Corrosion Inhibition Efficiencies of Polymeric Materials on Alloy Steel in Dilute Hydrochloric Acid and Sodium Hydroxide Solutions at Ambient Temperature

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Abstract. A corrosion control test was conducted on alloy steel, using polymeric coatings (polyurethane, bitumen (medium airing), and high-density polyethylene) in dilute HCl solutions of pH values 4, 7, and 12, respectively for acid, neutral and alkaline solutions at ambient temperature. In the study, Eighty-four coupons of alloy steel were used. The coupons were mechanized, ground, polished, etched with natal, and weighed using a digital weighing balance (Beva 206B). The mass of each coupon was recorded according to the tag number on them. Twenty-one of the coupons were coated with polyurethane, 21 coated with medium curing bitumen (MC), and 21 coated with high-density polyethylene, while 21 were left uncoated. Seven polyurethane-coated samples, bitumen coating, and uncoated coupons were suspended in dilute HCl solutions of pH values 4, 7, and 12. Every week, one sample is taken from each of the solutions, the coatings and the corrosion products were removed, and the coupons were etched with natal. Then the coupons were reweighed, and their masses were recorded in accordance with their tag number. The weight loss per unit area of the coupons, corrosion rate, and percentage corrosion inhibition efficiencies of the coatings was calculated over seven weeks. The results obtained were tabulated and represented graphically. From the results obtained, it is seen that the corrosion inhibition efficiency of polyurethane coatings is higher compared with bitumen and polyethylene. It is also seen from the graphs that the corrosion rate of the coupons is higher in acid, a little bit lower in alkaline, and much lower in neutral solution. It is also observed that the corrosion rates fall with time as the inhibition efficiency also falls with time.

Keywords: alloy steel, ambient temperature, inhibition efficiency, polymeric coatings.

1 Introduction

Due to its improved mechanical properties, including yield strength, hardness, toughness, etc., alloy steel is widely used in engineering works. Alloy steel has a yield strength of up to 500 MPa, a density of about 7800 kg/m³, the melting point of about 1400 °C, and good creep resistance. It is used in structural fabrication, pipelines, concrete reinforcement, etc. However, alloy steel has low corrosion resistance. As a result of alloy steel's corrosive nature, its mechanical properties fall over time when exposed to an aggressive environment. This can lead to the poor performance of the steel in service, short durability, or catastrophic failure. To avert this problem, there is a need to mitigate corrosion.
Corrosion is also defined as the degradation of metals due to a redox reaction between the metal to different substances in their environment, which produces an undesirable compound [2]. Corrosion occurs if the half-cell reaction that releases electrons is connected with the half-cell reactions that receive electrons. Corrosion occurs in various forms: uniform attack, galvanic corrosion, crevice corrosion, pitting corrosion, inter-granular corrosion, selective leaching, erosion, and stress-corrosion cracking [3].

Several researchers have made a reasonable effort, and significant results have been obtained on the appropriate measures for mitigating alloy steel corrosion in various corrosive media. Corrosion control of alloy steel can start from the liquid state of the steel. Corrosion-resistant elements are used to alloy the steel, such as chromium, which reduces the diffusion rate of carbon from the matrix to the steel’s grain boundaries. This minimizes the chances of intergranular corrosion of the steel. This is achieved by the chromium tieing itself with the carbon in the matrix, forming chromium carbide (Cr₃C₂) against carbon migrating to the grain boundary to form cementite or iron carbide (Fe₃C), which is a hard phase and corrosion site.

Inorganic coatings and organic inhibitors have been developed to fight the corrosion of metals. Material selection in design and electrical methods are also effective methods widely adopted in fighting the corrosion of metals. Inorganic inhibitors have an active group. They are amino which decreases the corrosion rate of metals [4].

They include Sodium Nitrite, Chromate, Phosphate, Zinc, etc. Sodium nitrite is not always recommended because it is required at a high concentration compared to others, usually (300–500 mg/L), so it is not economical. Chromate and zinc are toxic, and phosphate is considered a pollutant [5]. Other than the inorganic inhibitors, organic inhibitors are in use. They are classified into synthetic and organic from nature’s extractions [6]. Compounds used as organic inhibitors usually consist of nitrogen, sulphur, or oxygen atoms having a pair of free electrons [7].

