxide nanocomposite coatings, (iii) carbon-based polymer nanocomposite coatings, and (iv) hybrid polymer nanocomposite coatings [Fig. 3].

![Fig. 3. Different types of PNCs.](image)

3.1. Polymer-inorganic nanocomposite coating system

To improve compatibility with the polymer matrix, polymers are grafted onto the nanoparticles surface by polymerization. Using a simple esterification procedure, Feng et al. grafted poly(methylmethacrylate) (PMMA) onto the SiO$_2$ surface. They suggested that this simple esterification approach may be used to graft nanoparticles with a variety of polymers [94]. In-situ polymerization of nanoparticles has been utilized to increase the dispersity and homogeneity of nanofillers in polymers [95]. The in-situ particle production method improves the dispersity of nanofillers by synthesizing inorganic nanoparticles inside the pore of the polymer matrix. To generate diverse inorganic oxide nanoparticles in polymer networks, the sol-gel method is a typical in-situ particle creation method. The nanoparticles generated inside the polymer matrix can be kept in a well-distributed state, successfully preventing agglomeration. The development of silica, titania, or alumina nanoparticles in polymers using in situ sol-gel has been extensively explored to produce nanocomposite coatings. Organometallic precursors such as TEOS [96,97], tetrabutyl titanate (TBOT) [98], and others are routinely utilized to generate metal oxide nanoparticles in polymer matrix.
3.2. Polymer-metal oxide nanocomposite coating system

Polymer-metal oxide nanocomposite coating is an attractive new technology for numerous applications reinforced with nano sized SiO$_2$, TiO$_2$, Al$_2$O$_3$, ZnO and CeO$_2$ [Fig. 4].

![Polymer-metal oxide nanocomposite coating system](image)

**Fig. 4.** Polymer-metal oxide nanocomposite coating system.

3.2.1. Nano-SiO$_2$

Due to unique qualities of high hardness, low refractive index, facile functionalization, and exceptional chemical and thermal durability, SiO$_2$ nanoparticles have been widely used in a variety of applications, including paints and polymers. Sol–gel procedure, reverse microemulsion method, and flame spray pyrolysis can all be used to make silica nanoparticles with high reliability [99]. SiO$_2$ nanoparticles can increase the mechanical characteristics, durability, and anticorrosion qualities of polymeric coatings [100]. As a result, SiO$_2$ nanoparticles in nanocomposite coatings have a lot of promise [101].

To improve anticorrosion properties, the inclusion of SiO$_2$ nanoparticles into polymer matrix has been extensively explored. The addition of SiO$_2$ to resin coats can significantly reduce total free volume and disaggregation during curing [102,103]. If you're looking for a unique way to express yourself, Because of its strong adhesion for many substrates, low cost, great chemical resistance, and outstanding corrosion and abrasion resistance, the SiO$_2$/epoxy nanocomposite has been widely used as a major anticorrosive coating material [104-106]. Another potential method for using SiO$_2$ is that porous SiO$_2$ nanoparticles can be used as an inhibitor reservoir, slowing down the corrosion process [107,108]. Yeganeh et al. [107] designed a corrosion inhibitor (sodium molybdate) loaded in mesoporous SiO$_2$ nanoparticles to create a protective epoxy nanocomposite covering.
3.2.2. Nano-TiO$_2$

The steadily increasing tortuosity of the diffusion pathway of external aggressive molecules has been realized as mechanism of polymer/TiO$_2$ nanocomposite coatings. TiO$_2$/poly(carbonate urethane) nanocomposite was created by L. D’Orazio et al. as a protective layer for outdoor cultural heritage. The coating with 1 wt% TiO$_2$ nanoparticles has excellent self-cleaning and durability properties. [109] According to Khademian et al., adding 1.5 wt% of PANI-TiO$_2$ nanohybrid to poly (vinyl acetate) coatings improves heat stability, dispersion, and anticorrosion properties significantly [110]. Weng et al. established electroactive polyimide–TiO$_2$ (EPTs) hybrid nanocomposite coatings with well-dispersed TiO$_2$ nanoparticles, which can strengthen anticorrosion performance on cold-rolled steel electrodes substantially [111].

