



# Chemistry and application of emerging ecofriendly antifouling paints: a review

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**Abstract** There has been a global concern about the use of tributyltin-based coatings in combating biofouling in the marine industry. Although there have been alternatives to tributyltin in preventing biofouling, the emphasis is now on the use of nontoxic and/or ecofriendly natural materials which do not negatively affect the environment upon application. Natural materials are ecofriendly, biodegradable, cost-effective, and can be employed as precursors in the synthesis and formulation of biodegradable antifouling coatings. Consequently, many researchers are investing time into the synthesis and formulation of natural, ecofriendly antifouling coatings, comprised of higher biofiber, which would perform analogous antifouling like other conventional coatings, thus minimizing the more toxic base polymer proportion. A safe environment is surely the signal of a bright future; hence, cost-effective, biodegradable raw materials result in a long-term attainment of sustainability of these products to replace the expensive conventional ones. This review presents an overview of ecologically friendly, cost-effective, and legally acceptable ways of preventing and mitigating the growth of algae and other marine organisms from settling on the hull of a ship and other static constructions in oilfields.

**Keywords** Biofouling, Ecofriendly, Natural materials, Biodegradable, Coatings, Sustainability

## Introduction

The link between society, technology, and environment is the key determinant of a safe and comfortable society. Technology has indeed contributed to the growth of our society in diverse fields but with untold harmful consequences to the environment. Science and industrialization are now focusing on sustainable future technologies, which incorporate the environmental impact from such technologies. The interaction between humans and their environment has become more of our culture and should not only focus on raw materials but also green, ecofriendly, and biodegradable raw materials. Meeting this development need has focused research into materials that have little or no toxicity, are economical, and are socially accepted. So far, antifouling paints have been extensively formulated and used in the marine industry in many parts of the world. Their application has been critiqued over the years due to the harm they cause to the natural environment.<sup>1,2</sup> The challenge is that most of these products are not degradable after disposal or may take millions of years to be broken down. A bright future calls for the production of green materials and products. Renewable materials and products, usually synthesized from natural products, are environmentally friendly.

Antifouling in this context is basically any strategic application that prevents the attachment of micro- and macroorganisms to manmade surfaces.<sup>3,4</sup> In anticorrosive systems, a physical barrier such as paint is created that keeps out and decelerates the perforation of water and oxygen.<sup>5,6</sup> Over the years, antifouling paints have played diverse and significant roles ranging from prevention of marine growth to acting as a barrier

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against corrosion on metal hulls. Several antifouling and anticorrosion paints have been synthesized over the past few years. Application of these coatings in the 1970s continued for about 20 years until some environmental concerns were raised. Several studies into antifouling paints have proven that biocides are the active ingredients that prevent the settlement, adhesion, and growth of organisms to a painted surface and are arguably the second most hazardous ingredient to tributyltin which is a major component. Antifouling paints leach into the marine environment after application, thereby destroying aquatic life. This resulted in a total ban in early 2008 following a resolution from governments in many countries.<sup>4,7–10</sup> This created a need for the development of ecofriendly conventional coatings which have lower toxicities. Coatings made from environmentally friendly, ecologically acceptable, and readily available precursors have received much attention, as evidenced in several studies.<sup>6,11–16</sup>

Green antifouling and anticorrosion paints are basically made of natural precursors from plants and marine organisms and are mostly of lower toxicity and/or are nontoxic as compared to other booster biocides on the market.<sup>11,17,18</sup> Over the past few years, natural product antifouling and anticorrosion paints have been synthesized by many researchers. According to earlier research,<sup>13</sup> coatings synthesized from plant extracts are responsible for bacterial and fouling inhibition. After 25 days of immersing acrylic plates coated with natural (tannin-based) antifouling paints, the leaching rate of tannin from insoluble matrix paint decreased considerably, reaching a constant value. A green synthesis of polyethylene glycol-based silver nanocomposites and their application in marine environment resulted in a better antifouling protection due to the self-cleaning property.<sup>19</sup> Ethanolic extracts of African bush pepper (*Piper guinensis*) exhibited corrosion inhibition on mild steel.<sup>17,20</sup> Copper-based antifouling paints, which are less toxic than tributyltin in an aquatic environment, have been synthesized and applied in many countries. It was found out that the coatings are only effective against marine fauna. Combating weed growth may require incorporation of herbicides which are is environmental friendly.<sup>7,9,21–23</sup> Although tin-free antifouling paints have proved adequate on passenger ferries in Korea, their contamination in the marine world is high.<sup>7,24,25</sup>

The challenge in replacing conventional coatings with biodegradable types is to synthesize materials that possess structural and functional stability during application and yet effectively prevent growth of microorganisms with rapid biodegradability devoid of any major environmental impacts.<sup>26</sup> Environmentally benign antifouling coatings would not only save the marine industry huge sums of money invested in fuel, maintenance, and labor but would also have significant benefits for our citizens and society.<sup>12,27,28</sup> Local sourcing of raw materials for antifouling paint formulation is currently being explored. Of late, scientists have been investigating the use of agro-wastes as a

source of raw materials (precursors) in synthesizing a number of benign functional products. This development has led to a cost-effective way of introducing diverse products in combating some of the production challenges in oil fields.

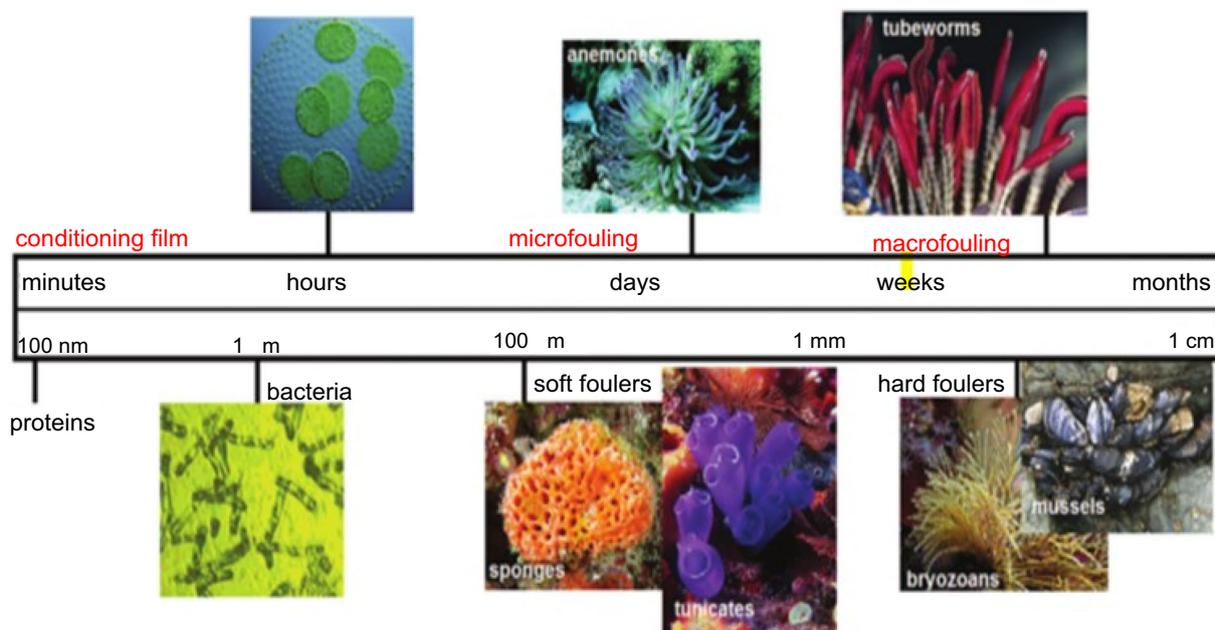
This work aims at providing a holistic overview of the research achievements that are driving the emerging commercially available antifouling paint technologies for both large and small vessels. It also seeks to introduce ecologically friendly, cost-effective, and legally acceptable ways of preventing and mitigating the growth of algae and other marine organisms from settling on the hull of a ship and other static constructions in oilfields.

