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Renewable Resources in Corrosion Resistance

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1. Introduction

Corrosion of metals or alloys occurs due to chemical or electrochemical reactions with their environment, which often results in drastic deterioration in the properties of metals or materials comprising thereof. Corrosion takes place on a steel surface, due to the development of anodic and cathodic areas, through oxidation and reduction reactions, forming of oxides of metals alloys. There are several corrosion causing agents or “corrodents” such as soot, sulphate salts, chloride ions, temperature, salinity, pH, dissolved gases, humidity, bacteria, sand, gravels, stones, mechanical stresses and also several protection methods employed for corrosion resistance such as the application of alloys, composites, inhibitors, cathodic and anodic protection, protective linings and coatings (Bierwagen, 1996; Ghali et al., 2007; Raja & Sethuraman, 2008; Sorensen et al., 2009). Notwithstanding, corrosion has become a gigantic problem today for every nation. The colossal detrimental impact of corrosion on the economy of a country can be manifested in billions of dollars spent annually to combat or control it.

In the past two decades, research and development efforts in the field have undergone vast changes globally, because of the everyday growing consumer expectations of good quality and performance coupled with lower cost, enormous hikes in the prices of petro-based chemicals out of fear of depleting stocks by the end of twenty first century, serious concerns pertaining to energy consumption and environmental contamination, regulations such as Clean Air Act Amendments [CAAA, 1990], and above all the “cost of corrosion”. These predictions, regulations and innovations have posed constant threats and challenges for anticorrosion industry forcing to change its gears worldwide. The corrosion chemists, researchers and engineers in industry and academics are actively engaged to explore and formulate new strategies to meet the mandatory limits of performance, cost and legislations. The ultimate solution is foreseen through the “excessive utilisation of our naturally available resources” primarily, to cut off the escalating prices of raw materials, to formulate environmentally benign materials, to expedite their post-service degradation, and to add value to a waste material. Consequently “environmentally friendly” or "green" coating technologies (waterborne [WB], powder, high-solid, hyperbranched and radiation-curable) have evolved, with special emphasis being laid on the excessive utilization of naturally available renewable resources thriving on acres of our agricultural lands. These may be formulated as corrosion resistant alloys, corrosion resistant composites, corrosion resistant pigments, corrosion resistant coatings, paints and corrosion inhibitors. Renewable resources provide cheaper and abundant biological feedstocks with numerous advantages, such as
cost effectiveness, low toxicity, inherent biodegradability and environment friendliness. They yield versatile materials through chemical transformations with plethora of applications, particularly in corrosion resistance against various corrosives [Fig. 1]. (Derksen et al., 1995, 1996; Gandini & Belgacem, 2002; Metzgar, 2001; Weiss, 1997; Ahmad, 2007).

Fig. 1. Renewable resource based materials provide corrosion resistance against various corrosives.

2. Renewable resources in corrosion resistance

Corrosion generally occurs when mild steel comes in contact with oxygen and water. The presence of anodic and cathodic sites on steel surface and their reaction with water and oxygen transforms metal (iron) atom to ions, finally through a series of chemical reactions, hydrated ferric oxide forms (iron) rust. Another anaerobic (without oxygen) corrosion, micro-biological corrosion may occur if conditions favor the growth and multiplication of microbes, i.e., bacteria and fungi (Witte et al., 2006). The preliminary steps to reduce, combat or completely eradicate corrosion require the elimination or suppression of such chemical reactions by the use of corrosion inhibitors, pigments, cathodic protection, coatings and others, providing barrier properties, adhesion between substrate and coatings, corrosion reducing activity and overall an active anticorrosion effect. The effectiveness of coatings as potential anticorrosion agents depends upon their type, the type of substrate, corrosives to which these are exposed and others. For efficient service, coatings should bear very good adhesion to the substrate resulting in low permeability (to oxygen, water) and good “wet” adhesion. The renewable resources or natural biopolymers such as lignin, starch, cellulose, cashewnut shell liquid, rice husk, sucrose, caffeic acid, lactic acid, tannic acid, furan, proteins, glycerol, and vegetable oils contain hydroxyls, aldehydes, ketones, carboxyls, double bonds, ester, ether and other functional groups. These functional groups impart good adhesion and corrosion resistance performance to the substrate. Also, the performance can be further improved by chemical transformations, use of modifiers (inorganic reinforcements, nanomaterials) and other methods.

The proceeding sections provide a brief description of some natural biopolymers and their utilisation in corrosion resistance.
2.1 Cellulose

Cellulose is the largest biopolymer obtained by photosynthesis. It is a crystalline polysaccharide. It is a linear long chain polymer of $\beta(1\rightarrow4)$ linked D-glucose units (5,000-10,000), that condense through $\beta(1\rightarrow4)$-glycosidic bonds (Fig. 2). It is mainly obtained from wood pulp and other plants but can also be extracted from algae and bacteria for industrial purposes. Cellulose and their derivatives are used in paper, paperboard, card stock, textiles, cellophane, smokeless gunpowder, pharmaceuticals, biofuels, foods, sponges, cosmetics, reinforced plastics, water-soluble adhesives, binders and coatings.