3.2.3. Nano-Al$_2$O$_3$

The addition of nano-sized Al$_2$O$_3$ to a polymer to produce a polymer nanocomposite system could give the coating exceptional chemical and mechanical resistance, as well as UV and temperature stability [112]. Mechanical synthesis [113], reverse microemulsion [114], sputtering [115], hydrothermal [116], combustion [117] and sol–gel method [118] and other methods for the manufacture of nano-sized alumina have been documented in the literature. Mallakpour et al. presented an overview of recent developments and properties research in Al$_2$O$_3$/polymer nanocomposites [119]. Al$_2$O$_3$ nanoparticles are also a promising material that is widely utilised to modify coatings for corrosion resistance [120]. The inclusion of stiff spherical Al$_2$O$_3$ nanoparticles in a polymer matrix at an adequate concentration can fill porosities in coatings, strengthen particle–matrix interactions, and improve coating hardness and corrosion resistance dramatically [121]. According to Golru et al., epoxy/polyamide coatings modified with 3.5 wt% Al$_2$O$_3$ nanoparticles had superior barrier characteristics, compact structure, and hydrolytic resistance [122]. Rout [123], Li [124], and Babaei-Sati et al. all found that Al$_2$O$_3$ plays a similar role in alumina/polymer nanocomposite coatings with strong anticorrosive properties. Because of their high chemical activity and surface energy, Al$_2$O$_3$ has a limited potential as a reinforcement due to poor dispersion of the nanofillers and the tendency of NPs to coalesce [125-127]. Surface modification of Al$_2$O$_3$ NPs, such as chemical surface functionalization using silane coupling agents and surfactant grafting, is a viable method for addressing this problem [128,129].

3.2.4. Nano-ZnO

Thermal conductivity, dielectric characteristics, mechanical qualities, thermal stability, and antibacterial capabilities could all benefit from the addition of ZnO to the polymer matrix. D. Ponnamma et al. presented an overview of recent developments in ZnO- based polymer nanocomposites [130]. High temperature sputtering [131], molecular beam
epitaxy [132], chemical vapor deposition [133], electrophoretic deposition [134], microwave-assisted technique [131], solvothermal [135], hydrothermal reactions [136], and chemical bath deposition are just a few of the methods that can be used to create various morphologies of nano-ZnO [137].

Nanosized ZnO with a large aspect ratio and small size could block pinholes and cavities in polymeric coatings, preventing corrosion specimens from penetrating through the pores in the coating film. At the same time, ZnO nanoparticles can zigzag corrosive species' diffusion pathways, enhancing corrosion protection [138]. Several studies have shown that ZnO nanoparticles play a significant role in improving the anticorrosion properties of conventional polymer or CP coatings [139,140]. For example, Hossein et al. found that in a 3.5 wt% NaCl solution, the anticorrosion life of a polypyrrole (PPy) coating containing ZnO nanorods was much longer than that of a pure (PPy) film, which they attributed to the corrosion molecules' longer diffusion pathway and more compact coating due to the addition of ZnO nanorods [141]. The addition of 6 wt% ZnO nanoparticles to the polymer improved the coatings super hydrophobicity, which helped to prevent corrosion [142].

3.2.5. CeO$_2$

CeO$_2$ has the ability to inhibit general corrosion, which is thought to be due to the deposition of cerium cations diffused from CeO$_2$ nanoparticles at corroding sites; however, increasing the nanoparticle number reduced the barrier qualities of coatings [143]. Furthermore, it has been demonstrated that the addition of CeO$_2$ nanoparticles to polymer coatings improved their barrier properties. Sababi et al. encountered that combining 3 wt % ceria nanoparticles with 3 wt% PANI doped with phosphoric acid in a polyester acrylate coating provided a synergistic protection effect, improving the coatings barrier property and stability while also providing active carbon steel protection [144]. According to Li et al., adding 1.0 wt% CeO$_2$ nanoparticles to a nanocomposite coating containing 1.0 wt% PANI improves the corrosion protection performance, where PANI and CeO$_2$ have a synergistic passivation effect as barrier-type protection to metals [145].

