Anticorrosion performance of zinc ferrite pigmented lignin/phenol epoxy novolac resin based coating

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Abstract. Corrosion in most processing equipment has always been a key research area. It is an important threat that needs to be prevented and controlled. Application of epoxy-based coatings on the surfaces of metallic parts is among the preventive measures but it is toxic and expensive. In this work, the anticorrosion performance of zinc ferrite pigmented bio-based epoxy-novolac coatings was studied. Initially, bio-based novolac resins were prepared by condensation from the reaction between phenol, bio-oil phenolic fractions and formaldehyde in an acidic medium. The prepared novolac was later transformed to epoxide with epichlorohydrine and 30 percent sodium hydroxide solution. The final coating formulation was obtained by mixing the prepared epoxy with zinc ferrite (a nontoxic anticorrosion pigment) and solvent. Anticorrosion tests using the formulated coatings and two other conventional coatings for comparison were conducted by simulating actual field conditions in a closed autoclave loop system that used 3 percent sodium chloride and water medium. The results showed that the zinc ferrite pigmented bio-based formulated coatings are very efficient in protecting the substrates since they exhibit similar protection ability with the conventional ones. The prepared epoxy can be said to be an eco-friendly and cheap source of resin for coating formulation that will reduce production cost and negative environmental effects as compared to conventional materials.

Introduction

The need to adequately and efficiently transfer energy or fuel for energy production can be found in a wide range of systems such as chemical, refinery, biological, electronics and petrochemical systems. After some operational period, surfaces of the equipment used for the transfer of the heat or fuel may no longer be in the same condition found upon installation. The surfaces can become coated with deposits from the process or cooling streams or become coated with corrosion products which can crates additional resistance to the heat transfer and a decrease in performance. Corrosion is the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings [1,2]. Disintegration implies deterioration of physical properties of the material. This can be a weakening of the material due to a loss of cross-sectional area, it can be the shattering of a metal due to hydrogen embrittlement, or it can be the cracking of a polymer due to sunlight exposure [1].

Coating on the surfaces of metallic parts is among the preventive measures. The use of polymer materials for the production of high performance coating has evolved and matured into a cost-effective remedy to reduce typical fouling and corrosion problems intrinsic to various
processing equipment. These polymeric materials have superior mechanical, thermal and anticorrosive characteristics ideally suitable for adverse environmental conditions [3]. On the other hand, most of the coating materials are toxic and harmful to the environment [3]. As such, recycle waste materials or biomass in general, is a promising option for coating agents (chemicals). Chemicals produced from such resources can be safe and environmentally friendly [4].

The objective of this study is test the anticorrosion performance of zinc ferrite pigment bio-based epoxy novolac resin based coating with the view of having a formulation that would be highly anticorrosive and eco-friendly.

Materials and Methods

Fractionation of bio-oil. The bio-oil was first separated into water-soluble (light) and insoluble (heavy) components by mixing the bio-oil with water at 2:1 V/V ratio under ambient condition [5]. It employed the use of magnetic stirrer where the measured amount of water was gradually added to the bio-oil which was in vigorously stirred condition for 3 hours. It was then allowed to stand for 24 hours and after which the bio-oil was separated into two phases.

Synthesis of Novolac Resin. The bio-based novolac resin was prepared by condensation reaction between phenol, bio-oil phenolic fraction and formaldehyde in acidic medium. This was synthesized in a 2.0L glass reactor equipped with a thermometer, reflux condenser and a stirrer. The pH was adjusted to 2.0 with aid of 0.1M HCl (used as catalyst) and the contents was heated to 90°C with constant stirring. The required amount (1 mole) of formaldehyde (37% formalin solution) was added over a period of 2.5 hours through a dropping funnel. The mixture was then stirred for an additional 30 minutes. Finally the water was removed under vacuum [6].

Epoxidation of Novolac Resin. The novolac resins prepared above was then reacted with epichlorohydrine and 30% NaOH solution was later added to the reaction vessel over a period of 2.5 hrs. The content was then washed with hot water in order to completely remove any salt that will be formed during the reaction. The epoxidation process was conducted in a 2.0L glass reactor equipped with a thermometer, reflux condenser and a stirrer. Finally the residual moisture in the resin was removed under vacuum [6].