![Fig. 2. Structure of cellulose.](image)

### Use in corrosion resistance

Cellulose is crystalline in nature. In desirable quantities, it may be used as a modifier rendering toughness in fragile coatings. The primary hydroxyl groups present in the chain may further facilitate adhesion to the substrate. Hydrophobically modified hydroxyethyl cellulose used in WB coatings and paints provided good gloss, levelling and sag resistance (Kroon 1993). Films obtained from regenerated cellulose (from cotton linter) by coating Castor oil polyurethane/benzyl konjac glucomannan semi-interpenetrating polymer networks were water resistant and biodegradable (Lu et al., 2004). Ethyl cellulose based aqueous dispersions and solvent based films were plasticized with $n$-alkenyl succinic anhydrides -2-octenyl succinic anhydride (OSA) and 2-dodecen-1-ylsuccinic anhydride to overcome the brittleness of cellulose films (Tarvainen et al., 2003). Films obtained showed excellent mechanical properties, low permeability, and good flexibility. Amoxicillin doped cellulose acetate films showed good corrosion resistance on AA2024-T3 substrate (Tamborim et al., 2011). Films doped with 2000ppm of the drug showed good anti-corrosion behavior as observed by Electrochemical Impedance Spectroscopy [EIS] results. These films showed lower current densities up to 3 days of immersion under anodic polarization. Scanning Vibrating Electrode Technique [SVET] results were found to be in close agreement with EIS and polarization results, also informing about the defects in coating. The results also showed a decrease of the electrochemical activity in the doped cellulose acetate films, relative to their undoped counterparts. Liu et al prepared cellulose acetate phthalate free films with diethyl phthalate/triethyl citrate as the plasticizer by spray method under heat-only (50°C for 24 h) and heat-humidity curing (50°C/75% RH for 24 h) conditions (Liu & Williams III, 2002). The latter (despite retaining higher content of plasticizer due to suppressed evaporation) provided increased mechanical strength and decreased water vapor permeability of the films. Triethyl acetate films showed increased % elongation, decreased tensile strength and elastic modulus relative to diethyl phthalate films, however, the latter showed low permeability.
2.2 Lignin

Lignin is the second most common organic polymer. About 50 million tons of lignin is produced worldwide annually as residue in paper production processes. It consists of methoxylated phenyl propane structures. The biosynthesis of complex structure of lignin is thought to involve the polymerization of three primary monomers, monolignols: p-coumaryl, coniferyl, and sinapyl alcohols (Figure 3), which are linked together by different ether and carbon-carbon bonds forming a three-dimensional network. The monolignols are present in the form of p-hydroxylphenol, guaiacyl and syringyl residues in lignin structure. Lignin is non-toxic, inexpensive and abundantly available (Sena-Martins et al.; 2008). It is hydrophobic, smaller in size and forms stable mixtures (Park et al.; 2008). It is used in dye dispersants, dispersants for crop protection products, to produce low molecular weight chemicals like dimethyl sulphoxide. It is also used as filler in inks, varnishes and paints (Belgacem et al., 2003) and as a dispersing agent in concrete, as binders for wood composites, chelating agents, for treating porous materials, in coatings and paintings (Stewart, 2008; Park et al., 2008; Mulder et al., 2011).

Use in corrosion resistance

Lignin contains hydroxyl, carboxyl, benzyl alcohol, methoxyl, aldehydic and phenolic functional groups. It adsorbs on the metal surface and is capable of forming a barrier between the metal and corrodents (Altwaiq et al., 2011). Extracted alkali lignin as investigated by Altwaq et al has shown corrosion inhibition behavior in the corrosion of different alloys immersed in HCl solutions. This was investigated by weight loss analysis, surface analysis on the corroded metals by scanning electron microscope (SEM), and micro-beam X-ray fluorescence (μ-XRF), inductively coupled plasma–optical emission spectroscope (ICPOES) and others (Altwaq et al., 2011). Lignin doped conductive polymers [polyaniline-PANI] are used in corrosion protection. Sulphonated kraft lignin conductive polymers are more dispersible in water and other solvents. Electrochemical analysis revealed that Ligno-PANI is an efficient corrosion inhibitor. A very low loading (1-2%) of the inhibitor brings much (10-20 fold) reduction in corrosion, presumably by the formation of a passive oxide layer (Xu, 2002). Corrosion behavior of Ligno-sulphonate doped PANI coatings on mild steel in neutral saline conditions (salt spray/immersion) was investigated by Sakhri and coworkers by EIS, potentiodynamic measurements [PD] and visual observations. The coatings with highest PANI performed well both in the salt spray and immersion tests (Sakhri et al., 2011).