3.2.6. Nano-iron oxide

Iron oxide nanocrystals are abundant in nature and are mostly found in three states: FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$. Corrosion and abrasion resistance can be improved by incorporating iron oxide nanoparticles into PANI coatings, which combine both conducting and mechanical capabilities of nanocomposites [146,147]. Using a Fe$_3$O$_4$/PANI (1:1) nanocomposite coating on carbon steel in 3.5 % NaCl for 60 min, Bagherzadeh et al. observed a high protection efficacy of 96.8 % [148]. The Fe$_3$O$_4$/PANI nanocomposite coating has a better resistance to corrosive ions, which can be attributed to the nanofillers’ strong barrier, adhesion, and locking properties. Furthermore, because they may create a potential p-n type junction at the Fe$_3$O$_4$/PANI interface, Fe$_3$O$_4$/PANI nanocomposite
exhibit good corrosion inhibition. The injection of very small quantities of modified Fe$_3$O$_4$ nanoparticles is thought to significantly improve the corrosion resistance of epoxy or PU coatings, which is linked to improved adhesion, barrier characteristics, and anodic corrosion inhibition action of Fe$_3$O$_4$ nanoparticles [149-151]. Liu et al. used a high-energy ball milling method to produce surface modification of iron oxide in epoxy, which reduced interface flaws and improved coating anticorrosion properties [152].

3.3. Carbon based polymer nanocomposite coating system

3.3.1. Carbon black (CB)

Carbon black (CB), a low-cost pigment, is commonly used in ink and painting [153]. Large surface area, great coloring qualities, strong electrical and thermal conductivity, and the ability to be easily functionalized are all characteristics of CB nanoparticles [154]. CB nanoparticles with a large specific surface area and high surface activity, like other nanoparticles, tend to agglomerate, which can be avoided by surface functionalization and careful control of the polymer content [155].

Only a few research papers discuss the use of CB-based polymer nanocomposite coatings. Zhang et al. discovered that polyvinyl alcohol (PVA) coatings containing 1% CB nanoparticles have a strong anticorrosion effect on steel in saline solution [156]. According to Ghasemi-Kahrizsangi et al., the optimum concentration of modified CB nanoparticles in epoxy coatings to prevent corrosion was 0.75 wt%. CB nanoparticles also have high UV stabilizing properties, which helps epoxy last longer. In comparison to unfilled coatings, Foyet et al. found that filling CB in epoxy to generate CB/epoxy nanocomposite coatings reduced the delamination rate of Aluminum AA2024 alloy by a factor of 10. A corrosion protection mechanism was proposed in which electrons might migrate into the coating, slowing oxygen reduction and coating delamination [157].

3.3.2. Carbon nanotubes (CNTs)

Several researches have shown that combining CNTs with polymers results in a nanocomposite with amazing characteristics [158]. The most prevalent procedures for fabricating CNTs/polymer nanocomposites are solution mixing [159], melt mixing [160], and in situ polymerization [161]. A homogeneous dispersion of CNTs into the polymer matrix has been proven to be crucial for high-performance coatings in a number of studies [162]. CNTs agglomerate into enormous bundles due to their intrinsic electrical arrangement, high surface energy, and incompatibility with the polymer matrix. Defect functionalization with concentrated acids, covalent functionalization, and non-covalent functionalization with compatibilization additives are the most common compatibilizing techniques [163,164].

Due to their unique electrical properties, Souto and coworkers demonstrated that combining CNTs and CPs, such as CNTs/PANI, can result in outstanding epoxy coating
corrosion resistance [165]. According to Rui et al., the interfacial - interactions between CNT and PANI give PANI/CNT nanocomposites of high redox capacity, which improves electrochemical activity and passivation protection. PANI/CNT nanocomposites added to acrylate-amino resin (AA) improved the protective effect by providing effective anodic protection and a physical barrier [166]. PANI nanocomposite containing 0.8 % CNT was used as an anticorrosive covering for aluminum bipolar plates in the acidic solution inside fuel cells, according to Deyab et al. [167]. To slow the corrosion rate of carbon steel, Hong et al. suggested using polydopamine/CNT nanocomposite coatings. The physical barrier on the surface and the inhibition of cathodic partial reaction by CNTs are strongly linked to the coating’s corrosion mitigation property [168].