Metals are also protected against corrosion using polymeric coatings, ceramic coatings, and concrete coatings. Polymeric coating in use includes epoxy resin, high density and low-density polyethylene, polyurethane, bituminous coatings (slow curing (SC), medium curing (MC) and Rapid curing (RC), etc. Comparatively, polyurethane has several good qualities against corrosion even at elevated temperatures (up to 40 °C). Such qualities include good hardness, good flexibility, strong adhesion to a metal surface, good resistance against steam penetration, chemical resistance, etc. [8]. This investigation aims to determine the most effective polymeric coating against alloy steel in acid, alkaline, and neutral solutions, looking at the corrosion inhibition efficiencies of polyurethane, high-density polyethylene, and medium curing bitumen as the coatings.

2 Research Methodology

2.1 Rusting

Rusting is the most common form of corrosion. The oxidation of iron from iron (II) ion to iron (III) ion in water and oxygen gives a reddish-brown deposit called rust. Generally, rusting is given by the equations.

\[
\text{Iron + water + oxygen = rust}
\]

\[
\begin{align*}
\text{Fe(s)} + 6\text{H}_2\text{O(l)} + 3\text{O}_2(g) &= 4\text{Fe(OH)}_3(s) \\
\text{Fe(OH)}_3 &= \text{Fe}_2\text{O}_3 + \text{nH}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Rust}
\end{align*}
\]

2.2 Corrosion rate

Generally, the corrosion rate is given by:

\[
CR = \frac{\Delta W}{D \times A \times T}
\]

where \(CR\) – corrosion rate, \(\Delta W\) – weight loss, \(D\) – density, \(A\) – the surface area of metal exposed to corrosion environment, \(T\) – exposure time.

2.3 Corrosion inhibition efficiency

Corrosion inhibition efficiency is a parameter that shows the effectiveness and durability of corrosion control measures over a given time. It is generally expressed as follows:

\[
\%IE = \frac{CR^0 - CR}{CR^0} \times 100
\]

where \(\%IE\) – percentage corrosion inhibition efficiency; \(CR^0\) – corrosion rate without inhibitor in the medium.

Al Aisha and Moubaraki [9] give the percentage corrosion inhibition efficiency:

\[
\%IE_{WL} = \left(1 - \frac{e_{WL}}{e_{WL}^0}\right) \times 100
\]

where \(\%IE_{WL}\) – percentage inhibition efficiency in terms of weight loss; \(e_{WL}\) – corrosion rate with inhibitor; \(e_{WL}^0\) – corrosion rate without inhibitor.

2.4 Experiment

Three coupons, each of dimension 4 mm x 40 mm x 45 mm were cut off from a bar of mild steel or alloy steel. The coupons were analyzed in a laboratory using a spectrometer (spectromax). The average composition of the coupons was determined and recorded as shown in Table 1:

\[
s = \frac{s1 + s2 + s3}{3}
\]

Table 1 – Chemical composition of the mild steel used for coupons
### Chemical composition, %

| Coupon | C    | Mn   | Mo   | V    | Cr   | Cu   | Ni   |
|--------|------|------|------|------|------|------|------|
| s1     | 0.2250 | 0.6120 | 0.0022 | 0.0033 | 0.0048 | 0.0056 | 0.0037 |
| s2     | 0.2249 | 0.6076 | 0.0023 | 0.0036 | 0.0053 | 0.0059 | 0.0035 |
| s3     | 0.2251 | 0.6104 | 0.0021 | 0.0036 | 0.0052 | 0.0059 | 0.0036 |
| s4     | 0.2250 | 0.6100 | 0.0022 | 0.0035 | 0.0051 | 0.0058 | 0.0036 |

Eighty-four pieces of coupons of the stated dimension were cut from the bar.

Each of the coupons was ground and polished with grade 60 and 120 emery cloth, respectively. The coupons were then etched with nital. Each of the coupons is tagged and weighed, and their masses are record accordingly. Twenty-one of the coupons were then coated with polyurethane and tagged with U, 21 coated with high-density polyethylene tagged with P, 21 coated with medium curing bitumen (MC) tagged with B, and 21 left uncoated tagged with X. Seven coupons, each of the polyurethane-coated, polyethylene coated, bitumen coated and uncoated were suspended in dilute solutions of HCl of pH values 5, 7 and 12 (for acid, neutral and alkaline) respectively. Every week, one coupon is taken from each of the solutions and reweighed without coatings. The weight loss per unit area, corrosion rate, and corrosion inhibition efficiency was also calculated and recorded. The results obtained were represented graphically.