2.3 Tannic acid [TA]

TA is commercial form of Tannin. It is a polymer of gallic acid molecules and glucose. The pure form of TA is a light yellowish and amorphous powder. It is contained in roots, husks, galls and leaves of plants. It is also found in bark of trees (oak, walnut, pine, mahagony), in tea, nettle, wood, berries and horse chestnuts. TA has astringent, antibacterial, antiviral and antienzymatic properties. TA is used in tanning of leather, staining wood, a mordant for cellulose fibres, dyeing cloth, disinfectant cleansers, pharmaceutical industry, food additives, metal corrosion resistance as rust convertor, slime treatment of petroleum drilling, paper, ink production and oil industry. The structure of TA is shown in Fig. 4.
Use in corrosion resistance

TA has been extensively utilized in anticorrosion methods as investigated by infrared, Mössbauer, Raman spectroscopies, EIS, PD and others (Morcillo et al., 1992; Nasrazadani, 1997; Jaén et al., 2003, 2011; Al-Mayouf, 1999; Ocampo et al., 2004; Galván Jr et al., 1992; Chen et al., 2009). TA is used as conversion coating to prevent corrosion of iron, zinc, copper and their alloys. The (ortho) hydroxyls react with metals forming metal-tannic acid complexes, which protect metal from rusting (Chen et al., 2008). TA based conversion coating can be formed on AZ91D magnesium alloy (Sudagar et al., 2011). Chen et al. proposed the formation of organic chromium-free conversion coating on AZ91D.
magnesium alloy obtained from solution containing TA and ammonium metavanadate. The corrosion resistance performance of these chromate free coatings was compared with the traditional chromate conversion coating. PD revealed that the said coating showed more positive potential and obvious lower corrosion current density relative to traditional chromate conversion coating; salt spray tests also showed the improved anticorrosive behavior of the former (Chen et al., 2008). In another report, mildly rusted steel surface were pretreated with TA based rust converters followed by the application of a Zn rich coating. The rust converters react with iron and rust to form a sparingly soluble iron tannate film on metal surface, which renders low pH adjacent to corroding interface by the diffusion of the unreacted acidic constituents of the rust converter in alkaline concrete solution. The low pH facilitates the formation of passive hydrozincite layer within 50h of exposure to chloride contaminated concrete pore solution relative to 150h for normal zinc coating without rust converter. The mechanism of film formation was investigated by EIS, Potential-time studies, Raman Spectroscopy, SEM, energy dispersive X-ray analysis [EDXA] and X-ray diffraction studies [XRD] (Singh & Yadav, 2008). Methacrylic derivatives of TA [m-digallic acid], toluylene 2,4-diisocyanate [TDI] and 2-hydroxyethyl methacrylate [HEMA] formed UV curable urethane coatings (in molar ratio 1:3:3). The formation occurred by the coupling reaction between TA and TDI followed by HEMA addition (Grassino et al., 1999).

Fig. 4. Structure of tannic acid.
2.4 Chitosan [CHTO]

Chitin and CHTO are polysaccharides. They are chemically similar to cellulose, differing only by the presence or absence of nitrogen. CHTO is deacetylated chitin (degree of deacetylation of chitin ~50%), obtained from the outer shell of crustaceans (crabs, lobsters, krills and shrimps). CHTO primarily consists of β linked 2-amino-2-deoxy-β-D-glucopyranose units. CHTO shows biocompatibility, low toxicity, biodegradability, osteoconductivity and antimicrobial properties (Fig. 5). CHTO is a cationic polyelectrolyte. CHTO forms complexes with metal ions and can gel with polyanions. It contains reactive hydroxyl and amine groups that undergo chemical transformations producing chemical derivatives with plethora of applications. It is used in cosmetics, as preservative, antioxidant, antimicrobial agent and coatings in food, fabrics, drugs, artificial organs and fungicides (Rinaudo, 2006; Bautista-Baños et al., 2006), as metal adsorbants for the removal of metals (mercury, copper, chromium, silver, iron, cadmium) from ground and waste water (Lundvall et al., 2007).