## Biofouling and corrosion—brief details and problems

In the marine industry, surfaces normally become encrusted with unwanted materials: a phenomenon known as fouling. Marine biofouling therefore is the amassing of unwanted micro- and macroorganisms as well as their metabolites, plants, and animals on structures submerged in seawater.<sup>29–31</sup> These organisms settle not only on submerged structures but on buoys, piers, undercover cables, offshore platforms, heat exchange equipment, and other static constructions.<sup>30,32,33</sup> This problem increases drag resistance which causes an increase in fuel consumption to as much as 30–40%,<sup>11,29,30</sup> thereby increasing the emission of greenhouse gases into the atmosphere, i.e., an environmental concern.<sup>34</sup> Consequently, additional cost is incurred in production and maintenance of ship hulls. Other issues of biofouling include metal corrosion and microbial-induced corrosion due to hydrogen sulfide formed by the bacteria.<sup>33,35</sup> Biofouling results in a corrosive environment (corrosion fouling) which involves a chemical reaction between the metal surface and a reactant. Equipment performance and other installations in seawater are some of the problems related to corrosion.<sup>36</sup> Microbiologically induced corrosion, also known as biocorrosion, is influenced by sulfate-reducing bacteria on the metal surface causing extensive damage to aquatic, maritime, and process industries.<sup>37,38</sup>

### The biofouling process

Normally, when a solid is immersed in the seawater, there is the colonization of a substratum. The attachment of marine biofouling occurs in four main stages, namely formation of primary film, formation of microbial biofilm, development of a more complex community, and attachment of larger invertebrate larvae (Fig. 1).



**Fig. 1: Stages of marine biofouling<sup>41</sup>**

#### *Formation of primary film*

During this stage, there is adsorption of organic and inorganic macromolecules onto the surface/substrate immersed in the seawater (usually proteins, polysaccharides, and nucleic acids). This is a physical interaction which leads to the formation of a nonliving chemical/biochemical film, a process known as conditioning which occurs within seconds to minutes<sup>10</sup> and sets the solid for further attachments.

#### *Formation of microbial biofilm*

The second stage involves bacteria transport/absorption, reversible adhesion, irreversible adhesion, and maturation and dispersion of biofilm. Microbiological cells are adhered onto the surface and immobilized onto the surface via reversible adhesion. The microorganisms are permanently attached during this chemical (irreversible) reaction to the substratum through extracellular polymeric substances.<sup>22,39</sup> Afterward, nutrients in the conditioned film enhance the growth and settlements of larger marine invertebrates and microalgae on the substratum. The entire process takes between minutes to hours.<sup>10,27</sup>

#### *Development of a more complex community*

Within days to weeks after immersion of a new substratum, a colony of multicellular species, microalgae, debris, and sediments develop on the surface leading to a sophisticated community.<sup>27,40</sup>

#### *Attachment of larger invertebrate larvae*

The final stage encompasses the settlement and/or growth of larger invertebrate including marine fungi, protozoa, algal spores, barnacles, and mussels. This stage normally occurs after several days to weeks of immersing a solid in seawater. During this period, the roughness of irregular microbial colonies and the existence of extracellular polymeric substances enhance trapping of more microorganisms.<sup>10</sup>

Persistent growth of these biofouling layers depends on a number of environmental conditions such as salinity, temperature, conductivity, pH, dissolved oxygen content, organic material content, hydrodynamic conditions, current, light, depth, and distance from the shore.<sup>41</sup> Additional factors are the organism and the substrate. Also, the strength of bio-adhesion depends on the organism type, the surface on which the organism is growing, and the separating fluid which are all regulated by electrostatic forces and surface wettability.<sup>29</sup>

#### *Characteristics of biofouling organisms*

Biofouling organisms are diverse, and most of them live along the coasts. Generally, there are two types of processes that drive biofouling as far as microorganisms are concerned, namely micro- and macrofouling. Over 400 biofouling species have been reported worldwide; but generally they have been categorized into two classes: (a) microfouling/biofilm organisms—bacteria and diatoms and (b) macrofouling organisms—algae, barnacles mussels, polychaete worms, bryozoans, and seaweeds.<sup>14</sup> According to the

literature,<sup>29</sup> “micro-fouling consists of microbes like bacteria, unicellular algae, and diatoms; macrofouling contains fouling organisms such as mussels, algae, and barnacles.” Several authors have confirmed the categorization of biofouling organisms. According to Chapman’s group,<sup>42</sup> antifouling classification of biofouling organisms was comprised of three categories: (1) microfoulers comprising bacteria, diatoms, fungi, and microalgae biofilms, (2) soft macrofoulers (macroalgae) and (3) hard macrofoulers—barnacles, mussels, tubeworms, and bryozoans. Others include microorganisms with a hard outer layer, such as encrusting bivalves (oysters, scallops, chamas), encrusting bryozoans, and hard corals, and those with soft exteriors, i.e., sponges, anemones, foliose bryozoans, soft corals, and hydroids.<sup>43,44</sup> These macroorganisms ranging from bacteria to seaweeds and molluscs colonize on submerged surfaces that already have a microbial film present which in turn attracts larger microfoulers. Favorable conditions would result in a permanent attachment, thereby facilitating initial growth, final growth, and dispersion.<sup>29</sup> Table 1 shows characteristics of some macrofouling organisms.

### What are antifouling paints?

Combating biofouling in the twentieth century informed the development of antifouling paints. An interesting feature about antifouling paints is that they combine material properties in ways not found in nature. Antifouling paints, therefore, are coatings, paints, and surface treatments employed on a solid substrate (e.g., ship hull) to control or prevent the attachment of unwanted organisms.<sup>29</sup> The problem researchers found with antifouling paint is the leaching out of biocides into seawater after its application. It has been discovered that biocides leach out into seawater, killing barnacles and other marine organisms, and thus harm the environment.<sup>7,45,46</sup>

Currently, the most widely used commercial antifouling coatings are biocide-based. Table 2 lists categories of commercial antifouling paints currently used in the marine industry.

