Polyester-graphene primer coatings: corrosive and mechanical properties

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Abstract. This study developed and characterized of the polyester (PE)-graphene (GR) primer coating in corrosion resistance and mechanical properties. PE coatings varied with 0-8% of GR were prepared using ultrasonication method and undergone the morphology characterization using Field Emission Scanning Electron Microscopy (FE-SEM), and also being evaluated using various corrosion and mechanical tests, namely tafel test, immersion test, adhesion test and hardness test. The FE-SEM analysis shows that the homogeneous dispersion of GR in PE resin at 2% of GR loading, whilst at higher loading of GR produced agglomeration that reduced the corrosion inhibition properties of the coatings. The corrosive properties were characterized using autolab potentiostat for determination of corrosion rate and immersion testing using 3.5% NaCl for 9 days. The results show that the optimum corrosion rate of coatings was found at 2% of GR loadings which is 0.586 mmpy. This is due to at 2% GR is optimum as a physical barrier and inhibit the diffusion pathways of corrosive species as there is no agglomeration of GR which is showed that very well dispersion of GR in the PE resin. Whilst, immersion observation also shows the optimum condition at 2% of GR loading, which has a lower corrosion property. On the other hand, adhesion and hardness testing were enhanced by increasing of GR loadings (0-8%) as the properties of GR imparted high strength, rigidity, and durability. Therefore, the incorporation of GR is very efficient materials to enhance both mechanical and corrosive properties of polymeric coatings.

1. Introduction
Coating is the application of covering layers on the top of the substrate to hinder it from corrosion. It offers many advantages like improved adhesion, corrosion resistance, or wears resistance [1-2]. A primer is a surface of coating that applied on materials before being painted with the finished products [3]. The purpose of priming is to diminish corrosion of the metal substrate, to defend against mechanical degradation of the paint system, to provide adhesion to the substrate and to promote the good of the coating system’s visual by reducing surface roughness [4]. The most commonly used primer is the epoxy, polyurethane and polyester primer Polyester (PE) contains the ester group in their main chain as a polymer. PE resins have an excellent adhesion, high strength, hardness, and impact resistances; make it commonly used in coatings industry. PE resins also affordable, easy to handle, and available in broad range of grades [5-8]. However, PE has disadvantages which is easily corroded [9],
lack of fire resistance [10], and high shrinkage during cured [11]. The PE resin also can absorb the seawater easily which leads the corrosion to occur. Previous research by Pathak & Khanna [12] the PE coatings showed chalking on the surface when being exposed to the ultraviolet (UV) light, but after being incorporated with organosilane, the chalk performances, gloss retention, hardness as well as the anti-corrosion ability were improved. Hence, the PE resin would be incorporated with graphene (GR) as a reinforcement filler to overcome the mentioned problem.

GR is the most basic form of carbon. It is widely used in coatings system for applications in different fields as GR has advantages such as absorbs most of the incident light and prevents degradation of the polymer coatings by solar irradiation [13, 14, 15]. In addition, GR tends to make the surfaces of the coatings hydrophobic and reduced the damages of the coatings surfaces from any attacks to improve both mechanical and corrosive properties of polymeric coatings [15, 16]. According to research studies by Berhanuddin et al., [17], the Young modulus of the epoxy-GR coatings was 31% greater than the pure epoxy matrix in the presence of 0.5 wt% of filler. Besides that, the tensile strength of the pristine epoxy was enhanced by around 40% with the same amount of GR loadings. Besides that, Prasai et al., [18] stated that the copper - GR coatings showed the corrosion rate that is 7 times slower than the corrosion rate of bare copper. Furthermore, he also stated that the GR-nickel coating corrodes 20 times slower than bare nickel on Tafel analysis testing.

Therefore, in this research studies, the primer coating of polyester reinforced graphene has been developed to study the corrosive properties and mechanical properties based on different loading of graphene from 0-8%.

2. Experimental Procedures

The chemicals used in this research were ethanol, sodium chloride (NaCl), polyester resin (SYNOLAC 9605S65 MY), methyl ethyl ketone peroxide (MEKP), graphene powder (900561 ALDRICH) and acetone. The instruments and equipments that used in this research were carbon steel plate (15 cm × 10 cm × 0.2 cm), hand brushes, ultrasonicator (Cress ultrasonic model 4HT-1014-6), Autolab PGSTAT240, Field Emission Scanning Electron Microscopy (FE-SEM), hardness pencil tester and Nichiban tape. The chemicals used in this research were purchased from Fluka and used without further purification.