3.3.3. Graphene (GN) and its derivatives

GN has shown considerable promise in a wide range of applications. The most common ways for producing graphene are micromechanical stripping, redox [169], and CVD [170]. The degree of dispersion of nanofiller in the polymer has a significant impact on the characteristics of graphene-based nanocomposites. GN derivatives such as graphene oxide (GO), reduced GO (rGO), and electrochemically exfoliated graphene (ECG) have been created using various ways to obtain well distributed graphene-based nanocomposites [171]. GN/polymer nanocomposites have been created by physically or chemically mixing graphene nanosheets or derivatives with polymer, mostly through in-situ polymerization, solution mixing, and melt intercalation techniques [172].

GN and its derivatives with amazing lamellar structure have been described in numerous investigations as improved nanofillers for high-performance anticorrosive polymer coatings [173,174]. The enhanced anti-corrosion property of graphene-based polymer nanocomposite coatings is most likely due to larger contact areas between modified graphene or GO nanosheets and polymers, which is beneficial in elongating the diffusion pathway (tortuosity) of corrosive molecules in the matrix and providing superior physical barrier [175]. Chan et al. [176] reported anticorrosion performance which is coated by adding 0.5 wt. % well-dispersed graphene nanosheets to epoxy, as well as 0.5 wt.% polyaniline (PANI). Huang et al. [177] also created a high-barrier novel graphene oxide nanosheet (GONS)/PVA nanocomposite film. The oxygen and water vapor permeability coefficients of nanocomposite films could be reduced by 98 % and 68 %, respectively, by adding just 0.001 wt. % of GONS to PVA. Ding et al. [178] and Cui et al. [179] recommended using functionalized graphene in epoxy coatings in hostile conditions to improve corrosion resistance.

3.3.4. Nano-graphitic carbon nitride (g-C3N4)

Graphitic carbon nitride (g-C3N4) is a metal-free polymeric semiconductor having a 2D graphene-like structure with only one or a few atomic layers. The 2D frameworks of g-C3N4 are made up of repeating units of s-triazine or tri-s-triazine linked by planar amino
groups [180]. When compared to graphene, g-C₃N₄ has the following advantages: lower cost, stronger mechanical stability, and high in-plane nitrogen concentration. Preparation methods for g-C₃N₄ include PVD, CVD, solvothermal, single step nitridation, and thermal condensation.

The integration of g-C₃N₄ nanoparticles into a protective polymer matrix is critical for improving the coating’s anticorrosion characteristics [181]. Zuo et al. used chemical oxidative polymerization to create the PANI/g-C₃N₄ nanocomposite coating, which displayed improved corrosion inhibition behavior of g-C₃N₄ over individual components on iron panels in saline solution. Chen et al. modified the surface of g-C₃N₄ with MoOₓ to achieve a homogenous dispersion in epoxy coatings [182]. The ability of g-C₃N₄ nanoparticles to fill the coating porosities and free volumes, resistance to electrolyte permeation, coatings degradation, and delamination are significantly improved when 3 wt% of g-C₃N₄/MoOₓ nanoparticles are added to epoxy, with no negative effect on the adhesion strength of the coating on Al substrates. For Al alloy protection, Xu et al. developed a novel poly(urea-urethane)-g-C₃N₄ (PUU-g-C₃N₄) nanocomposite material [183]. They discovered that PUU-g-C₃N₄ worked as a smart anticorrosion coating with good antipenetration and self-healing properties, even when exposed to high humidity.