Contact leaching paints contain biocides or toxicants that are released slowly after application, thereby weakening the protection effect of substrates. Controlled depletions adapt a similar mechanism but

**Table 1: Characteristics of macrofouling organisms<sup>22</sup>**

Groups	Algae (plants)	Invertebrates (animals)							
Subgroups	(a) green (b) brown and (c) red	Hard shell organisms				Grass type organisms	Small bush organisms	Spineless organisms	
Designation	(a) Euteromorpha, Ulva and Cladophora, (b) Ectocarpus, and Fucus, and (c) Ceraminum	Balanus	Barnacles	Molluscs	Fouling bryozoans	Hydroids or bryozoans	Hydroids or bryozoans	Ascidians	Sponges and sea anemones
Example of typical aspect									
Designation	Green algae	Balanus	Calcareous polychaetes	Molluscs	Fouling bryozoans	Bryozoans	Ascidians		
Example of typical aspect									
Short description	Only plants that become attached to immersed surface: (a) closed to surface; (b) at mid depth (c) at depth	Attached trunco-conical or cylindrical crustaceans	Barnacles are Balanus that are fixed to surfaces via a stem	Bivalves containing a spineless animal in their interior	Calcareous incrustations that multiply from a central individual	Organisms that cover surfaces with an open grass or fur	Like bushes of several centimeters and with branches	Constituted by a spineless bag with two tubular openings or starry plates	Spineless and spongy aspect (sponges) and sea anemones

**Table 2: Behavior of biocide-based antifouling system**

Paint type	Components	Biocide?	Lifetime	References
Contact leaching coatings (insoluble matrix)	Chlorinated rubber polymer, copper, and zinc oxides	Yes, decreases over time/slow	12–24 months	26 47
Controlled depletion (soluble matrix)	Synthetic organic resin, copper, arsenic, zinc, mercury, or iron oxides	Yes, short sustained period of time	36 months	37 48
Self-polishing/ablative	Methacrylic polymer, zinc oxide, and insoluble pigments	Yes, sustained period of time	5 years	47

**Table 3: Commercial biocides and their effects on microbiological organisms**

Biocide/booster	Target species	Reason for application	Consequence	References
TBT, TBTO	Microorganisms	Prevention of growth	Toxic effect on the marine food chain	29
TBT	<i>Stenoglossan gastropods</i>	Impairment of development	Masculinization in female leading to population decline	53,55
	<i>Oryzias latipes</i>	Prevention of growth	Delayed developmental rate; tail abnormalities	53
Copper, copper oxide	Crustaceans, algae, barnacles, bivalves	Deterring growth	Toxic effect on marine organisms	29
Irgarol, zinc pyrithione, copper pyrithione	<i>Chroococcus minor</i> , <i>Synechococcus</i> sp.	Prevention of growth	Pollution of environment/water due to high toxicity	56
Chlorothalonil	Crustaceans, molluscs, tunicates	Antifungal activity	Toxic effect on marine organisms	15
Dichlofluanid	<i>Glyptocidaris crenularis</i>	Antifouling activity	Toxic effect (embryotoxicity)	51,52
Diuron	Phytoplankton organisms	Antifoulant herbicide	Highly toxic, impacting the food chain	57
TCMS pyridine	<i>Botryllus schlosseri</i>	Antifoulant	Immunotoxic effects leading to oxidative stress	51
Zineb	<i>Salmo gairdneri</i>	Antifoulant fungicide	Toxic effect (embryotoxicity)	51

TBT tributyltin, TBTO tributyltin oxide, TCMS 2,3,3,6-tetrachloro-4-methylsulfonyl

release the biocides for a short period of time but at a sustained pace. Ablative systems erode and release the biocide over a sustained period of time.<sup>37,47</sup> Biocides in antifouling paints prevent the attachments of organisms on the ship hulls by killing them. This is a threat to the ecosystem, and researchers should focus on substituting antifouling systems containing copper and organotin compounds with additives containing non-toxic biocides that are equally effective as tin and copper-containing biocides.<sup>29</sup>

Antifouling paints have two main components, namely the polymer/binder/resin and the pigment. There is also a vehicle (solvent) in which the main components are dissolved plus other additives (e.g., catalysts, plasticizers) which may be included at low levels.<sup>5,9,49</sup> Ecofriendly antifouling paints are synthe-

sized incorporating local raw materials as pigments and binder. The composition of antifouling paints may vary but not without the two main components.

### ***Biocides employed in antifouling systems***

It is believed that antifouling paints, in their bid to kill or deter attached microorganisms, release biocides or toxins into the aquatic environment. Throughout history, diverse biocides have been employed for this purpose. Until today, biocides such as cuprous oxide (Cu<sub>2</sub>O), tributyltin, tributyltin oxide (TBT/TBTO), and organic additives/booster biocides (e.g., Irgarol 1050<sup>®</sup>, Sea Nine 211<sup>®</sup>, dichlofluanid, chlorothalonil, zinc pyrithione, and Zineb) released from antifouling

systems can have toxic effects on organisms<sup>50,51</sup> at all points in the food chain, including mammals.<sup>29</sup> Several reviews have described and compared the extent of toxicity of biocides.<sup>10,51–53</sup> According to the findings,<sup>54</sup> some booster biocides are more toxic than biocides; in that some applications result in high-level accumulation, resulting in a higher toxic effect on nontarget marine species (Table 3).

The fact that the alternatives to tributyltin are also toxic has generated a keen interest among researchers to study their contamination in the aquatic environment. To secure a congenial atmosphere in the aquatic environment, there is a need to develop nontoxic technologies.<sup>56</sup> Formulation of antifouling paints comprising environmentally safe natural products would not only give us a safe environment but also secure the future of the marine industry.

### Mechanism of ecofriendly antifouling coatings

Antifouling is a chemical reaction between the fluid that reacts and the surface of the component.<sup>4</sup> The mechanism of operation of traditional biobased coatings is based on a dual mode of action, namely nonstick properties and release behavior (inlay) on a biological scale.<sup>58</sup> Pei and Ye<sup>59</sup> hypothesized that antifouling coatings prevent the organisms from adhering in the first place or reduce the adhesion force of those that adhere, so that they can be easily removed by the shear forces generated by the movement of the ship or by the soft mechanical cleaning devices. In general, an antifouling agent or compound should avoid biofilm formation, which is considered a signal for further settlement of invertebrate larvae in the marine environment. The mode of action of antibiofilm activity of microbial strains related with marine macroorganisms

includes antibiotic activity and antiadhesion property and impacts the production of extracellular polymers (EPS), which is necessary for biofilm formation.<sup>60</sup>

The antifouling mechanisms of ecofriendly biobased coatings have been extensively studied. Feng et al.<sup>61</sup> reported that compounds synthesized from indole derivatives exhibited a good antifouling activity with low toxicity against algal cells by a molecular inhibition mechanism. Del Grosso et al. dissolved antioxidants into host coatings and evaluated their antifouling characteristics on mussels in the laboratory. It was found that all the coatings with antioxidants minimized adhesion via a reduction process, thereby discontinuing the crosslinking reactions required to form glues.<sup>62</sup> The above results not only reveal that natural antifouling compounds are ecofriendly, but they also help us to understand the mechanisms of bio-adhesion for marine applications.

Under normal circumstances, the ecofriendly bio-based coatings act through diverse ways and subsequently prevent the formation of biofilms and/or the attachment of microorganisms on a substratum. The strategies given as follows summarize the mode of action of ecofriendly antifouling coatings/paints:

- Inhibition of adhesive production: These compounds inhibit the production or release of adhesives during settlement on a surface.
- Biofilm inhibition: Antifouling compounds inhibit the fixing of microbes on surfaces.
- Quorum blockers: The communication between cells between microbial cells is inhibited.
- Protein expression regulation: Regulators inhibit the sedimentation of contaminating organisms by altering their protein expression.
- Neurotransmission blocking: Blockers interrupt signal transduction during settlement.