![Fig. 5. Structure of chitin and chitosan.](image)

**Use in corrosion resistance**

CHTO dissolved aqueous solution forms tough and flexible films. CHTO is utilized as anticorrosion material, however, it absorbs moisture from atmosphere, which penetrates the film easily and deteriorates its performance (Lundvall et al., 2007; Sugama & Cook, 2000). As
a remedial approach to employ CHTO as an environmentally green water-based coating system for aluminum (Al) substrates, Sugama et al modified CHTO with polyacid electrolyte, poly(itaconic acid) [PI], containing two negatively charged carboxylic acid groups, with CHTO: PI ratio of 100:0, 90:10, 80:20, 70:30, 50:50, 30:70, and 0:100, by weight, applied on 6061-T6 aluminum (Al) sheet by a simple dip-withdrawing method. –COOH and –NH$_2$ groups of PI and CHTO, respectively, formed (hydrophoebic) secondary amide linkages, which lead to the grafting of PI on CHTO backbone, and at higher temperature crosslinking occurred. Increased “grafts” and “crosslinks” formed coatings that were less susceptible to moisture and prevented the penetration of corrosive electrolyte species, providing good corrosion protection to the substrate. CHTO:PI ratio 80:20 was found to be an ideal composition for efficient corrosion protection (Sugama & Cook, 2000). Sugama et al also modified CHTO with corn-starch derived dextrin and applied on Al-6063. CHTO:dextrin ratio 70/30 provided low moisture resistance and could withstand salt spray test up to 720 h (Sugama & Milian-Jimenez, 1999). CHTO shows high hydrophilicity and poor adhesive strength with Al 2024 T3 alloy. CHTO was modified with epoxy functional silanes [2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane and (3-Glycidoxypropyl)-trimethoxysilane] as coupling agents and vanadates as corrosion inhibitor (Kumar & Buchheit, 2006). The derivatives of CHTO such as acetylthiourea CHTO, carboxymethyl CHTO are used as efficient corrosion inhibitors as assessed by PD, EIS, SEM, weight loss measurements, conductometric titrations and other studies (Fekry & Mohamed, 2010; Cheng et al., 2007). Hydroxyapatite-CHTO composite coatings on AZ31 Mg alloy by aerosol deposition produce well adherent, corrosion resistant biocompatible coatings (Hahn et al., 2011)

2.5 Starch

As a carbohydrate consisting of a number of glucose units joined together by glycosidic bonds, starch is a low cost, renewable and biodegradable natural polymer. It consists of two types of molecules, amylose (linear) and amyllopectin (branched) (Fig. 6). It is the energy store of plants (Sugama & DuVall, 1996). Commercial refined starches are cornstarch, tapioca, wheat and potato starch. Industrial applications include pharmaceutical, papermaking, textile, and in food preparation.

![Fig. 6. Structure of starch.](image)

Use in corrosion resistance

Starch is used as a natural corrosion inhibitor. A few reports are available in literature where starch is used to protect metal against corrosion (Sugama & DuVall, 1996). When used at low pH, starch shows low water solubility and poor stability. Thus, for improved performance, certain physical and chemical modifications become necessary. These involve...
the reactions of their hydroxyl groups with functional groups of the synthetic polymers, such as carboxylic acids, anhydrides, epoxies, urethanes, oxazolines, and others. Another alternative method is via free-radical ring-opening polymerization occurring between their glucose rings and vinyl monomers. Sugama et al carried out the preparation of polyorganosiloxane grafted starch coatings for the protection of aluminium from corrosion (Sugama & DuVall, 1996). The protocol involved the modification of potato starch [PS] with N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole [TSPI]. The constant threat with the use of PS was active bacterial and fungal growth, which caused diminution of its corrosion resistance behavior. TSPI protects the bacterial and fungal growth on PS solution; this was analysed by SEM technique (Sugama & DuVall, 1996). The grafting of organosiloxane occurred by the opening of glycosidic rings. The coating properties were investigated by EIS and salt spray test. PS/TSPI 85/15 and 90/10 ratio-derived coatings displayed good protection of Al against corrosion (salt spray test-288 hours, impedance >10^5 Ω cm^2). In another report, Sugama attempted to investigate the effect of cerium (IV) ammonium nitrate modified PS as primer coatings for aluminium substrates (Sugama, 1997).

Bello et al. used modified cassava starch as corrosion inhibitor of carbon steel in an alkaline 200mgL\(^{-1}\) NaCl solution (chemical composition of tap water) in contact with air at 25°C. One was cassava starch modified through gelatinization and activation [GAS] and carboxymethylated starch [CMS] with different degrees of substitution [DS]. These were characterized by NMR spectroscopy; estimation of DS was also performed, which was about 0.13±0.03 (CMS 0.13) and 0.24±0.04 (CMS 0.24). Electrostatic potential [V(r)] mapping of the repetitive unit of GAS and CMS was based on the model proposed by Politzer and Sjoberg (Bello et al., 2010). Corrosion studies were performed by EIS coupled with a rotating disk electrode with a fixed rotation speed of 1000 rpm. The polarization resistance values followed the order CMS 0.13 < CMS 0.24 < GAS. The studies confirmed that starch acts as corrosion inhibitor of carbon steel; the extent of protection against corrosion depended on the amount and type of active groups present [carboxylate (–COO\(^{-}\)) and alkoxy (–CO\(^{-}\)) groups for CMS, and alkoxy (–CO\(^{-}\)) groups for GAS] and also on DS (Bello et al., 2010).