### 3 Results

In this section, the experiments' results are presented in Fig. 1–6 and Tables 2–7.
Figure 6 – Percentage corrosion inhibition efficiency of coatings

Table 2 – Alloy steel coupons in a dilute acid solution of HCl (pH = 5)

| TAG | U1  | U2  | U3  | U4  | U5  | U6  | U7  | B1  | B2  | B3  | B4  | B5  | B6  | B7  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Time, days | 7   | 14  | 21  | 28  | 35  | 42  | 49  | 7   | 14  | 21  | 28  | 35  | 42  | 49  |
| Wₒ, g  | 58.200 | 57.980 | 58.110 | 58.020 | 58.060 | 57.980 | 58.140 | 58.080 | 58.150 | 58.010 | 57.910 | 58.400 | 58.060 | 58.090 |
| W, g   | 57.635 | 57.380 | 57.479 | 57.309 | 57.286 | 57.191 | 57.329 | 57.490 | 57.530 | 57.369 | 57.190 | 57.620 | 57.279 | 57.276 |
| ΔWₒ, g | 0.565 | 0.600 | 0.631 | 0.711 | 0.741 | 0.789 | 0.811 | 0.590 | 0.620 | 0.641 | 0.720 | 0.780 | 0.781 | 0.814 |
| ΔW/A, g/cm² | 0.016 | 0.017 | 0.018 | 0.020 | 0.022 | 0.022 | 0.023 | 0.017 | 0.017 | 0.018 | 0.020 | 0.022 | 0.022 | 0.023 |
| CR     | 0.154 | 0.082 | 0.057 | 0.049 | 0.042 | 0.036 | 0.032 | 0.161 | 0.085 | 0.058 | 0.049 | 0.043 | 0.036 | 0.032 |
| IE, %  | 56.639 | 56.172 | 55.280 | 51.534 | 48.843 | 48.932 | 48.703 | 54.720 | 54.711 | 54.571 | 50.920 | 48.447 | 49.450 | 48.514 |

Table 3 – Alloy steel coupons in a dilute acid solution of HCl (pH = 5)

| TAG | P1  | P2  | P3  | P4  | P5  | P6  | P7  | X1  | X2  | X3  | X4  | X5  | X6  | X7  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Time, days | 7   | 14  | 21  | 28  | 35  | 42  | 49  | 7   | 14  | 21  | 28  | 35  | 42  | 49  |
| Wₒ, g  | 58.100 | 58.110 | 58.000 | 57.980 | 58.200 | 58.000 | 58.100 | 58.120 | 59.000 | 57.780 | 58.020 | 58.100 | 58.030 | 58.040 |
| W, g   | 57.500 | 57.467 | 57.319 | 57.229 | 57.416 | 57.187 | 57.286 | 56.817 | 57.631 | 56.369 | 56.553 | 56.587 | 56.485 | 56.459 |
| ΔWₒ, g | 0.600 | 0.643 | 0.681 | 0.751 | 0.784 | 0.813 | 0.814 | 1.033 | 1.369 | 1.411 | 1.467 | 1.513 | 1.545 | 1.581 |
| ΔW/A, g/cm² | 0.017 | 0.018 | 0.019 | 0.021 | 0.022 | 0.022 | 0.023 | 0.023 | 0.037 | 0.039 | 0.040 | 0.041 | 0.043 | 0.044 |
| CR     | 0.164 | 0.088 | 0.062 | 0.051 | 0.043 | 0.037 | 0.032 | 0.035 | 0.187 | 0.128 | 0.100 | 0.083 | 0.070 | 0.062 |
| IE, %  | 53.952 | 53.031 | 51.736 | 48.807 | 48.182 | 47.379 | 48.514 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