**Table 4: Mode of action of antifouling biobased coatings**

Antifouling strategy	Mechanism	Consequence	References
Surface topography	Hydrophobic surface, hence low surface energy leading to low/no adhesion	Detachment of biofoulants	64 65
DOPA-based antifouling materials	Adherence to the substrate surviving harsh conditions	Prevention of protein adsorption and interruption of formation of biofilm	66
Quorum-sensing inhibitory compounds (Quorum quenching)	Inhibition of cell-to-cell transfer and exchange of signals in bacteria	Biofilm mitigation and antifouling	67
Neurotransmission disruption	Release of adhesive cement to interrupt settlement signals/cues in larvae	Inhibitory activity	68
Metabolic-signaling pathways inhibition	Alterations in redox–regulatory mechanisms governing the settlement	Inhibitory/antisettlement effect	69 70

- Surface modification: Surface modifiers block the bacterial binding site and prevent biofilm formation.<sup>60</sup>

Development of antifouling coating mechanisms based on the principles of biofouling has become an effective way of combating the menace. Thus, the biobased coatings upon application oppose the formation of a conditioning film and/or release sitting biofoulants before the secretion and differentiation of natural adhesives occur, thus keeping the adhesion strength to a minimum.<sup>60,63</sup> Table 4 shows a summary of the mode of action of antifouling coatings.

The mechanisms in Table 4 give an insight into how biobased compounds react with the target organism and/or prevent the attachment of biofilms to surfaces in the marine environment.

### Natural products as precursors in antifouling paints

Following the ban on tributyltin and other booster biocides in antifouling paints, there has been an interest in the synthesis of effective and novel ecofriendly compounds from natural resources. Diverse natural products have been successfully employed as starting materials in the development of antifouling paints.<sup>56,71</sup> Notably, ecofriendly natural antifouling agents are found in seaweed,<sup>31,72</sup> bacteria,<sup>16,27</sup> algae,<sup>15,73</sup> corals,<sup>27,74</sup> sponges,<sup>60,75</sup> and terrestrial plants.<sup>10,26,64</sup>

It is believed that tannins found in aquatic and terrestrial plants contain special pigments that exhibit antifouling properties. Thus, they are complex polyphenolic compounds, which have antimicrobial and anticorrosive properties. Application of tannins in antifouling coatings has successfully prevented the attachment of barnacles.<sup>11,27,72,76</sup> The antifouling activity of an active compound from *Andrographis paniculata* plant extracts has been reported. It showed an outstanding antifouling activity against marine bacteria.<sup>27</sup> Normally, fouling inhibition of these pigments is enhanced by complexation with metal ions, which results in less leaching of polyphenol. Several studies have affirmed this with the incorporation of metal ions with tannins.<sup>11,22,71</sup> Hemaida et al.<sup>8</sup> synthesized copper(II) and cobalt complexes of 3-(2-furylidene)hydrazine-5,6-diphenyl-1,2,4-triazine and discovered in vitro antifouling activity against barnacle larvae. After a 12-month immersion test, copper dodecanoate antifouling paint showed similar antifouling inhibition when compared with those with commercial coating.<sup>77</sup>

The use of agricultural by-products or waste in solving environmental problems has become an emerging area in the world of research. This approach could be a strategy of reducing waste through improved design, recycling, and reuse, i.e., turning waste to

wealth. In the formulation of natural ecofriendly antifouling paints, extracts from peanut skin, onion skin, grapes, nuts, vegetables cereals, etc. could be used as sources of phenolic compounds<sup>78</sup> for the synthesis of pigments. Naturally occurring polymers, including plant exudates and extracts such as gum Arabic,<sup>79,80</sup> shellac,<sup>81</sup> rosin,<sup>32</sup> gum tragacanth,<sup>82,83</sup> and galactomannans,<sup>84</sup> are good sources of polymer/binder. Cashew nut shell, also an agro-waste, could be deployed by extracting the liquid from the shell and subsequently using it as a precursor for the synthesis of polymer/resin.<sup>85</sup>

Natural antifoulants work through various physical and chemical control mechanisms, including low drag, low adhesion, wettability, microtexture, grooming, sloughing, and chemical secretion.<sup>29</sup> Natural products as antifoulants coated on substrates could exhibit a low drag flow, thus removing microorganisms from the surface.<sup>58,64</sup> When the adhesion strength of the surface is reduced, attached microorganisms are released easily; this is low adhesion.<sup>29,37</sup> Adhesive interactions (strong or weak) between marine organisms and the substratum are dependent on the wettability of the surface. As noted in reference (14), fouling diatoms cling more securely to a hydrophobic polydimethylsiloxane substratum than to glass. Some marine organisms crave for suitable surfaces of attachment, known as microtextured surfaces. Once they settle on such surfaces, attachment of fouling organisms is prevented or early release of already attached ones is enhanced.<sup>86,87</sup> Examples of such are barnacle, mussels, and shark-skins. *Cypris* larvae, a type of barnacle, are turned away by microtextured surfaces if the features are the same in size.<sup>29</sup> Furthermore, other marine organisms possess brush-like structures for removal of fouling from substrates. This method, known as grooming, is normally employed by decapods, crustaceans, and echinoderms. Pedicellaria, a special structure in echinoderms and bryozoans, is used in grooming macroepibionics.<sup>29</sup> One other physical means of defense against biofouling is sloughing. This involves the periodic shedding of surface tissue or outermost layer of an organism. It has been<sup>88</sup> reported that sloughing is an effective mechanism for getting rid of foulants, although it occurs rarely. Another interesting mechanism is chemical secretion, which involves the secretion of a lubricant which enhances the repulsion of extraneous foulants and also self-cleaning attributes. Retention of the lubricant onto the substrate occurs either by wetting into the configuration of the surface or by grafting to substrates through chemical bonds.<sup>89,90</sup>

Natural product antifouling mechanisms have motivated researchers to develop effective antifouling systems, otherwise known as bioinspired antifouling methods or biomimicry. In confirming the efficiency of this method, they have invented many microtextured surfaces. Some of these techniques include: Sharklet antifouling<sup>TM</sup> microtopographical structures,<sup>29</sup> laser ablation,<sup>42</sup> silver nanoparticles,<sup>91</sup> casting,<sup>92</sup> and

