A Brief Review on Conducting Polymer Nanocomposite Based Epoxy Coatings for Marine Applications

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Abstract. Recently, fouling has become the main concern in the marine, naval and shipping industries. Furthermore, fouling has caused an increase in ship drag and fuel consumption whilst reducing the hydrodynamic performance of ships. Marine structures that partly or fully submerged such as oilrigs, submarine pipes and marine buoys are also impacted. Therefore, research and numerous studies had conducted to propose the best antifouling coating. The main objective of this review is to provide an overview of polymer-based surface coatings for protection from marine biofouling organisms. The physicochemical and mechanical properties of polymers had found to make these materials promising as polymeric coating that can be used in marine applications. Furthermore, this review will discuss the utilization of nanocomposites as additives, modifiers and nanofillers in order to enhance the properties of the polymer for antifouling coating.

1. Introduction

Antifouling (AF) known as the ability of specifically designed coatings to remove or prevent biofouling by any number of organisms on wetted surfaces. For example, AF paints are usually used to prevent the settlement of marine organisms on ship hulls including smaller vessels most of which are made of steel, polymeric resin and wood. Figure 1 shows the development in antifouling research by number of publications in respective years.
Figure 1. Statistics of Antifouling Research Paper By Year (Source: Web of Science)

In addition, a few requirements have to be fulfilled to produce an effective coating including adhesion to the substrate, mechanical and functional properties, wear resistance, hydrophobicity and hydrophilicity, antibacterial and chemical resistance [1]. Temperature is also included as one of the important conditions required for coating application. Therefore, figure 2 shows the types of coatings based on their usage and application in marine paint industry.

Figure 2. The types of coatings as per ACA and US Census Bureau Current Industrial Report

| METHOD                        | STRATEGIES                                      | REF  |
|-------------------------------|------------------------------------------------|------|
| Physical and biological       | Biomimetic                                      | [2]  |
| Chemical, biological and physical | Chemical: Traditional and modern methods. Biological: Enzymes. Physical: Electrolysis & radiation, modification of surface topography and changing the zeta potential. | [3]  |
| Biological                    | Tara Tannin (TT)                                | [4]  |
Improvement in polymer material structure and altered by the coatings environment on polymer nanocomposites that each paints this engineering resins [11]. Year by year, tortoise shells and horns have shown in Table 1. In addition, polymers have the ability to be used as additives in antifouling paints besides protecting metals against corrosion [12]. Figure 3 shows the percentage of publications on polymer nanocomposites that each subject area and category comprises.

Other than that, polymers have been a part of our lives, from the early ages - such as in tar, shellac, tortoise shells and horns until more recently in synthetic offerings like polyolefins, epoxies and engineering resins [11]. Year by year, many researchers find interest in the study of polymer coatings. This has shown in Table 1. In addition, polymers have the ability to be used as additives in antifouling paints besides protecting metals against corrosion [12]. Figure 3 shows the percentage of publications on polymer nanocomposites that each subject area and category comprises.

| Physical and biological | Functional properties & biomimetic using natural products, cells & enzymes. | [5] |
|-------------------------|--------------------------------------------------------------------------|-----|
| Chemical                | Tin free self-polishing copolymer, polymer coating                        | [6] |
| Chemical                | Tributyltin (TBT), copper, organic additives and polymers.               | [7] |
| Physical                | Microstructures of Cancer pagurus by using Poly(methyl methacrylate) (PMMA). | [8] |
| Biochemical             | Biodegradable polymer based polyurethane.                                | [9] |
| Biochemical             | Biodegradable polyurethane with low surface energy polydimethylsiloxane. | [10]|
Table 2. Improvement of Polymer Coatings on Value Addition of Nanoparticles [1]

| POLYMER MATRIX     | NANOPARTICLE EMBEDDED                      | % WT LOAD /RATIO | REF |
|--------------------|-------------------------------------------|------------------|-----|
| Polyurethane       | Molybdenum disulfide                      | 20-55.6          | [14]|
| Fluorinated polysiloxane | Steric acid-modified ZnO       | 13:7             | [15]|
| Teflon tailings    | Tetrafluoroethylene and hexafluoropropylene | -                | [16]|
| Fluoride latex     | Phosphating material                     | 40 vol%          | [17]|
| Epoxy resin        | Fatty acids and epoxidized oleic acid     | 5                | [18]|

2. CONDUCTING POLYMER NANOCOMPOSITE BASED EPOXY AS ANTIFOULING COATING

2.1. Epoxy Based Coating

Epoxy resin that is used as a coating material has been shown to have good mechanical and chemical properties that are relatively simple and safe [19]. In addition, epoxy is desirable for its easy processing, high safety, excellent solubility, good chemical resistance and toughness, low shrinkage on cure, good electrical insulating properties and corrosion resistance with strong adhesion to a lot of substrates [19]. Nanofillers were added into the epoxies to improve their antifouling properties [20]. Furthermore, blending two polymers through the incorporation of epoxy resin with additional fillers and modifiers into the base polymer matrix had seen to enhance the coating properties as in the figure 4.

![Figure 4. Properties of Epoxy-PDMS filled and unfilled systems [1]](image)

Dispersion of polysiloxane into an epoxy resin matrix has been achieved using suspension polymerization technique by utilizing the core-shell microsphere analogy [1]. Figure 5 shows siloxane core and epoxy shell lead to the creation of elastomeric microspheres. Based on the results of SEM
and X-ray microanalysis, the microhardness and the gradient of domain size were homogenized to present mixable and fully compatible microstructures [1].

Figure 5. The Synthesis Route of Epoxy-PDMS Core-shell Microspheres [1]

2.2. Polyaniline (PANI) as Antifouling Coating

Polyaniline has good potential for use as an antifouling agent to provide a coating that is non-toxic, low density and has stable electrical conductivity [21]. Fazli-shokouhi et al. has conducted research on PANI combined with graphene oxide nanosheets making PANI-GON nanocomposite by using in-situ polymerization method to form an epoxy based paint coating that showed significant antifouling properties [22]. Based on figure 6, the samples had shown the lowest and highest antifouling behaviour for which the reason was the ability of inorganic nanoparticles like graphene oxide to disperse and fill the micropores of epoxy [22].

Figure 6. Coating samples after immersion in simulated seawater for 3 months [22]

Furthermore, the pure epoxy coating on metal is colourless and the micropores that are not filled with any nanocomposites can allow the droplets of electrolyte to diffuse easily into the metal surface while the micropores of the epoxy coating that are filled with nanocomposite prevent the diffusion of electrolyte droplets from reaching the metal surface [22].

Other than that, with the good conductivity of PANI coupled with the excellent photocatalytic effect of zinc oxide in a polymer nanocomposites has shown ability to reduce the adhesion of marine bacteria [23]. Mooss et al. studied the embedding of polymer nanocomposite of PANI-ZnO in the basis of thermoplastic polyurethane that had good hydrolytic stability as well as chemical and microbial resistance as shown in Figure 7 [23].
3. Conclusion and Remarks

This review article has shown the development of antifouling coating that utilize a polymer basis for marine application. Nanocomposites, for antifouling coating, were used as additives in the coating in order to enhance the properties of antifouling and reduce the adhesion behaviour of the biofouling organism attached to the coating surface materials. However, there is little research on the use of polymer nanocomposite for marine antifouling coating. Therefore, further investigation focusing on conducting polymer nanocomposite for marine coating is needed, as the marine field requires more surveys for surface coating applications.

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