3.4. Other types of PNCs

3.4.1. Nano-clay

Toyota Research Group discovered that adding clay to Nylon-6 matrix improves mechanical qualities, which sparked interest in clays in advanced nanocomposites in the early 1990s [184]. Clay is a 2D nanofiller with an extremely high aspect ratio (10-1000) and a large surface area made up of layered silicates or clay minerals with traces of metal oxides and organic materials. Clay in a polymer matrix can give a clay/polymer nanocomposite exceptional impermeability and barrier qualities, allowing it to be used in a variety of applications, including packaging and coatings [185].

For contrast, adding clay nanosheets modified by a surfactant can improve the compatibility and interfacial contact between nano-clay and polymers, resulting in better nanocomposite coating barrier properties [186]. Clay/polymer nanocomposite structures can be classified into three categories based on the clay's dispersion degree: phase separated, intercalated, and exfoliated [187]. Exfoliated clay layers are completely separated sheets, resulting in a homogeneous nanoscale dispersion in the polymer matrix; complete exfoliation of the layered clay in the matrix is thus the most desirable state, in which clay has the highest aspect ratio and thus the best barrier performance [188,189].

Montmorillonite (MMT) is a type of clay that is utilised as one of the most frequent nanofillers in clay/polymer nanocomposites for corrosion resistance. MMT/polymer nanocomposite coatings have shown to be quite effective at preventing corrosion. For example, Shabani-Nooshabadi et al. investigated the effect of MMT/PANI nanocomposite coatings on the anticorrosion properties of aluminium alloy 3004 in saline solution,
finding that the MMT/PANI nanocomposite coatings reduced the corrosion rate by about 190 times and lowered the corrosion current values from 6.55 A cm\(^2\) (uncoated Al) to 0.102 A cm\(^2\) (MMT/PANI-coated Al) [190]. Madhup et al. found that alkyl quaternary ammonium salt modified sepiolite and hectorite clays are excellent reinforcement fillers for anticorrosive clay/polymer nanocomposite coatings. The addition of sepiolite and hectorite clay to the epoxy coating significantly increased the water vapor barrier and salt spray anticorrosion capabilities [191].

3.4.2. Nano-cellulose

Various nano-sized organic or organometallic compounds have been adopted to combine with polymer for the development of high-performance nanocomposite coatings, in addition to the standard inorganic nanoparticles. One of most ubiquitous polysaccharides in nature, cellulose, is a renewable and "green" polymer. Cellulose nanoparticles are elongated rod-like materials having a highly crystalline structure, a large specific area of roughly 150 m\(^2\)/g, and excellent mechanical capabilities, making them ideal for use as reinforcement in anticorrosive polymer coatings [192,193]. Dimethyldidodecylammonium bromide (DDAB) has been deployed to alter cellulose nanocrystals to increase their water contact angles by 100-200 percent, making them much more dispersible in epoxy matrices. Simultaneously, modified cellulose nanocrystals provided an impressive barrier against corrosive substances [194]. The inclusion of cellulose nanowhiskers into polylactic acid reduced the water and oxygen permeability of nanocomposites by 82 % and 90 %, respectively, according to Sanchez-Garcia et al. [195].

3.4.3. Nano-hexagonal boron nitride

Hexagonal boron nitride (h-BN) is a novel type of nanomaterial with a crystalline structure that is similar to graphene in two dimensions. Because of its unique structure, remarkable thermal stability, electrical insulating capabilities, and great impermeability, h-BN has also been used to make anticorrosive nanocomposite polymer coatings [196]. Husain et al. found that polymer coatings with h-BN on stainless steel demonstrate corrosion resistance with low corrosion current density and corrosion rate [197]. Cui et al. used poly (2-butyl aniline) (PBA) as a surfactant to make thin h-BN nanosheets, which they then laminated into epoxy coatings for corrosion resistance. They discovered that adding PBA scattered h-BN boosts long-term corrosion resistance, [198]. Other studies by Wu and He et al. found that epoxy coatings with 0.3 wt% h-BN non-covalently modified by GO had exceptional impermeable performance and corrosion resistance [199]. Aside from mechanical exfoliation, chemical dispersants such as carboxylated aniline trimer derivative (CAT) [200], poly(ethyleneimine) (PEI) [201], and poly (dopamine) [202] have been used to diminish the incompatibility of h-BN with polymer matrix.
3.4.4. Nano-glass flakes