**Table 5: Green antifouling natural products deployed in the twenty-first century**

Antifouling natural compound	Source species	Activity/target species	Toxicity		References
			EC <sub>50</sub> (mg/mL)	LC <sub>50</sub> (mg/mL)	
Zinc tannate	Plant	Bacteria, diatoms, barnacles			13
Isocyanoterpenes	Sponges, Nudibranchs	Larval recruitment	0.046	> 30	75
Alkyl and phenyl formamides	Plant	<i>Balanus amphitrite</i> larvae			75
5,6-Dichloro-1-methylgramine (DCMG)	Plant	Barnacles	0.01	1.0	75
Poly-APSs (linear 3-octylpyridinium polymers)	Marine sponges				75
Zosteric acid	Marine plants	Zebra mussels			75
<i>Agelas tabulata</i>	Colombian Caribbean Sea sponges	biofilm and barnacle			94
<i>Holoturia glaberrima</i>	Sea cucumber	Barnacle larvae			94
Tween 85 (polyethylene glycol sorbitan trioleate)	Plant	Green algae, bryozoans, spirorbis worms, barnacles.	1000	Nontoxic	56
Terpenes( <i>Sphaerococcus coronopifolius</i> )	Marine red algae	Barnacle ( <i>A. amphitrite</i> )	0.23	>100 mg/L	88
Chromanols( <i>Sargassum horneri</i> )	Brown seaweed	Mussel larvae ( <i>Mytilus edulis</i> )	0.11–3.34 µg/mL		88
Thymol	Plant	Barnacle ( <i>Bugula sp.</i> , <i>Ciona intestinalis</i> )	4.41 mM	2.260 mM	12
Eugenol	Plant	Barnacle ( <i>Bugula sp.</i> , <i>Ciona intestinalis</i> )	0.059 mM	0.024 mM	12
Proteolytic enzyme	Bacteria ( <i>Pseudoalteromonas issachenkonii</i> )	Antibacterial ( <i>bryozoans B. neritina</i> , <i>Schizoporella sp.</i> )	0.001 µg/ml	–	69
Kalihinol A & 10-B-formamidokalihinol A	Sponge ( <i>Acanthella cavernosa</i> )	Antifouling ( <i>H. elegans</i> )	(LC <sub>50</sub> /EC <sub>50</sub> = 200)		69
Diketopiperazines and benzene-type secondary metabolites	Bacterium ( <i>Pseudomonas rhizosphaerae</i> )	Antibacterial ( <i>B. neritina</i> , <i>B. amphitrite</i> larvae)	(LC <sub>50</sub> /EC <sub>50</sub> = 17; 22)		69
Poly-APS	Bacteria ( <i>B. Amphitrite</i> )	Antifungal	(EC <sub>50</sub> = 0.27 µg/ml)	(LC <sub>50</sub> /EC <sub>50</sub> = 111)	69
<i>Sarconema furcellatum</i>	Seaweed	Antibacterial			71
Mangrove tannins ( <i>Rhizophora apiculata</i> )	Mangrove plant	Antibacteria ( <i>Bacillus cereu</i> )			11

#### Poly-APSs polymeric 3-alkylpyridinium salts

molds.<sup>93</sup> Several green antifouling natural products have been used around the world. Table 5 gives a summary of these products. For this matter, ecofriendly natural products could be deployed as reliable and motivating precursors in arresting biofouling in oilfields.

#### Biodegradable polymers as matrices for antifouling coatings

As a result of the ban of tributyltin-based or toxic coatings, researchers and the marine industry have developed a keen interest in coatings formulated from less toxic, biodegradable raw materials (pigments and polymers). The global concern for a safe environment due to complete degradation of these materials has increased the demand for biodegradable products. Waste generation and management have become a costly global menace, and researchers have resorted to converting waste to biodegradable polymers. Moreover, biodegradable polymers when incorporated with

pigments with antifouling properties increase the antifouling period.<sup>95</sup> A biodegradable polymer, according to reference 96, is the polymer type that disintegrates by the action of microorganisms (fungi, bacteria, algae) through photodegradation, oxidation, and hydrolysis to yield carbon dioxide, methane, inorganic compounds (biomass), and other natural substances in a specified period of time (Fig. 2). For example, a polymer synthesized from a renewable or biodegradable precursor is a “green polymeric material,” and interestingly, the biodegrading process has become a carbon source in the environment.<sup>96</sup> Figure 2 is a summary of the life cycle of degradable polymer.

Biodegradable polymers are of two sources—natural/renewable and synthetic. Although natural polymers exist in a perfect combination, a detailed comprehension of how they are formed, inconsistencies in biological and chemical composition with respect to geographical and weather conditions, etc. remain to be understood. Synthetic polymers, however, have varied applications in medicine and the chemical

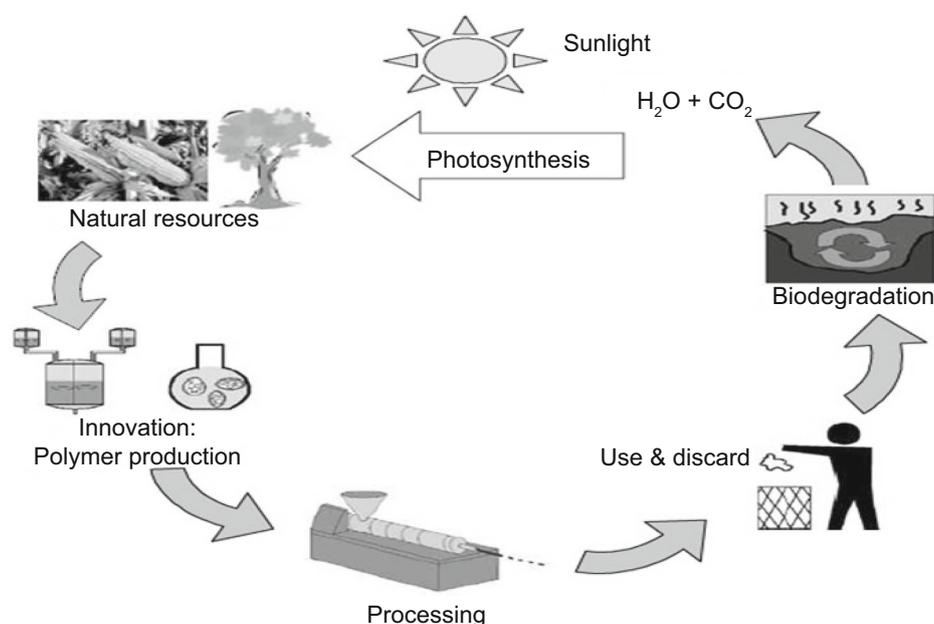


Fig. 2: Life cycle of biodegradable polymers<sup>96</sup>

industries.<sup>97–99</sup> Our focus in this review is on polymers synthesized from naturally occurring biodegradable phenolic compounds such as cashew nut shell liquid (CNSL), lignin, tannins, vegetable oil, or palm oil, which can be used as monomers. One interesting property of these naturally occurring phenols is that they can be used for the synthesis of sustainable polymers with or without modification.<sup>98</sup>

Many natural and synthetic biodegradable polymers have been employed as matrices in antifouling systems. Properties influencing the decomposition of these polymers are chemical composition, physico-mechanical characteristics (density, melting point, tensile strength), and morphology.<sup>100,101</sup> Some researchers<sup>102</sup> synthesized a biodegradable polymer from a blend of poly( $\epsilon$ -caprolactone) and poly(butylene succinate). It was then employed as a marine antibiofouling polymer which exhibited good antifouling ability over a long period of time. In a recent study, a copolymer of 2-methylene-1,3-dioxepene (MDO), tertiary carboxybetaine ester (TCE), and 7-methacryloyloxy-4-methylcoumarin (MAMC) was prepared and found not only with strong adhesion to the substrate, but also with a good inhibition of bacteria adhesion.<sup>95</sup> As we appreciate the fact that biodegradable polymers are promising antibiofouling matrices, the demanding situation regarding their stability and time span for the degradation should not be relegated to the background.<sup>96,103</sup>