Rosliza and Nik studied the corrosion resistance conferred by tapioca starch [TS] to AA6061 alloy in seawater. The weight loss of AA6061 alloy specimens in seawater diminished with increasing TS concentration as a result of corrosion deposits. PD results revealed that as the concentration of TS increased, corrosion potential \([E_{corr}]\) values shift to more positive value, corrosion current density \([i_{corr}]\) reduced remarkably, the numerical values of both anodic and cathodic Tafel slopes decreased, polarization resistance \([R_p]\) value of AA6061 alloy increased (higher the \(R_p\) value, lower the corrosion rate), double layer capacitance value \([C_{dl}]\) decreased, indicating that anodic and cathodic processes are suppressed by TS, that acts as corrosion inhibitor, preferentially reacting with Al\(^{3+}\) to form a precipitate of salt or complex on the surface of the aluminum substrate (Rosliza & Nik, 2010). Inhibition efficiency \([IE(\%)\)] values obtained from all the measurements viz. gravimetric, PD, linear polarization resistance \([LPR]\) and EIS were in close agreement with each other. IE (%) of TS increased with the corrosion inhibitor concentrations ranging from 200 to 1000 ppm. The protection conferred by TS is attributed to the adsorption on AA6061 alloy surface through all the functional groups present in starch (linear amylose constituted by glucose monomer units joined to one another head to tail forming alpha-1, 4 linkage, and highly branched...
amyllopectin with an alpha-1,6 linkage every 24–30 glucose monomer units). Other uses of starch include their potential application in edible coatings (Vásconeza et al., 2009; Pagella et al., 2002), coatings for colon-specific drug delivery (Freirea et al., 2009), and in blast cleaning of artificially aged paints (Tangestaniana et al., 2001).

2.6 Plant extracts

Plants naturally synthesize chemical compounds in defence against fungi, insects and herbivorous mammals. Some of these compounds or phytochemicals such as alkaloids, terpenoids, flavonoids, polyphenols and glycosides prove beneficial to humans in unique manner for the treatment of several diseases. These compounds are identical in structure and function to conventional drugs. Extracts from parts of plants such as roots, stems, and leaves also contain such extraordinary phytochemicals that are used as pesticides, antimicrobials, drugs and herbal medicines.

Use in corrosion resistance

Plant extracts are excessively used as corrosion inhibitors. An interesting review in this context is compiled by Raja & Sethuraman, 2008. Plant extracts contain a variety of organic compounds such as alkaloids, flavonoids, tannins, cellulose and polycyclic compounds. The compounds with hetero atoms-N, O, S, P coordinate with (corroding) metal atom or ion consequently forming a protective layer on the metal surface, that prevents corrosion. These serve as cheaper, readily available, renewable and environmentally benign alternatives to costly and hazardous corrosion inhibitors (e.g., chromates). Plant extracts serve as anticorrosion agents to various metals such as mild steel, copper, zinc, tin, nickel, aluminium and its alloys. Literature reveals that there are exhaustive numbers of plant extracts that have shown proven anticorrosion activity as corrosion inhibitors. Examples are Swertia angustifolia, Accacia conicianna, Emblica officianilis, Terminalia chebula, Terminalia belvia, Sapindus trifolians, Pongamia glabra, Eucalyptus leaves, Annona squamosa, Eugenia jambolans, Azadirachta indica, Accacia Arabica, Vernonia amydalina, Carica papaya, Rosmarinus officinalis, Hisbiscus subdarifla, Opuntia extractd, Mentha pulegium, Occum virdis, Datura metel, Ricinus communis, Chelidonium majus, Papaia, Poinciana pulcherrima, Cassia occidentalis and Datura stramonium seeds, Papaia, Calotropis procera B, Azydracta indica, Justicia gendarussa, Artemisia pallens, Auforpio turkiale sap, Black pepper extract, henna extract and several others (Zucchi & Omar, 1985; Dahmani et al., 2010; Ostovaria et al., 2009; Satapathy et al., 2009).