The amount of 1-4g of GR was dispersed in a 5ml ethanol (solvent) by ultrasonication for 1 hour at 27°C. Then 5ml of UPE resin was added into the mixture and mixed for another 10 minutes. After that, 0.3ml of the curing agent (MEKP) was added into the mixture and continues to stir. Then, the mixture was coated onto the carbon steel plates at three layers with the total of 1mm thickness of coating to fully wet the steel surface and to provide good adhesion for subsequently applied coats and then, they were left to cure for 7 days at room temperature [6].Then, the tafel test, immersion test, hardness test, and adhesion test of the painted PE-GR primer coatings were carried out to obtain the optimum properties of the coatings.

2.1 Characterization

2.1.1. FE-SEM analysis. FE-SEM analysis was characterized to study the surface morphology of the PE-GR coatings. The samples that were scratched off from the plate was stacked on a metal sample holder and then coated with gold. Analysis was done at an accelerating voltage of 10 kV.

2.1.2. Tafel test. The tafel test was measured by immersing the coated steel plate into the 3.5% NaCl solution that placed in the beaker together with platinum foil and a saturated calomel electrode which act as counter electrode and reference electrode, respectively using an Autolab PGSTAT204.

2.1.3. Immersion test. All the carbon steel plate was scratched as "X" scratch presenting to the substrates on the covering surface of the plate. Then, the coated carbon steel was immersed in seawater and salt solution (3.5% of NaCl) for 9 days at room temperature and observed visually to
obtain the immersion testing results.

2.1.4. Adhesion test. The adhesion strength test was measured using ASTM D3359.

2.1.5. Hardness test. Pencil hardness test was conducted according to standard procedure of ASTM D3363.

3. Results and discussions

3.1. FE-SEM analysis

The FE-SEM analysis results were illustrated in figure 1. Figure 1 (a), the control sample which is pure PE showed very brittle and uniform structure of the coating as it does not contain any other materials beside of PE resin itself. In figure 1 (b), the cross-section of PE-GR 2% coating showed a smooth structure as the GR loading was suitable enough for the well dispersion. This finding is similar with the research done by Bora et al., [6]. However, the higher the loading of GR more than 2%, the morphology shown the agglomeration of GR [6, 19] as illustrated in figure 1(c). Moreover, restacking occurs frequently during mixing the GR with the polymer matrix due to strong van der Waals forces between the GR fillers and causes cracks, pores, and pin holes in the coatings structure. These defects decrease the beneficial properties of the GR- polymer coatings [20-25].

![Figure 1. The SEM Photograph of the Primer Coatings: (a) Pure PE, (b) PE-GR 2%, (c)PE-GR 4% at 1000X Magnification.](image-url)
3.2. Tafel test
The tafel test results were tabulated in Table 1. Based on Table 1, the highest corrosion rate and the lowest polarization resistance is the control sample at 75.023 mmpy and 10.569Ω, respectively. This is due to the ions easily penetrates the substrate as it was not covered with the GR that has higher corrosion resistance [6].

The optimum condition was found at 2% of GR, which exhibit the lowest corrosion rate at 0.586 mmpy and the highest polarization resistance at 57.394Ω. This is due to the compact oxidation protective film was formed on the surface of stainless steel. Hence, the anodic dissolution reaction was inhibited greatly subsequently the corrosion rate was slowed down. The corrosion potential Ec, of 2% of GR loadings has more positive values in comparison to bare coatings. This signifies that PE-GR 2% acts as a very strong passivation layer against ion diffusion and corrosion. PE-GR 2% proved that GR coating acts as a barrier to the underlying coating surface and therefore inhibits the coating attrition [7]. In a word, the addition of GR could effectively improve the corrosion resistance of base metal, and the coating with the 2% content had the optimum corrosion resistance. This is also due to the well dispersion of GR into the PE resin promotes the inhibition properties of coating towards corrosive elements as the pores on the coating surface was completely filled with the filler [26] as shown in SEM image in figure 1 (b).

Whilst, PE-GR coatings at 4%, 6% and 8% gives the corrosion rates at 4.002 mmpy, 10.392 mmpy and 12.028 mmpy, respectively. It is believed, the higher the content of the GR on the coating, the agglomeration occurred as the poor dispersion of the constituent's materials [20-25] as supported by SEM analysis in figure 1 (c). The agglomerations also induced the pores opening on the surface of the coatings. Therefore, the electrolyte solution gradually permeated into the coating that gives the higher corrosion rate [26-27]. The increment in the value of GR loadings also increased the micro-defects in polymer coating which will lead to the weak coating barrier property [28].