Other alternatives for polymer coating additives are nano-glass flakes (GF) with a parallel-arranged 2D structure, which have low permeability and high weathering and chemical resistance [203]. González-Guzmán et al. constructed a porous, non-barrier epoxy/polyamine organic film with GFs as a pigment that demonstrated improved protection and carbon steel adhesion [204]. Due to the effect of GF nanoparticles on extending the diffusional path of gases and vapors in epoxy coating, Ghaffari et al. noticed a noticeable reinforcement on the barrier protection performance of epoxy coating by adding 0.5 wt% GF nanoparticles in a sodium chloride solution [205]. Furthermore, Nematollahi et al. assessed epoxy coatings containing 3 wt% GF and 3 wt% montmorillonite organoclay (OMMT) in a 5 wt% NaCl solution.

Other nanostructures, such as ceramics, have been reported with augmented polymer coatings in addition to the nanocrystals mentioned above niobium pentoxide (Nb$_2$O$_5$) [206], phosphate [207], starch [208], chitosan [209], zinc molybdate (ZM) [210], silicon–aluminum–oxygen–nitrogen (SiAlON) [211], fluoride–doped diopside [212], CaCO$_3$ [213], zinc chromates and zinc phosphates [214], siloxane [215], phthalocyanine [216], micaceous iron oxide (MIO) [217], nickel oxide [218], and triethanolamine nanoparticles [219].

3.5. Hybrid PNCs

Nanohybrid structures, which combine many functional components into a single structural unit, have sparked a lot of attention in the research interests. Nanohybrids containing various inorganic nanoparticles, which are then incorporated into polymers, are predicted to increase coating performance. Zhan et al. created an innovative epoxy nanocomposite covering with co-modified GO/Fe$_3$O$_4$ hybrids. Yu et al. also promoted the usage of a GO-alumina nanosheet hybrid structure as a promising material for improving epoxy coating corrosion resistance [220]. Ramezanzadeh et al. grafted PANI nanofibers and CeO$_2$ nanoparticles onto GO nanosheets, and then incorporated the nanocomposite coating into an epoxy matrix. The corrosion inhibition performance of PANI-CeO$_2$-GO nanohybrid particles is highly active [221]. The incorporation of CPs and CNTs into traditional coatings has a high potential for corrosion resistance. Rui et al. demonstrated that adding PANI/CNT nanohybrids to acrylate-amino resin improved protection against corrosion, which they attribute to the nanohybrids efficient physical barrier effect as well as PANIs passivation catalytic and anodic protection [222].
Table 1. Comparison of nanofillers for polymer nanocomposite coatings.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Polymer</th>
<th>Fabrication method</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>PANI</td>
<td>Electrochemical Polymerization</td>
<td>High hydrophobicity, outstanding anti-permeability, good mechanical properties, and strong adhesion.</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Alkyd resin</td>
<td>Mechanical mixing</td>
<td>Inhibition of both hydrogen evolution and carbon steel dissolution reaction.</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Poly(o-anisidine) (POA)</td>
<td>Electrochemical Polymerization</td>
<td>Good uniformity and strong adhesion property.</td>
</tr>
<tr>
<td>ZnO</td>
<td>PANI, Epoxy</td>
<td>In situ chemical oxidative polymerization</td>
<td>Prevention of the delaminating and degradation of coatings; increase of durability.</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>PPy</td>
<td>Electrochemical Polymerization</td>
<td>High thermal stability, distinct compact and denser morphologies and outstanding corrosion resistance.</td>
</tr>
<tr>
<td>CNTs</td>
<td>PANI</td>
<td>Electrochemical Polymerization</td>
<td>The addition of f-CNTs enhanced the mechanical behavior and hydrophobic nature.</td>
</tr>
<tr>
<td>GO</td>
<td>Epoxy</td>
<td>Solution processing technique</td>
<td>Low viscosity and desirable adhesion to substrate.</td>
</tr>
<tr>
<td>MMT</td>
<td></td>
<td>Electrochemical Polymerization</td>
<td>Environmental friendly, strongly adherent property.</td>
</tr>
</tbody>
</table>