2.7 Vegetable oils [VO]

VO are triglycerides of fatty acids (Fig. 7). They find versatile applications as biofuel, lubricants, adhesives, antimicrobial agents, coatings and paints [Mar et al., 2007; Bruning, 1992. The extensive utilization of VO in several diverse fields is manifested in their rich chemistry—a storehouse of functional groups such as esters, carboxyls, hydroxyls, oxirane, double bonds, active methylene and others. These functional groups on VO backbone may undergo a host of chemical transformations yielding “green” polymer derivatives, e.g., alkyds, epoxies, polyols, polyurethanes, polyesters, polyesteramides, polyetheramides and others, with versatile applications.
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Use in corrosion resistance

VO is the single, largest, well-established, non-polluting, non-toxic, biodegradable family used in coatings and paints, since primeval times particularly in corrosion resistance. Depending on their Iodine value \([IV]\), VO are classified as non-drying, semi-drying and drying, as indicated by their drying index \([DI]\) \((DI=\text{linoleic}\%+(2\times\text{linolenic}\%); \text{“drying” VO: } IV>130 \text{ and } DI> 70); \text{“semi-drying” VO: } 115<IV<130 \text{ and } DI 65-75; \text{“non-drying” VO: } IV<115; DI< 65)\). Usually, drying VO are used in coatings and paints. Drying VO are film formers, i.e., they have the tendency to form films over the substrate by drying themselves, without the use of any drier. In drying VO, drying occurs as a natural phenomenon through auto-oxidation initiating from the active methylene groups on VO backbone. However, since these films are not tough enough to meet the desirable performance characteristics, VO are chemically transformed into several derivatives as polyesters, alkyds, polyestheramides, polyetheramides, polyurethanes (Fig. 8) and others, to meet the stringent environmental conditions. These have been further modified through chemical pathways including acrylation, vinylation, metallation, and others, for improvement in their drying, gloss, scratch hardness \([SH]\), impact resistance \([IRt]\), flexibility \([FL]\), and corrosion resistance of coatings produced therefrom. The presence of hydroxyls, esters, oxiranes, amides, carbonyls, metals, acrylics, carboxyls, urethanes, imparts good adhesion to the substrate due to good electrostatic interactions with the metal substrate.

Fig. 7. Chemical structure of VO.

Today, the advancements in knowledge, rise of several innovative technologies, human awareness and concerns related to energy consumption and environmental contamination have brought about manifold changes in the world of VO based coatings and paints. They include VO based low/no solvent coatings, high solids coatings, hyperbranched coatings, WB coatings, UV curable, organic-inorganic hybrids and nanocomposite coatings.
Aigbodion et al prepared WB coatings from rubber seed oil (Aigbodion et al, 2000, 2001, 2003, & 2010). WB polyurethanes with dimer fatty acids showed excellent water and hydrolytic resistance (Liu et al, 2011). Commercially procured acrylated soybean oil modified with acrylated sucrose [ACSU] and hyperbranched acrylates [HYAC], was formulated into UV curable coatings, (Chen, et al., 2011). The addition of HYAC and ACSU improved the adhesion and toughness of coatings, respectively. ACSU acted as reactive flexibilizers in coating formulations. ACSU (in an optimum concentration) modified coatings showed good stability in water, after immersion for seven days, except for slight haziness in smaller portion of the films. Soy alkyd/ PANI conducting coatings showed good SH, IRt, FL and conductivity due to good adhesion between PANI and metal substrate.
While the virgin Soy alkyd coating succumbed to corrosion resistance tests in different corrosive media after 2 h, relatively, Soy alkyd/PANI showed higher performance as monitored for a period of 960 h. The corrosion rate decreased with increased concentration of PANI, being minimum for the highest PANI loading in alkyd. Minimum corrosion rate of $35 \times 10^{-2}$ mpy in 5% HCl, $32 \times 10^{-2}$ mpy in 5% NaOH and $30 \times 10^{-2}$ mpy in 3.5% NaCl was observed for 2.5%-Soyalkyd/PANI (Alam, et al., 2009). Metal containing VO coatings have shown antimicrobial behavior due to the presence of metal, either embedded or incorporated into the matrix. Metal/VO corrosion resistant materials interact with the microbes by adhering to their surface, the long hydrophobic VO chains engulf the microbes completely cutting off their nutrients, making the cell weak and finally dead.

