Study on the making of corrosion resistant steel (ASTM A36 Steel) coatings from a mix of graphene oxide + waterborne paint

P H Tjahjanti*, A R Hidayat1, R Firdaus1, Iswanto1, Nurcahyo R1 and G A N Fitri2
1 Department of Mechanical Engineering, University of Muhammadiyah Sidoarjo, Indonesia
2 Department of Mechanical Engineering, State University of Surabaya, Indonesia
*E-mail: prantasi@gmail.com

Abstract. Steel coating as long as including ASTM A36 steel is generally carried out by galvanizing or coating to provide corrosion resistance. However, the problems that occur with the commonly used layer will break and peel off when the steel is removed. The purpose of this study is to make of corrosion resistant steel coatings especially for ASTM A36 steel from a mix of graphene oxide + waterborne paint. Weight loss method for calculate Corrosion Penetration Rate (CPR). Corrosion testing by immersing ASTM A36 steel samples in seawater (NaCl), and corrosion test for room temperature and 500°C. Final results showed that CPR values for ASTM A36 steel samples with graphene oxide + waterborne paint coating obtained CPR value that did not exceeded the allowable standard rate (0.5 mm/yr).

1. Introduction
ASTM A36 steel is a low carbon steel with a carbon content of about 0.1%, commonly used for building construction, tanks, and strip steel pipes. This steel is susceptible to corrosion, causing the appearance to be ugly, dirty and discolored. The impact of the corrosion process on steel, among others, steel becomes porous and damaged, the surface becomes less attractive, and can cause a steel construction to collapse if the damage is severe. Therefore, galvanized coatings and coatings are generally carried out to provide corrosion resistance. But the problem that occurs is on the coating, meaning that the layer that is commonly used will generally break and peel off when the steel is removed [1]

Therefore, research was conducted to make an alternative layer of graphene material. Since it was discovered by Geim dan Novoselov, graphene attracted many researchers’ attention to develop its application in the world of engineering. Graphene has good conductivity electrons, high thermal conductivity, and 207 times stronger than steel [2]. Besides graphene can form a barrier for gas and salt, because it has a geometric hole lattice that is smaller than the smallest atom [3]. So graphene has the potential to be used as corrosion protection for materials that tend to be reactive.

Several studies have made other alternative layers more closely and strongly fused with the steel by using a layer of nanomaterial graphene-polymer, which is a type of graphene oxide dispersed in water. This material is very potential in anti-corrosion technology. This is based on the nature of graphene which is resistant to water and air and by making a nano composite coating, the effect of graphene as a protective corrosion can be seen even at low concentrations. Nanomaterial graphene-polymer materials
have never been applied for metal coating, especially steel, so that it becomes an interesting and
important innovation for the development of steel industry in the country.

The aim of the research is to make other alternative layers that are more sticky and stronger fused
with ASTM A36 steel by using a nanomaterial graphene-polymer layer that is a type of graphene oxide
which is dispersed in water that is not toxic (carcinogenic) and mixed with Waterborne paint, which is
waterborne technology namely products that contain more elements of water, including for the purposes
dilution, there are no toxic compounds such as thinner which is very disturbing to the environment.

2. Experimental Studies
The composition of the sample consists of: (1) 15% graphene + 85% waterborne, (2) 20% graphene +
80% waterborne, and (3) 25% graphene + 75% waterborne. The initial stage, the mixtures are stirred for
30 minutes then left to stand for one day, the results are like Figure 1.

The second stage is preparing ASTM A36 steel hollow cylindrical pipe (centre hole) was cut into 15
pieces, each had a size of pipe height, diameter and thick is 3.0 cm, 33.4 mm, and 2.95 mm. The samples
were then divided into five (5), (a). We distinguished the sample into 5 types. The sample without
coating (A), coated with galvanized (G), coated with 15% graphene + 85% waterborne coating (GW15),
coated with 20% graphene + 80% waterborne coating (GW20), and were coated with 25% graphene +
75% waterborne coating (GW25).

Figure. 1 (a) solution of graphene and waterborne paint (b) bare sample of ASTM A36 (c) sample of
ASTM A36 steel coated with galvanizing

Corrosion test was then performed in two ways; those are (1). Corrosion Wet in which the sample
cylinder was dipped in a solution of sea water (NaCl) with concentrations of 0.1M for 6 hours. Every
interval 2 hours, samples were removed and cleaned, (2) Corrosion Dry in which the sample cylinder
were heated at a temperature of 500ºC for 72 hours with a 24 hour time interval. The unit for
measuring the Corrosion Penetration Rate (CPR) is expressed in mile per year (mpy) or millimetre per
year (mm /yr). Where, the material density (D), testing time (T) and weight are parameter which to be
known during the testing process, the CPR can be calculated by the equation:

\[ \text{CPR} = \frac{KW}{ADT} \] (1)

CPR is Corrosion Penetration Rate (mpy) or reduction in the thickness of the material per time unit.
Unit: mile per year (mpy) or millimeter per year (mm/yr). W is weight loss during testing (mg) = mo −
m, m is weight after corroded, mois weight before corroded. K is constant depends on unit used, when
K = 534 the mpy will be used. When K = 87.6, mm/yr will be used. D is density (gr/cm3), T is time
(hours), A = surface area (cm²) (same units other such as CPR wear mpy). When the value of CPR was
less than 20 mpy (0.5 mm/yr), the value/coefficient was still acceptable. Clearly shown in flow chart Figure 2.