4. Nanofillers for PNC Methods

The ultimate purpose of embedding nanofillers into polymer coatings is to eliminate the issues that regular polymers have, such as susceptibility to surface abrasion, wear, low chemical and mechanical durability, and so on. Because they provide hostile ions easy access to the underlying metal surface, these restrictions have a significant impact on the barrier, adhesion, and anticorrosive properties of polymer coatings, resulting in localized corrosion. As a result, nanofillers can improve the barrier property of virgin polymer coatings, which is influenced by the fillers miscibility with the polymer matrix. This result not only addresses the defects listed above, but it also reduces porosity and produces a zigzag diffusion path for active/destructive species penetration [223].

PNC manufacturing is an environmentally friendly operation when compared to other corrosion prevention technologies [224]. Furthermore, the presence of nanomaterials reduces polymer disaggregation during the curing process, leading to more homogeneous PNC systems. NMs can cover tiny gaps and pinholes that arise inside the polymer network due to shrinkage during curing, as well as act as connecting materials between polymer chains, thanks to their high surface area and nanoscale structure [225]. As a result, the polymer networks free volume decreases while the cross-linking density increases [226]. Because they prevent delamination from the metal surface, PNCs with a small number of nanofillers (< 4 % of polymer weight) often exhibit a strong barrier performance for anticorrosive applications [227]. Numerous academic researchers are
interested in the role of NMs in strengthening the anticorrosive processes of PNCs. Wei et al. [228] used multiwalled carbon nanotube (MWCNT) nanocomposites to investigate the anticorrosive capabilities of conductive polyurethane nanocomposite coatings. The type and nature of nanofillers has also been discovered to have a significant impact on the corrosion prevention mechanism of PNCs. Incorporating conductive fillers (such as conductive polymers, metals, and metal oxides) into polymer matrices, for example, makes it easier to form an oxide passive layer at the metal-coating interface, which serves as a secondary barrier and improves PNC corrosion resistance. A new system has been introduced by Ali et al., modified nanohybrid composite resin bonded with a one step self-etching bonding system and was compared to the conventional microfilled composite resin bonded with a one step-etching bonding system [229].

4.1. Effect of physical properties of inorganic nanofiller on PNC methods

In general, nanoscale inorganic fillers materials for reinforcing polymeric materials for a wide range of applications are the emphasis. These micron-sized fillers have a substantial surface area and length (length/thickness or length/diameter ratio). As a result, several characteristics such as "particle size, porosity," drying technique, and polymer network structure influence the reinforcing effect. Particle size affects superabsorbent characteristics, particularly swelling dynamics. In comparison to clay-free hydrogels, composite hydrogels often have a slower swelling rate [230]. The effect of calcium carbonate granular particle size on the physical properties of latex films was studied by Manroshan and Bahrain in 2005 [231]. The results show that the time it takes for the rubber to mature is mostly determined by the rate of filler loading due to interaction or bonding between the fillers and the matrix.

Zaini et al. [232] evaluated the effects of the inorganic filler "sepiolite (sep) hybridized with CaCO₃, SiO₂ or CB" on the hardening technique, mechanical characteristics, thermal stability, and flammability of ethylene propylene diene monomer (EPDM) rubber composites. The small particle sizes of carbon black and silica allow increased diffusion of each filler, curatives that are more refined, as well as a good interaction of the CB-sep filler network and EPDM chains, and a speedier beginning of crosslinking reactions. The addition of "calcium carbonate" to EPDM/sep composites, on the other hand, reduced tensile strength. This could result in poor stress shift and low tensile strength due to the greater particle size of carbonate, which does not give an outsized region to work with the rubber matrix. As a result, the combined same "EPDM/sep/CB composites had the greatest tensile strength improvement, followed by EPDM/sep/Sil and EPDM/sep/CaCO₃ composites. EPDM, sep, and CB described the good thermal stability and flammability concentration. Furthermore, the smaller particle size of inorganic fillers resulted in the highest interaction between filler and polymer, reducing swelling due to the formation of "bonds" in close proximity to the filler, which physically and chemically collaborated to limit swelling [232].
6. Scope of the Work