Table 4 – Alloy steel coupons in an alkaline solution of pH 12

| TAG | U1  | U2  | U3  | U4  | U5  | U6  | U7  | B1  | B2  | B3  | B4  | B5  | B6  | B7  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Time, days | 7   | 14  | 21  | 28  | 35  | 42  | 49  | 7   | 14  | 21  | 28  | 35  | 42  | 49  |
| Wₒ, g  | 57.980 | 58.200 | 58.000 | 58.100 | 58.200 | 57.980 | 58.110 | 58.110 | 58.000 | 57.980 | 58.200 | 58.000 | 58.100 | 57.980 |
| W, g   | 57.479 | 57.680 | 57.460 | 57.490 | 57.532 | 57.265 | 57.455 | 57.595 | 57.457 | 57.409 | 57.559 | 57.335 | 57.397 | 57.264 |
| ΔWₒ, g | 0.501 | 0.520 | 0.540 | 0.610 | 0.668 | 0.715 | 0.655 | 0.515 | 0.543 | 0.571 | 0.641 | 0.665 | 0.703 | 0.716 |
| ΔW/A, g/cm² | 0.014 | 0.015 | 0.015 | 0.017 | 0.019 | 0.020 | 0.018 | 0.014 | 0.015 | 0.016 | 0.018 | 0.019 | 0.020 | 0.020 |
| CR     | 0.137 | 0.071 | 0.049 | 0.042 | 0.036 | 0.033 | 0.026 | 0.141 | 0.074 | 0.052 | 0.044 | 0.036 | 0.032 | 0.028 |
| IE, %  | 59.400 | 59.533 | 59.060 | 54.748 | 52.286 | 50.690 | 54.921 | 58.266 | 57.743 | 56.710 | 52.448 | 52.500 | 51.517 | 50.723 |
Table 5 – Alloy steel coupons in an alkaline solution of pH of 12

| TAG | P1 | P2 | P3 | P4 | P5 | P6 | P7 | X1 | X2 | X3 | X4 | X5 | X6 | X7 |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Time, days | 7 | 14 | 21 | 28 | 35 | 42 | 49 | 7 | 14 | 21 | 28 | 35 | 42 | 49 |
| W₀, g | 58.020 | 58.060 | 57.980 | 58.140 | 58.110 | 58.000 | 57.980 | 58.200 | 57.980 | 58.200 | 58.000 | 58.100 | 58.200 | 58.100 |
| W, g | 57.940 | 57.496 | 57.380 | 57.508 | 57.430 | 57.259 | 57.308 | 56.966 | 56.695 | 56.881 | 56.652 | 56.700 | 56.750 | 56.647 |
| ΔW, g | 0.530 | 0.564 | 0.600 | 0.632 | 0.680 | 0.741 | 0.672 | 1.234 | 1.285 | 1.319 | 1.348 | 1.400 | 1.450 | 1.453 |
| ΔW/A, g/cm² | 0.015 | 0.016 | 0.017 | 0.016 | 0.019 | 0.021 | 0.019 | 0.035 | 0.036 | 0.037 | 0.038 | 0.039 | 0.041 | 0.041 |
| CR | 0.145 | 0.077 | 0.055 | 0.043 | 0.037 | 0.034 | 0.026 | 0.337 | 0.175 | 0.120 | 0.092 | 0.076 | 0.066 | 0.057 |
| IE, % | 57.050 | 56.109 | 54.511 | 53.116 | 51.429 | 48.897 | 53.751 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

Table 6 – Alloy steel coupons in a neutral solution of pH of 7

| TAG | U1 | U2 | U3 | U4 | U5 | U6 | U7 | B1 | B2 | B3 | B4 | B5 | B6 | B7 |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Time, days | 7 | 14 | 21 | 28 | 35 | 42 | 49 | 7 | 14 | 21 | 28 | 35 | 42 | 49 |
| W₀, g | 58.000 | 58.100 | 58.200 | 57.980 | 58.110 | 58.200 | 58.000 | 58.200 | 57.980 | 58.110 | 58.020 | 58.060 | 57.980 | 58.240 |
| W, g | 57.555 | 57.647 | 57.730 | 57.468 | 57.520 | 57.558 | 57.347 | 57.740 | 57.515 | 57.635 | 57.476 | 57.437 | 57.329 | 57.584 |
| ΔW, g | 0.445 | 0.453 | 0.470 | 0.512 | 0.590 | 0.642 | 0.653 | 0.460 | 0.465 | 0.475 | 0.544 | 0.623 | 0.651 | 0.656 |
| ΔW/A, g/cm² | 0.013 | 0.013 | 0.013 | 0.014 | 0.017 | 0.018 | 0.018 | 0.013 | 0.013 | 0.013 | 0.015 | 0.018 | 0.018 | 0.018 |
| CR | 0.121 | 0.062 | 0.043 | 0.035 | 0.032 | 0.029 | 0.025 | 0.126 | 0.063 | 0.043 | 0.037 | 0.034 | 0.030 | 0.026 |
| IE, % | 62.352 | 62.250 | 61.317 | 60.062 | 55.337 | 53.512 | 52.715 | 61.083 | 61.250 | 60.905 | 57.566 | 52.839 | 52.860 | 52.498 |