*Mesua ferrea* L. seed oil polyester/clay silver nanocomposite coatings have shown antimicrobial behavior against *Escherichia coli* and *Psuedomonas aeruginosa* (Konwar, et al., 2010). Zafar et al have reported antibacterial activity of Zn containing Linseed polyesteramide coatings (Zafar, et al., 2007, 2007). Sharmin and co-workers recently investigated the coating properties of copper oxide containing poly (ester urethane) metallohybrids from Linseed oil (Sharmin, et al., 2012). Castor polyurethane organo clay composite coatings prepared by Heidariani et al showed good corrosion resistance properties (Heidariani et al., 2010). At 3wt% loading of clay, good corrosion resistance properties could be achieved as determined by PP and EIS. The composite showed $i_{corr}$ (nA/cm$^2$)=0.139, $R_p$ (M$\Omega$cm$^2$) polarization resistance= 3819.41, $E_{ocp}$ (mV/Ag|AgCl) (open circuit potential)= $-132$ after 30 days immersion of samples in 5wt% NaCl. At higher clay loading (>3wt%), the coating material became viscous and the adhesion of the coatings to the substrate deteriorated. The composites prepared through ultrasonication technique did not show any phase separation contrary to their counterparts prepared by mechanical agitation. Zafar et al have for the first time reported the microwave assisted preparation and characterization of Castor oil based zinc containing metallopolylurethane amide coating material. Metallopolylurethaneamide containing 5% metal showed the best performance. The coatings showed good SH (3.5kg), IRt (150lb/inch), FL (1/8in.) and gloss (tested by standard methods and techniques). The coatings were tested by PD in 3.5% HCl, 3.5% NaOH, 3.5% NaCl solutions. IE% in 3.5% HCl, 3.5% NaOH, and 3.5% NaCl were found as 96.23, 90.81, and 94.50, respectively [Zafar, et al., 2011]. Ahmad et al recently reported the preparation and corrosion resistance performance of Linseed oil based polyurethanefattyamide/ tetraethoxyorthosilane [TEOS-20, 25, 30 phr] based organic-inorganic [PULFAS] prepared at ambient temperature (Ahmad et al., 2012). PD measurements were conducted in HCl (3.5%), NaOH (3.5%), NaCl (5%) and tap water (Cl- ion 63mg/l; conductivity 0.953 mS/A). PULFAS hybrid coatings with 30 phr inorganic content showed the best coating properties, $i_{corr}$ (A/cm$^2$) 2.65x10$^{-8}$ and IE% 99.77 in 3.5% HCl, $i_{corr}$ (A/cm$^2$) 1.09x 10$^{-7}$, IE% 99.34 in 3.5% NaOH. Salt spray test of PULFAS coatings was carried out in 3.5% NaCl solution; while the hybrid coatings could withstand the test for 240h, the coatings of virgin polyurethaneamide showed loss in weight and gloss after this time period. Araujo and co-workers investigated the influence of the type of VO on the barrier properties of alkyd paints pigmented with zinc phosphate. They selected Linseed and Soybean oils as modifiers of alkyd paints (Araujo, et al., 2010).

The research work on the use of VO in corrosion resistance is exhaustive. Numerous innovations in the field have occurred in recent years and still more is yet to take place.
2.8 Biofilms

A biofilm consists of a highly organized bacterial community with cells entrapped in an extracellular polymer matrix. Bacteria in biofilms show higher resistance to antibiotics, increased production of exopolysaccharide, morphological changes in cells, different responses to environmental stimuli, and distinct gene expression profile (Zuo, 2007; O’Toole et al., 2000; Videla & Characklis, 1992) (Fig. 9). Biofilm formation on metal surfaces may enhance or hamper corrosion process. The bacterial colonies on metal substrates form anodic (area below thicker colonies, due to more respiration activity and lower oxygen concentration) and cathodic (areas below thinner colonies due to less respiration activity and higher oxygen concentration) areas, resulting in the corrosion of metal surface. The biofilm matrix itself, contrarily, forms a transport barrier, impeding the penetration of corrosive agents (such as oxygen, chloride, and others), decreasing their contact with the metal surface, thus reducing corrosion. Often, the corrosion products themselves form a passive layer that may impede corrosion. The overall process (corrosion or anti-corrosion) depends upon the type of metal and activity of microbes. Some bacteria may become protective or corrosive, depending upon the pH of the medium (Zuo, 2007; O’Toole et al., 2000; Videla & Characklis, 1992; Videla & Herrera, 2005; Lopes et al., 2006). The mechanism involves the removal of corrosives such as oxygen by aerobic respiration of biofilms, elimination of corrosion causing bacteria by biofilms generated antimicrobials, biofilm secreted corrosion inhibitors form passive layer decreasing contact of metal and corrosives. Such corrosion inhibiting microbes include Pseudomonas cichorii, Bacillus mycoides, Bacillus licheniformis and several others. The use of biofilms as anti-corrosion agents requires extensive research to be focussed mainly on interactions between bacteria within the microbial community and interactions between certain bacteria and metal. This requires the collaboration of microbiologists and corrosion chemists for further fruitful results in the field.

2.9 Cashew nut shell liquid (CNSL)

CNSL is obtained as a by-product of the cashew nut industry, mainly containing anacardic acid 80.9%, cardol 10-15%, cardanol, and 2-methyl cardol (Fig. 10). CNSL occurs as a brown viscous fluid in the shell of cashewnut, a plantation product obtained from the cashew tree, Anacardium oxidentale (Bhunia, et al., 2000). CNSL is used in the manufacture of industrially important materials such as cement, primers, specialty coatings, paints, varnishes, adhesives, foundry core oils, automotive brake lining industry, laminating and rubber compounding resins, epoxy resins, and in the manufacture of anionic and non-ionic surface active agents. CNSL modified phenolic resins are suitable for many applications and perform improved corrosion and insulation resistance.