PNCs made of polymers have some advantages over other anticorrosive compounds. To name a few attributes, they have excellent environmental/chemical stability, exceptional mechanical and adhesive properties, and high thermal stability. Their structural properties can be tailored to meet the requirements of a certain application. Furthermore, their environmental friendliness can be improved by utilizing organically derived precursors.

PNCs on metals and alloys give excellent protection against oxidation, corrosion, and other harsh environments. The PNC manufacture methods changed the physical, microstructure, and mechanical properties of subsequent PNCs. Adhesion, compactness, and processability were all affected by these alterations, which are all essential in terms of stability and application. According to the research, structural modification of nanofillers through encapsulating, enveloping, decorating, and other ways is a promising strategy for improving the filler-matrix interactions. The PNCs have significantly enhanced the identification, qualification of disease biomarkers, improving the clinical trials [233].

6. Limitations of PNC Methods

Long-term shelf life causes nanofillers to separate from the matrix, resulting in an inhomogeneous PNC system with poor anticorrosive coating performance. The dispersion of nanofillers inside the polymer matrix, which affects storage and stability, is one of the most serious issues with PNCs. Building evenly dispersed stable PNCs remain a difficult task, despite the fact that several solutions have been used to tackle these challenges. Conversely, excessive use of nanofillers affects the physico-mechanical properties of polymer nanocomposite coatings, reducing stiffness and creating brittleness inside the coating, lowering performance at the application site. Color choice and the need for more aesthetic sense can occasionally limit certain nanofillers that fail to provide vibrant color but induce very strong anticorrosive characteristics in coatings and paints. As a result, these nanocomposites have been used as intermediate coating materials rather than top coats.

7. Future Prospects

We attempted to provide an overview of PNCs in both basic fundamental and recent developments in nanocomposite coating design, processing, and applications. PNCs are becoming smaller, cheaper, and more useful because to the rapid rise of nanotechnology and associated industries. Drug delivery systems, coatings for implants, anticorrosion barrier coatings, antimicrobial coatings, self-scratch repair, fire retardant coatings, reflective coatings, and screen effect coatings are all potential applications for polymer-based nanocomposite coatings in the future. Due to the presence of multifunctional nanofillers, the nanocomposite coating now serves as a protection for the materials as well as other functions. Antibacterial coatings and smart coatings, both used in sustainable energy domains, are two of the most common examples. In the first scenario, silver
nanoparticles based on nanofillers and associated goods have a bright future in the next decades.

8. Conclusion

PNC methods have become outstanding, cheaper, smarter, and more efficient as a result of rapid advancements in nanotechnology. Anticorrosion barrier coatings, self-repair coatings, and self-scratch repair coatings are all expected to benefit from PNC methods. Recently these coating methods have been used to protect metals from corrosion. Corrosion prevention is made easier with PNC methods. Although some corrosion prevention technologies have great inhibitory properties, they are constrained by time, temperature, and other considerations. However, when the film of polymer-based nanocomposite coated metals is broken by a harsh corrosive environment, the nanofillers/nanomatrix included in the nanocomposite release active elements, healing the injured surface and slowing the corrosion process. Because the modern world relies heavily on renewable energy, nanocomposites' smart or easy-to-clean coatings will be long-lasting and extremely efficient. The development of high-yield fabrication using eco-friendly composites will be the focus of future research on PNC methods.

References

7. E. Manias, Nat. Mater. 6, 9 (2007). https://doi.org/10.1038/nmat1812


Review Article: Polymer-Based Nanocomposite Coating


https://doi.org/10.1002/app.21595

https://doi.org/10.1007/s13726-018-0643-4

https://doi.org/10.3329/jsr.v13i3.53740