Coating formulation. A typical coating is composed of binders, carriers, pigments and additives. Binders provide the major properties to the coating while the carriers (solvents and/or water) adjust the viscosity of the coating for application [9]. Pigments impart specific properties to a coating such as corrosion resistance and colour. In this study, the coating composition was formulated by incorporating the prepared resins (epoxy-novolac) and zinc ferrite pigment with the curing agent (Phthalic anhydride). The nomenclatures for the coating used in the test are as follows:- CA- Laboratory prepared coating (solvent-borne); CB- Laboratory prepared coating (water-borne); CSA- Commercial coating 1(zinc-rich); CSB- Commercial coating 2.

Measurement of Corrosion Rate. Initially all the plates used for the test were cleaned mechanically (by 400# abrasive paper), degreased using acetone to remove all the oxidized surface and impurities, rinsed and pickled with hydrochloric acid solution at 1:1 dilution, and finally rinsed with de-ionized water and oven-dried. Thereafter, weight loss method which is a simple test for measuring corrosion is adopted. The weight loss from the testing plates was obtained by first measuring the initial weights (W1) of the empty cleaned plates. It was followed by measuring the weights of the dry coated plates (W2) and finally measuring the weights of the plates after the corrosion test (W3). This final measurement was done after removing the corrosion products from the plates. The coating solution was applied on the metallic plates by flow coating method and left in air for 3 h to evaporate the solvent. The coating samples were thermally cured in an oven to have
a uniform coating thickness of about 20-30 µm measured in accordance with ASTM D4138-94. The following expressions were used to assessed the corrosion rate [7].

\[
Corrosion\ Rate\ (CR) = \frac{W}{\text{Weight\ loss} \times \text{Density} \times \text{Exposed\ Area} \times \text{Exposed\ Time}}
\]

or

\[
CR = \frac{KW}{DAT}
\]

Where the values for variables are; \( A = 10\, \text{cm}^2, D = 7.85\, \text{g/cm}^3 \) (for carbon steel) and since the area is in \( \text{cm}^2 \) then corrosion rate constant, \( K = 3.45 \times 10^9 \) in order to get the CR in mills per year (mpy). Therefore,

\[
CR = \frac{3.45 \times 10^8 \, W}{7.85 \times 10^5 T}
\]

or

\[
CR = \frac{43949 \, W}{T}
\]

Results and Discussions

Fractionation of bio-oil. The separation operation was performed in order to separate the relatively stable top emulsion phase containing water soluble chemicals and light oily components which are mostly alkenes and low molecular lignin and precipitate the heavy oil of the bottom layer. The bottom fraction is a mixture of large oily molecule characterized by high viscosity and water insoluble (heavy oil). The heavy oil yield from this experiment was about 20% of bio-oil while that of the light oil was about 80%.

Corrosion rate. The results indicate that as time increases, corrosion rate also increase due to continuous dissolution of iron ion from the plate. The corrosion rate is faster in brine medium than the that of water. This may be due to the presence of chloride in NaCl. The summary of the results are presented in Figures (1-4).

![Figure 1](image1.png)  
(a)  
(b)  
Figure 1. Variation of weight loss with time of coated plates in (a) water (b) brine medium

![Figure 2](image2.png)  
(a)  
(b)  
Figure 2. Variation of corrosion rate with time of coated plates in (a) water (b) brine medium
Figure 3. Comparison of corrosion rate of the different coatings in (a) water (b) brine medium

Figure 4. Uncoated plates corrosion behavior showing (a) weight loss (b) corrosion rate

The coating performance on various coated and uncoated (blank) plate in terms of weight loss and corrosion rate was analysed. As indicated in Figures 1-4, it was observed that coating the metals with any of the coatings provide a significant protection against corrosion when compared with the blank plates. It was also observed the corrosion rate is faster under the brine medium which may due to chlorine presence.

Conclusion
No visible corrosion products were seen on the surface of the unscratched area of the coated panels at the end of the all the tests. Corrosion products were seen mainly on scratched area of the coated panels. Corrosion is lower in the case of commercial coating 1, 2 and the solvent based bio-based epoxy-novolac coated panels than the water-borne epoxy and blank (uncoated).

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