### Biodegradable polymers from cashew nut shell liquid

The cashew nut shell liquid (CNSL), an alkyl phenolic oil, is a reddish-brown viscous liquid from the cashew

nut shell, a by-product obtained from the cashew nut industry.<sup>104–106</sup> The cashew nut shell, an agro-waste, has now become a raw material for polymer synthesis<sup>105</sup> and a source of petrochemical phenolic compounds,<sup>107,108</sup> among others. The CNSL has the following components based on the method of extraction: anacardic acid (71.7%), cardanol (4.7%), cardol (18.7%), methylcardol (2.7%), and unnamed polymeric materials (2.2%) as shown in Fig. 3.<sup>109</sup> The side chain, R, comprises 15 carbon atoms in the meta-position from the hydroxyl groups.<sup>106</sup>

### Chemistry of CNSL

The chemistry is dependent on the presence of its reactive operational aromaticity, phenolic hydroxyl, and unsaturated alkyl phenol (side chain), R,<sup>108</sup> making it suitable for polymerization into resins. Consequently, modified CNSL has diverse industrial applications,<sup>110</sup> some of which are: plasticizers,<sup>98</sup> adhesives,<sup>105</sup> fuel additives,<sup>111</sup> surfactants,<sup>112</sup> resin additives,<sup>98,105,113,114</sup> friction materials as well as flame retardants,<sup>108</sup> and as intermediates or precursors for other chemical synthesis.<sup>105</sup> Recent reviews have captured the varied applications of CNSL.<sup>109,110,115,116</sup> CNSL is highly stable at room temperature due to the presence of strongly polar aromatic group.<sup>98</sup> Storage at high temperature will lead to polymerization.<sup>105</sup>

Extraction of the liquid from the cashew nut shell could be done by techniques such as hot oil processes,<sup>112,117</sup> solvent extraction,<sup>109</sup> mechanical processes,<sup>98</sup> vacuum distillation,<sup>112,118</sup> or supercritical fluids.<sup>105</sup> These techniques have been employed successfully in many research studies.<sup>104,105,119,120</sup> Car-

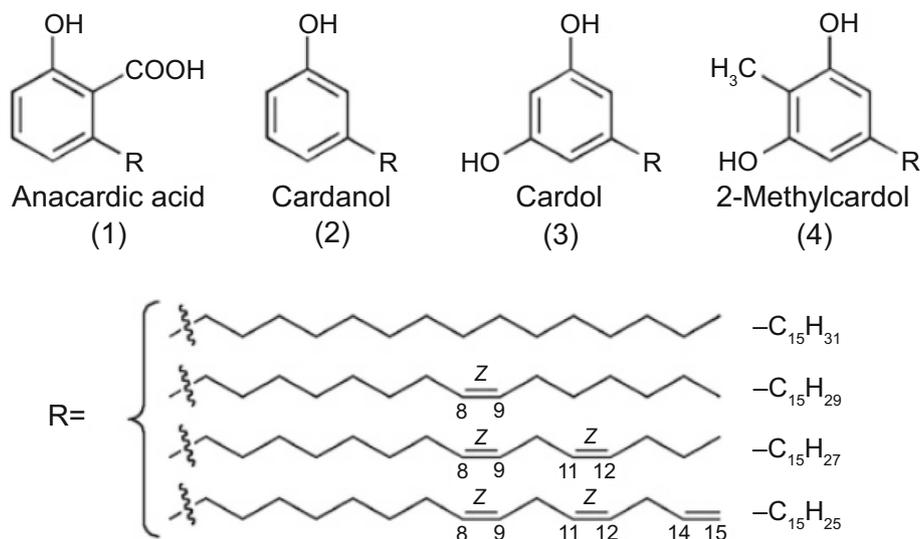


Fig. 3: Components in CNSL: (1) anacardic acid, (2) cardanol, (3) cardol, and (4) methylcardol<sup>106</sup>

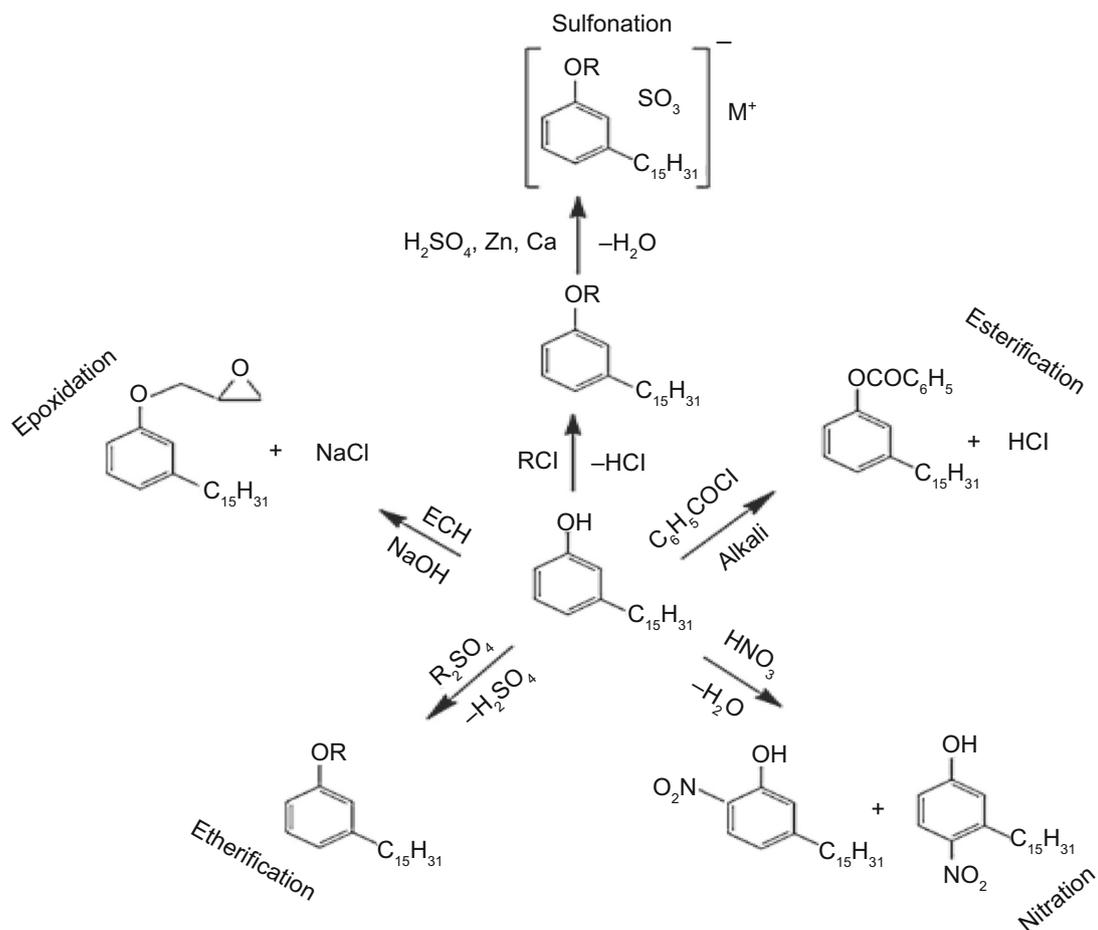


Fig. 4: Possible reactions of CNSL and their derivatives<sup>105</sup>

danol (52–60%) is a major component of a heat-extracted CNSL with cardol (10%) and polymeric materials (30%). Technical-grade CNSL (without polymeric material) has about 78% cardanol, 8% cardol, and 0–2% polymeric material.<sup>98,106,110</sup>

Structural and functional group properties of cardanol make it highly reactive and, hence, undergo reactions such as sulfonation,<sup>115,121,122</sup> nitration,<sup>105</sup> esterification,<sup>112</sup> halogenation,<sup>105,121</sup> etherification,<sup>123</sup> and epoxidation.<sup>107,124</sup> Figure 4 shows a summary of possible reactions of CNSL and their derivatives.