Table 1. Results for tafel test of PE-GR coatings.

| Formulations | Corrosion potential, Ec [mv] | Corrosion current, icorr [μA/cm²] | Corrosion rate [mmpy] | Polarization resistance [Ω] |
|--------------|-------------------------------|---------------------------------|-----------------------|-----------------------------|
| Control (PE) | -603.210                      | 6456.40                         | 75.023                | 10.569                      |
| PE-GR 2%     | -358.740                      | 50.4240                         | 0.586                 | 57.394                      |
| PE-GR 4%     | -470.880                      | 1724.20                         | 4.002                 | 37.083                      |
| PE-GR 6%     | -569.240                      | 1827.00                         | 10.392                | 24.041                      |
| PE-GR 8%     | -594.380                      | 1935.10                         | 12.028                | 19.250                      |

3.3. Immersion test
The observation of immersed sample in seawater and salt solution after 9 days is presented in figure 2. The utilization of GR in the coatings increased the corrosion protection of the steel plate. Based on figure 2, the most corroded sample is observed on control sample because it contains pure polyester that is very poor resistance towards electrolyte [29]. Hence, the ‘X’ scratched becomes completely corroded. The optimum corrosive properties of coating were found at 2% GR loadings, with no corrosion, flakes, and blister occurred. This is because of the nature of GR itself, which high in corrosion inhibition properties that impermeable to electrolytes, thus decline the rusting processes that ordinarily caused more destruction to metal surfaces [30]. Apart from that, the well dispersion of GR in the PE resin improved the corrosion inhibition properties of the coatings [26] as supported in the SEM images in figure 1 (b). Therefore, the coating was completely shielded, and no corrosion obtained.

The higher the loading of GR, the corrosion occurs on the steel plate as the galvanic corrosion takes place when seawater and salt solution comes in contact with steel and graphite interface [6]. Other than that, the inhomogeneous dispersion of GR with PE resin also would induce the corrosion [31, 32]. The immersion results of 3.5% of NaCl solution shows the higher rate of corrosion as compared to
the immersion in seawater as the salt solution was more aggressive towards carbon steel plate than the sea water [33].

| PE-GR 0% | PE-GR 2% | PE-GR 4% | PE-GR 6% | PE-GR 8% |
|----------|----------|----------|----------|----------|
| Seawater |          |          |          |          |
| Salt solution | | | | |

**Figure 2.** Results of immersion test for PE-GR coatings in seawater and salt solution after 9 days.

3.4. **Adhesion test**

The adhesion strength test results were illustrated in figure 3. As shown in figure 3a, some peeling and chipping of the coating were observed. This coating was rated as 3B by referring to the ASTM D 3359 standard. For other formulations, as shown in figure 3b–e, there were no removal of the coating being observed, indicating strong coating adhesion. These results indicate that the coatings containing GR (2-8%) can bind strongly to the surface of steel. The strong adhesion of GR containing coatings to the substrate might be attributed to the fact that the addition of GR modifies the physical properties of PE-GR coatings [6].

Therefore, the addition of GR (2-8%) can improve the interfacial bond established between the polymer coating and the substrate, leading to enhanced corrosion resistance.

**Figure 3.** Observation of cross-cut tape test: (a) PE, (b) PE-GR 2%, (c) PE GR 4% (d) PE-GR 6% and (e) PE-GR 8%.

3.5. **Hardness test**

Based on results in table 2, the increasing in the GR loadings shows the highest hardness of PE-GR primer coatings. This is due to properties of GR and PE themselves, which were very high in strength, durable, high rigidity, high in modulus [7, 29]. Therefore, the incorporation of GR into PE primer coatings improved the hardness of the coating materials.
Table 2. Hardness measurements of coatings.

| Type of sample | Hardness |
|----------------|----------|
| Control        | H        |
| PE-GR 2%       | 5H       |
| PE-GR 4%       | 5H       |
| PE-GR 6%       | 5H       |
| PE-GR 8%       | 5H       |

4. Conclusions
Corrosive properties and mechanical properties of PE primer coatings reinforced GR on steel plates were successfully developed. The FE-SEM analysis was successfully done to determine the morphology structure of the primer coatings. The well dispersion of GR was observed in PE-GR 2% coating as there is no agglomeration occurred, whilst; by further increasing the loading of GR, the agglomeration being spotted and produced inhomogeneous mixture of primer coatings. The corrosion rate for polyester coatings showed that the optimum formulation is at 2% of GR loadings as the corrosion rate was found at 0.586 mmpy, which is the lowest value. This is due to the inhibition of anodic dissolution of PE-GR and decreased the corrosion rate. For immersion testing, the results followed the same trend as the corrosion rate measurement test at 2% GR gave lower corrosion properties. However, the higher loadings of GR lead to the corrosion of the coatings. As the loadings were increased from 2-8%, the protection ability of the coatings is reduced as more of micro-defects occurred in the coating system due to the inhomogeneous dispersion of primer coatings and would affect the corrosive properties. Adhesion and hardness testing were enhanced by increasing the GR loadings as the properties of GR which very high in strength, rigidity, modulus and durability. The PE-GR coatings were improved in mechanical and corrosive properties of coatings.

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