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

AHMED Murtala Musa, NASRI Noor Shawal, HAMZA Usman Dadum, MOHAMMED Jibril, GARBA Abdurrahman and MOHD Zain Husna

Sustainability Waste-To-Wealth Unit, UTM-MPRC Institute for Oil and Gas, Energy Research Alliance, Research University, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
OUTLINE

Introduction
Objectives
Materials and Methods
Results and Discussions
Conclusion
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 create 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.
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.

On the other hand, most of the coating materials are toxic and harmful to the environment. 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.
The objective of this study is to 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.
**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. 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 Bio-novolac resin

- Condensation reaction between phenol, bio-oil phenolic fraction and formaldehyde in acidic medium

- Initially, the bio-oil phenolic fraction was added in three concentrations (5, 10 and 50 wt%) in total amount of the pure phenol needed (1.12 mole)

- pH adjusted to 2.0 with aid of 0.1M HCl (used as catalyst)

- Heated to 90° C with constant stirring

- The required amount (1 mole) of formaldehyde (37% formaline solution) was added over a period of 2.5 hours through a dropping funnel

- The mixture was then stirred for an additional 30 minutes
MATERIALS AND METHODS

Synthesis of Epoxy-novolac resin

- The novolac resins prepared above was reacted with epiclorohydrine.
- 30% NaOH solution was later added to the reaction vessel over a period of 2.5hrs.
- The content was then washed with hot water in order to completely remove any salt that will be formed during the reaction.
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. 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.
MATERIALS AND METHODS

or

Where the values for variables are; A= 10cm\(^2\), D= 7.85g/cm\(^3\) (for carbon steel) and since the area is in cm\(^2\) then corrosion rate constant, K=3.45x10\(^6\) in order to get the CR in mills per year (mpy). Therefore,

\[
CR = \frac{KW}{DAT}
\]  \hspace{1cm} (2)

or

\[
CR = \frac{3.45x10^6 W}{7.85x10^xT}
\]  \hspace{1cm} (3)

or

\[
CR = \frac{43949 W}{T}
\]  \hspace{1cm} (4)
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 %.
Ortho-connection and contra-connection in novolac had a greater influence on the curing time due to the fact that the contra-position of phenol showed higher activity than the ortho-position of phenol (Xu J, 2010). By using HCl as catalyst, the resin obtained was in high contra-connection which make the curing time to long. With the increased percentage use of the amount of the insoluble fractions, there is requirement for much more reaction time as well as the amount of HCl because the ortho-position and contra-position or both positions in these lignin derivatives were replaced by methyl, methoxy, propenyl, ketones, and aldehyde groups.
Synthesis of epoxy-novolac resin

From the IR spectrum, a prominent band is observed at 800-900 cm⁻¹ in all the formulated epoxies, which shows the presence of oxirane ring in epoxy resins. In general, these peaks at the stated range might be due to oxirane functionality of the epoxidized novolac resin (a peculiar feature for epoxy).

**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).
RESULTS AND DISCUSSIONS

Figure 1. Variation of weight loss with time of coated plates in (a) water (b) brine medium

Figure 2. Variation of corrosion rate with time of coated plates in (a) water (b) brine medium
RESULTS AND DISCUSSIONS

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
No visible corrosion products were seen on the surface of the unscratched area of the coated panels at the end of all the tests. Corrosion products were seen mainly on scratched area of the coated panels.

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 that the corrosion rate is faster under the brine medium and this may due to chlorine presence.

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).
ACKNOWLEDGEMENT

This study was supported by Ministry of Education through the University Research Grant (Q.J130000.2509.06H79) provided by Universiti Teknologi Malaysia, Johor Bahru
THANK YOU