### *CNSL resins and polymers*

A number of resins and polymeric derivatives can be synthesized from CNSL for diverse applications.<sup>106</sup> This is due to CNSL's phenolic construction and lengthy hydrocarbon chain with carbon–carbon double bonds which affords additional reaction sites. Reactions such as polycondensation with electron deficient species (e.g., formaldehyde) or polymerization of the reactive side chain with acid and/or base catalysts, followed by a linkage of a number of monomers, could yield CNSL polymers/resin.<sup>112</sup> The condensation reaction with formaldehyde is commonly employed. CNSL resins such as epoxy, alkyd, polyurethane, phenolic resin, vinyl, and acrylic can be put together for diverse modified coatings.<sup>105</sup> Various resins obtained from CNSL can be used in the following: coating of surfaces,<sup>105</sup> rubber or plastic modifiers,<sup>115,122</sup> brake lining or friction materials,<sup>112,125</sup> waterproof materials,<sup>112,121</sup> flame retardants,<sup>112</sup> ion-exchange resins,<sup>126,127</sup> and anticorrosive paints.<sup>118</sup> These novel biobased resins exhibit similar and periodically better chemical, mechanical, and thermal properties than other commercially available petro-based products.<sup>110</sup> Synthesis and application of resin from CNSL have been reported in many research papers and reviews. One of the earliest was the preparation of varnishes from cardanol–formaldehyde resins, with equally good chemical and mechanical properties as other commercial precursors.<sup>115,128</sup> Researchers<sup>129</sup> successfully synthesized CNSL-resin via a base-catalyzed formaldehyde reaction. The resin was coated on the surface of wooden samples, and it was found that the sample with the thickest CNSL-resin had the lowest wetness and water absorption capacity. Table 6 is a summary of some CNSL resins and their applications.

### *Biodegradable polymers from other sources*

Renewable naturally occurring phenolic compound precursors such as vegetable oil, lignin, and tannin matrix systems can also be employed for bio-composite applications. Over the years, several classes of phenolic resins have been developed from these matrices.<sup>98</sup> The reasons are not far-fetched: availability, affordability, and biodegradability.

Vegetable oil, which consists of monosaturated and polysaturated long-chain fatty acids, can be converted into vegetable oil-based polymer via polymerization reaction.<sup>110</sup> Over the past few years, polymerization has been a common method for synthesizing vegetable oil-based polymers.<sup>137,138</sup> Copolymerization of these resins with other materials yields products with comparable or better chemical and mechanical properties. Glass fibers (45%) were augmented with cationic copolymers of corn oil (COR), styrene (ST), and divinylbenzene (DVB). In this application, it was discovered that there was an increase in Young's modulus, tensile strength, crosslinking density, and other mechanical properties of the composites.<sup>139</sup> Earlier work<sup>140</sup> fortified free radical resins consisting of: 50 wt% conjugated linseed oil, aliquots of DVB, and n-butyl methacrylate (BMA) with 20–80 wt% of corn stover. In this work, varying proportions of increasing corn stover and decreasing length of fiber boosted the overall mechanical properties with a corresponding decrease in thermal sturdiness. The reaction of Nahar seed oil monoglyceride with phthalic and/or maleic anhydride yielded polyesters with acceptable qualities for application as surface coatings and resin for composites.<sup>141,142</sup>

The most abundant natural phenolic polymer, lignin, is a complex class of organic molecules which are linked together with ether and limited carbon–carbon molecules in a spiral construction.<sup>143</sup> They are primarily found in terrestrial plants, although some aquatic plants may be made up of lignin. Consequently, hardwood, softwood, fiber, grasses, and many plant materials contain varied compositions of lignin. They are alternatives to nonrenewable petroleum feedstocks in that they basically possess an alkyl–aryl–ether system of links, straight chain and aromatic hydroxyl groups, and low polydispersity. Major properties that determine the reactivity of lignin are attributed to the presence of hydroxyl, methoxy, carbonyl, and carboxyl functional groups. Reactions of lignin do occur under vigorous conditions, a property arising from the chemical stability of the polyphenolic group.<sup>144</sup> Lignin extracts from composite materials have proven to be excellent coating materials as per earlier reports.<sup>145</sup>

The literature<sup>73</sup> defined tannins as “inexpensive and ubiquitous natural polymers, polyphenolic secondary metabolites of higher plants mainly present in soft tissues (sheets, needles or bark).” They are unrefined, benign, biodegradable compounds containing more than one phenolic hydroxyl group. Sources of tannin include: diverse plant species,<sup>146</sup> mangrove bark,<sup>22</sup> wine wastes and chestnut peels,<sup>73</sup> and forest exploitation wastes.<sup>98</sup> They are divided into two main categories, namely hydrolyzable tannins (gallic acids easily hydrolyzed in acidic media) and condensable tannins, which are polymeric flavonoids.<sup>73</sup> Tannins have various applications including their use as: corrosion inhibitors in aqueous media,<sup>147</sup> constituents of rust convertors,<sup>146</sup> pigments in paint coatings,<sup>13</sup> natural antioxidants,<sup>148</sup>