Table 7 – Alloy steel coupons in a neutral solution of pH of 7

| TAG | P1 | P2 | P3 | P4 | P5 | P6 | P7 | X1 | X2 | X3 | X4 | X5 | X6 | X7 |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Time, days | 7 | 14 | 21 | 28 | 35 | 42 | 49 | 7 | 14 | 21 | 28 | 35 | 42 | 49 |
| W₀, g | 57.980 | 58.200 | 58.000 | 58.100 | 58.120 | 58.100 | 58.200 | 57.980 | 58.020 | 58.060 | 57.980 | 58.140 | 58.110 | 58.440 |
| W, g | 57.510 | 57.719 | 57.500 | 57.548 | 57.489 | 57.439 | 57.539 | 56.798 | 56.820 | 56.845 | 56.698 | 56.819 | 56.729 | 57.059 |
| ΔW, g | 0.470 | 0.481 | 0.500 | 0.552 | 0.631 | 0.661 | 0.661 | 1.182 | 1.200 | 1.215 | 1.282 | 1.321 | 1.381 | 1.381 |
| ΔW/A, g/cm² | 0.013 | 0.014 | 0.014 | 0.016 | 0.018 | 0.019 | 0.019 | 0.033 | 0.034 | 0.034 | 0.036 | 0.037 | 0.039 | 0.039 |
| CR | 0.14 | 0.014 | 0.014 | 0.016 | 0.018 | 0.019 | 0.019 | 0.033 | 0.034 | 0.034 | 0.036 | 0.037 | 0.039 | 0.039 |
| IE, % | 57.980 | 58.200 | 58.000 | 58.100 | 58.120 | 58.100 | 58.200 | 57.980 | 58.020 | 58.060 | 57.980 | 58.140 | 58.110 | 58.440 |

4 Discussion

Figures 1, 2, and 3 show that the corrosion rate of coupons in the acid environment is higher than those in an alkaline medium. It is also seen that the corrosion rate of the coupons in a neutral environment is appreciably low. From the graphical presentations, it is seen that the corrosion rate of polyurethane-coated coupons has a relatively low corrosion rate in all the test media and at all exposure time. It is also significant that the corrosion rate of the coupons falls over time and more rapidly within the first and the second week of exposure. Fig. 4 shows that the inhibition efficiency of polyurethane-coated coupons is always higher and in all mediums. However, it is observed that there is a fall in inhibition efficiency, which may be attributed to the degradation of the coatings over time in the test media. The decrease in corrosion rate may be due to the corrosion product's presence, which tends to form a passive film on the surface of the metal and hence mitigate corrosion. The fall in the coated coupons' corrosion rate over time indicates the degradation of the coatings in the exposure media. This data may be used to predict the useful life or durability of the coatings in each of the media. In Fig. 4, there is a sudden increase in inhibition efficiency at the end of the fifth week, decreasing at the sixth week. This may be related to the fall in acid concentration over exposure time. From Table 2, it is seen that the weight of the coupons increases with time for both the coated and uncoated coupons in the acid environment, which is applicable in all the exposure media used for this study.

The results obtained from this study also show polyethylene is more efficient than medium curing bitumen and polyethylene in mitigation of corrosion of alloy steel in acid, alkaline and neutral environment. It is also seen from figures 4, 5, and 6 that bitumen is comparatively better than polyethylene in fighting corrosion.

This study's overall result may be used as a guide in selecting the most suitable protective coating against...
corrosion of alloy steel in acid, alkaline, and neutral media. However, there may be variations in the results if the experiment is performed at various temperatures, applicable in real-life situations. On this basis, it is recommended to carry out a similar study in which the experiment is conducted at different temperatures. In this study, polyurethane coating has an average thickness of 100 microns; bitumen coating has an average thickness of 0.3 mm, and polyethylene coatings have an average thickness of 3 mm.

Naturally, an increase in coating thickness will impose more difficulty in the penetration of corrosive substances. Hence, the variation of coating thickness may also vary the results obtained in this study.

5 Conclusions

Looking at Figures 1–6, it can be said that polyurethane coating is more efficient than bitumen coating in the entire test environment. Comparatively, polyethylene has the least corrosion inhibition efficiency. However, polyethylene may be recommended in the absence of polyurethane for corrosion protection of alloy steel in acid, alkaline, and neutral environments at ambient temperature. It is also concluded that alloy steel corrosion is more severe in the acid environment than in alkaline medium and least in a neutral environment at ambient temperature. Another conclusion drawn from this work results is that the weight loss of the coupons increases with time. From Figure 6, it is concluded that the corrosion inhibition efficiencies of bitumen and polyethylene are almost the same after 28 days of exposure.

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