Use in corrosion resistance

CNSL has excellent combination of functional groups viz., hydroxyls, double bonds, long aliphatic chain, aromatic ring. It can impart good adhesion to coating material due to its structural attributes. Aggarwal et al prepared epoxy-cardanol resin based paints from epichlorohydrin, bisphenol-A and cardanol (Aggarwal, et al., 2007), in presence of Zn powder, Zn phosphate, micaceous iron oxide and synthetic iron oxide as pigments, some
fillers, additives and hardener (aromatic polyamine). The coated panels were subjected to immersion tests in water, 5% NaCl, urea and di-ammonium phosphate for 180 days and humidity cabinet test at 100% RH at 42-48°C. The coatings showed good SH, adhesion, FL; coatings with micaceous iron oxide showed minimum blistering in immersion and humidity cabinet tests (Aggarwal, et al., 2007). CNSL is also used as a modifier for phenol-formaldehyde [PF] resin. CNSL-PF modified natural rubber has shown improved physico-mechanical performance compared to pure CNSL (Menon, et al., 2002).

Fig. 9. Corrosion resistance by the formation of biofilm.
Corrosion Resistance

2.10 Others

Other examples include furan, polycaprolactone, glycerol, gums, proteins, pectin, drugs and others, which are also used in corrosion resistance (Hussain et al., 2002; Fabbri et al., 2006; Velayuthama et al., 2009; Umoren, 2008; Umoren et al., 2009; Zuo et al., 2005; Sugama, 1995; Abdallah, 2004; Obot et al., 2009). The role of antibacterial and antifungal drugs like Clotrimazole, Fluconazole, Cefixime, Ampicillin, Ampiclox, Cloxacillin, Tetracycline, Methocarbamol, Orphenadrine, Penicillin G, Azithromycin, and others, in corrosion resistance is basically as corrosion inhibitors. The inhibition mechanism is based mainly on adsorption, significantly influenced by the presence of functional groups –CHO, –N=N, R–OH, steric factors, aromaticity, electron density, molecular weight of inhibitor and others (Abdullah, 2004; Obot, et al., 2009; Naqvi et al., 2011; Eddy et al., 2010). Drugs may often compete with “green” corrosion inhibitors. Similarly, gums (Raphia hookeri gum, gum Arabic) also exert their anticorrosion effect as corrosion inhibitors through the formation of films on metal surface via adsorption and thus, blocking off the corrodents present in the environment (Umoren, 2008).

Fig. 10. Chemical structure of the constituents of CNSL, (a) anacardic acid, (b) cardanol, (c) cardol and (d), 2-methyl cardol.
In an excellent review by Shchukin and Mçhwald (Shchukin & Mçhwald, 2007), they have discussed about the nanoreservoirs containing active materials (corrosion inhibitors) for self-repairing coatings and surfaces. Such an approach can be employed on renewable resources in corrosion. In another review by Nimbalkar and Athawale, they have elaborated the use of VO in WB coatings (Athawale & Nimbalkar, 2011). In another excellent report, use of plant extracts as natural corrosion inhibitors has been briefly described (Raja & Sethuraman, 2008). The target of corrosion engineers and chemists, beyond the boundaries, is to achieve and come to a cost effective, environment friendly, user-friendly and long term solution to corrosion-the metallic cancer. For the present, persistent ongoing research efforts in the direction have shown proven results. The substitution of renewable resources based binders and corrosion inhibitors to conventionally used chemicals will pave way for a fruitful utilisation of our naturally available bioresources. With innovative technologies in hand, green chemistry, nanotechnology and green anticorrosion methods and materials as our tools, we can be fully equipped to combat corrosion and related problems, in near future.

3. Conclusion
Renewable resource based derivatives are cost-effective, abundantly available, biodegradable, environmentally benign alternatives for corrosion resistant coatings, paints and inhibitors. With advancements in knowledge and updated instruments and techniques available, further research in the field may be focussed on the enhanced use of the lesser and highly explored biomaterials for the development of anticorrosion agents in hand with “green” coating technology, for high performance high solids, hyperbranched, waterborne, hybrid and composite coatings that may compete with their petro-based counterparts, both in the terms of cost and performance, in near future. Though we have come a long way, much remains to be done on our palette; we still have a long way to go and explore.

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5. References

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The book has covered the state-of-the-art technologies, development, and research progress of corrosion studies in a wide range of research and application fields. The authors have contributed their chapters on corrosion characterization and corrosion resistance. The applications of corrosion resistance materials will also bring great values to reader’s work at different fields. In addition to traditional corrosion study, the book also contains chapters dealing with energy, fuel cell, daily life materials, corrosion study in green materials, and in semiconductor industry.

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