**Table 6: Summary of some CNSL resins and their applications**

Resin	Composition	Application	Properties	References
Tactix-based vinyl ester (VE) prepolymer	Tactix 756, cardanol, methacrylic acid	Biobased reactive diluents	Good thermal stability (300°C); $T_g$ values 100–130°C; good binders	130
Cardanol Formaldehyde (CF) resol resin	Formaldehyde, cardanol, ammonia	Reinforcing fillers in natural rubber (NR)	Mechanical properties and abrasion resistance enhanced	119
Cardanol Formaldehyde (CF) novalak resin	Formaldehyde, cardanol, sulfuric acid			
Thermosetting resin	Cardanol, substituted aromatic compound, furfural, hydrochloric acid	Selective adsorption of metal ions	Higher degradation temperature due to high stability of resins	125
Diazotized <i>p</i> -chloroaniline cardanol-furfural resin (DCFUR)	<i>p</i> -chloroaniline, cardanol, sodium nitrite, hydrochloric acid, furfural, sulfuric acid, dil. sodium hydroxide	Thermal and kinetic studies	Exhibited higher activation energy than the copolymers.	108
Diazotized <i>p</i> -chloroaniline cardanol-furfural organic compound resin (DCFUR-R1/R2/R3/R4)	<i>p</i> -chloroaniline, cardanol, sodium nitrite, hydrochloric acid, furfural, urea/ethylene glycol/resorcinol/o-hydroxy benzoic acid, sulfuric acid	Thermal and kinetic studies	Derivatives of aromatic co-monomer resins exhibited high activation energy, higher percentage of crystallinity and lower thermal stability than the aliphatic derivatives	108
CNSL-based polyol	Commercial CNSL-based diglycidal ether (NC-514), 2° amines	As a binder in formulation of polyurethane coatings	Coatings show good mechanical performance, excellent chemical resistance, good thermal stability and anticorrosive performance	118
Epoxy CNSL prepolymer (ECNP)	ECNP, diethylenetriamine (DETA)	Antimicrobial material	Good antimicrobial activity against <i>E. coli</i> and <i>S. aureus</i> bacteria.	131
Cardanol-based novalac resins (Nov-1, Nov-2)	Cardanol, oxalic acid, paranti-formaldehyde	Curing agents	Improvement in mechanical properties of cured resin, $T_g$ values increased ( $T_g = 10$ )	132
Novalac resin type	CNSL, petrochemical phenol, formaldehyde, oxalic acid	Curing agent by plasma treatment and hexamethylenetetramine (HMTA)	Thermal stability of HMTA-cured resin higher	104
Biobased cardanol (NC-514)	Epoxidized cardanol, commercial amine	Synthesis of epoxy networks	Good mechanical and thermal properties	107
Epoxy-cardanol resin	Epichlorohydrin, bisphenol-A, cardanol	Anticorrosion paints	Better mechanical and chemical properties, better binder media for formulation of anticorrosion paints	133
Phenalkamine-epoxy resin	Phenalkamine (from cardanol, formaldehyde, polyamines)	Curing of epoxy resin	Good adhesion on metal surface, good mechanical and thermal properties	134
Epoxide containing polycardanol	Polycardanol, hydrogen peroxide, organic acid	Curing agent	Improved hardness (9H) and good mechanical properties	135
Tetrafunctional cardanol epoxy resin	Cardanol, epoxy resin	Curing agent	Improved chemical resistance and mechanical properties	136

tanning agents in the leather industry,<sup>98</sup> and adhesives and polymers.<sup>147,149</sup>

### Biodegradable antifouling paints as alternatives to TBT coatings

The use of TBT-based antifouling paints in the twentieth century was globally patronized until its ban in 2003 due to its effect on aquatic organisms. This

consensus was reached globally after reports on higher concentrations of TBT in the coastal areas of many countries reached the International Maritime Organization in the early 1990s.<sup>65</sup> The formulation, use, and degradation of TBT antifouling paints have been scrutinized from an environmental point of view, after their global approval as the most efficacious antifouling paints ever produced.<sup>60,150</sup> This concern was attributed to the lifespan of TBT in the aquatic environment after its disposal, and the fact that it was exerting a negative

influence on nontarget creatures. Studies and reviews have confirmed that even low levels of TBT kill or weaken other species in the aquatic system.<sup>3,51,53,150–152</sup>

Antifouling paints are primarily made up of pigments and matrix polymer systems. A biodegradable antifouling paint should be composed of a biodegradable pigment and a biodegradable polymer or binder, among others. Such a system would be categorized as “completely biodegradable” since they are open to microbial and environmental mortification upon disposal without any negative environmental consequences.<sup>96,153</sup> Marine industry players would appreciate the potential in biodegradable antifouling paints if they can deliver the same or better performance as conventional antifouling systems.<sup>150,154</sup> Moreover, the biocides used in antifouling systems should have broad spectrum activity, low or no mammalian toxicity, and no bioaccumulation in the food chain.<sup>155</sup>

The formulation of antifouling paints with natural or biodegradable pigments and polymer composites has been reported. Researchers<sup>56</sup> have formulated ecofriendly antifouling paints using biodegradable polymer and lower toxicity substances. When these precursors or substances were deployed in the biodegradable polymer, they provided antifouling protection against biofouling for several months. Also, reference (156) reported the preparation of novel antifouling paints made up of biodegradable polymer, which, when incorporated with butenolide, exhibited antifouling properties for over 3 months. Biodegradability of the polymer in seawater was enhanced in the presence of marine organisms. Natural resin (rosin) was incorporated into the system, and the resultant effect was an increased release of the butenolide. The general concern has to do with novel, low-cost, and biodegradable natural raw materials with effective or excellent antifouling properties in the formulation of antifouling coatings for combating marine biofouling without impacting nontargeted organisms.

### **Sustainable biobased products: new materials for a new economy**

Sustainable chemistry (green chemistry) encompasses the use of less toxic precursors to formulate new products and processes without compromising the environment.<sup>157</sup> With sustainable development, our focus covers not only current generations, but also puts measures in place to ensure the concerns of posterity are not compromised.<sup>158</sup> Development today that does not jeopardize future development is the goal of all processes, ecosystems, communities, companies, and countries. The globe is now conscious of what is emitted into the environment and hence the inception of environmental legislation. Therefore, combating environmental problems should not only consider the ecofriendly starting materials but also the conse-

quences of application of the product. Furthermore, there is the need to formulate “green antifouling coatings” using sustainable and environmentally friendly raw materials, with no or less dangerous influence on the environment. Going forward, in assessing the sustainability of a novel antifouling coating as compared to TBT-based coatings, the technology development time gap between TBT-based coatings and biobased antifouling paints should be considered.

Cost-effective biodegradable precursors or raw materials which would inform a long-term attainment of sustainability were recommended to replace the expensive conventional ones. Indeed, green antifouling paints with over 50% cheap natural raw materials would not only be cost-effective, but also possess other environmental advantages, thus economic and environmental sustainability. A firm foundation for developing novel and/or benign and emerging biobased antifouling coatings will depend on a good comprehension of natural pigments, polymers, and their basic formulation concepts.

Natural biobased antifouling coatings are likely to be environmentally superior to conventional TBT-based coatings. The reasons are not far-fetched: (a) Natural biobased antifouling coatings result in lower or no environmental impact; (b) natural, ecofriendly antifouling coatings, comprising higher biofiber, perform analogous antifouling like other conventional coatings, thus minimizing more toxic base polymer proportion; (c) synthesis, formulation, and application of natural, ecofriendly antifouling coatings is a new, cost-saving solution to an old problem.

### **Conclusions and future perspectives**

To date, the marine industry is plagued with an old problem of biofouling. Several attempts have been made to solve this problem with new perspectives and concepts since it became a global concern in the nineteenth century. It has become necessary to develop environmentally benign antifouling coatings are developed as a means of finding a sustainable solution to this problem. Many researchers have recommended that green chemistry concepts are developed to highlight the use of biodegradable, natural precursors and other constituents in the development of new chemical compounds.

Contemporary environmental considerations have also justified the need to develop novel materials, policies, and procedures that will improve the quality of life, health, safety, and the environment. The inclusion of bio resources into these materials, policies, and procedures of today will meet these considerations and lessen extra reliance on TBT-based antifouling paints. Going forward, biodegradable and ecofriendly materials would become the best resort, with varied applications in the marine industry, because the pro-

duction, use, and removal of these materials are not harmful to the environment. Natural materials are ecofriendly, biodegradable, cost-effective, and can be employed as precursors in the synthesis and formulation of biodegradable antifouling coatings. These products then can become an unrivaled portfolio of effective products to replace nonbiodegradable materials on the market—thus providing a means of introducing sustainable and safe biobased products into the market.

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