**Figure 2** Flow chart of research

3. **Result and Discussion**

3.1 **Wet Corrosion Test (Dipped in 0.1 M NaCl solutions)**

The result for CPR data obtained from effect of time in wet corrosion test when dipped in solution of, 0.1 M NaCl, shown in Table 1 respectively. The fastest of corrosion rate for six hours was occurred in solution of NaCl for samples ASTM A36 steel were not coated. Samples ASTM A36 steel were coated with graphene and waterborne paint coating were seen that the corrosion attack is slow, meaning that the CPR of them is low when compared to the galvanized coated sample (Figure 3a, 3b, 3c).

When the sample is dipped in the solution of NaCl which contains of ions Na\(^+\) and Cl\(^-\), Cl\(^-\) ions tend to react with the oxygen bonding of aluminum, so the process of corrosion takes place more rapidly than in the alkaline environment. The corrosion rate values for the four samples when dipped in a solution of NaCl reach up to 0.034 mm/yr, with one-week period of 6 hours.
3.2 Dry Corrosion Test (Heated at a temperature of 500°C)

The results of temperature data 500°C, showed that the highest corrosion rate in samples without coating. While the lowest corrosion rate on ASTM A36 steel with 20% graphene + 80% waterborne coating with a corrosion rate of 0.067 mm/year with a corrosion time of 96 hours. It appears that.

| Sample | Time (hours) | Average CPR (mm/yr) |
|--------|--------------|----------------------|
| A      | 2            | 1.24                 |
|        | 4            | 1.38                 |
|        | 6            | 1.41                 |
| G      | 2            | 0.16                 |
|        | 4            | 0.21                 |
|        | 6            | 0.23                 |
| GW15   | 2            | 0.04                 |
|        | 4            | 0.04                 |
|        | 6            | 0.05                 |
| GW20   | 2            | 0.01                 |
|        | 4            | 0.02                 |
|        | 6            | 0.02                 |
| GW25   | 2            | 0.02                 |
|        | 4            | 0.03                 |
|        | 6            | 0.03                 |

*Figure 3. Corrosion Penetration Rate in NaCl 0.1 M*

High temperatures can cause corrosion rates to accelerate, because almost all processes or reactions at high temperatures result in increased speed and generally the reaction results also increase. Corrosion
attacks that occur in samples are direct air reactions forming an oxide layer. Complete CPR data on dry corrosion in Table 2 and Figure 4.

**Table 2. CPR obtained by dry corrosion test (500°C)**

| Sample | Time (hours) | Average CPR (mm/yr) |
|--------|--------------|---------------------|
| A      | 24           | 1.75                |
|        | 48           | 1.92                |
|        | 72           | 2.18                |
| G      | 24           | 0.37                |
|        | 48           | 0.41                |
|        | 72           | 0.48                |
| GW15   | 24           | 0.07                |
|        | 48           | 0.08                |
|        | 72           | 0.09                |
| GW20   | 24           | 0.04                |
|        | 48           | 0.06                |
|        | 72           | 0.07                |
| GW25   | 24           | 0.05                |
|        | 48           | 0.07                |
|        | 72           | 0.08                |

Figure 4. Corrosion Penetration Rate in 500°C

Graphene is produced by means of high shear liquid exfoliation which is then processed by a functionalization process mixed with 3-Aminopropyl triethoxysilane (APTES). The solvents used for graphene coatings are water to be more environmentally friendly and reduce production costs. The
results showed that graphene coated carbon steel had a lower corrosion rate (0.015 mpy) compared to commercial chromate coated coating (0.087 mpy) [4].

In addition to using GO as a mixture on coatings, other researchers also try on a large scale. [5] uses graphene which is synthesized from electro chemical processes of graphite or called electrochemically exfoliated graphene (EEG). EEG was obtained from graphite rods which were made electro in an electrochemical system with solution (NH4) 2SO4 as an electrolyte. The coating is made by mixing EEG and polydimethylsiloxane (PDMS) with ethanol as a solvent. EEG and PDMS mixtures produce coatings that have super hydrophobic properties. This coating is coated on Al 6061 material and provides a very perfect self-cleaning effect. Super hydrophobic surfaces show better corrosion resistance than pure Al 6061. This research opens new thinking about the design and fabrication of superhydrophobic materials with self-cleaning and anti-corrosion properties. Although Pourhasem and Wang were able to produce graphene - polymer coatings with an easy synthesis method, the solvents used were still organic solvents. Only a few references in the literature report the corrosion study of graphene coatings - polymers with easy method of synthesis and using water solvents. Therefore, investigations of graphene coatings - polymers with water solvents need to be studied further.

4. Conclusion
It has been successfully created ASTM A36 steel with graphene oxide + waterborne paint coating can protect low carbon steel (ASTM A36) from corrosion attacks when immersed in 0.1M NaCl solution and dry corrosion test at a temperature of 500°C. The final results showed that CPR values for ASTM A36 steel samples with graphene oxide + waterborne paint coating obtained CPR value that did not exceeded the allowable standard rate (0.5 mm/yr).

Acknowledgment
The work/research was financially supported by Universitas Muhammadiyah Sidoarjo and RISTEK DIKTI (grant-in-aid Penelitian Terapan Unggulan Perguruan Tinggi (PTUPT 2019) is acknowledged.

References
[1] Andik Suprayogi , Prantasi Harmi Tjahjanti,2017, Analysis Surface Preparation on Steel Plate ASTM A36, The 1st Asian Summit on Knowledge Advancements (ASKA 2017)
[2] Aneja, K.S., et al 2015. Nanoscale. 7 17879-17888
[3] Ambrosi, A., et al 2014. Chemical Reviews. 114 7150-7188
[4] ASTM G31-72, 1990.Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens
[5] Pourhashem, S., et al 2017. Corrosion Science. 115 78-92