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Comparison Studies on Corrosive Properties of Polyester Filled Graphene Primer Coatings via Sonication and Mechanical Method

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ABSTRACT

This paper investigates the mixing of the graphene (GR) particles in the polyester (PE) resin by using two different dispersion techniques which are mechanical stirring and sonication method. This paper shows that the mixing method has a significant effect on the corrosive behavior of the coatings. Fourier Transform Infrared Spectroscopy (FT-IR) characterization technique is done to analyze the functional group present and evaluate the graphene/polymer matrix interaction. The FT-IR analysis has successfully done and shows that graphene has grafted onto the polyester resin. The corrosive behavior testing is evaluated by using Tafel testing and immersion test which determines the corrosive properties of the coatings based on the mixing method with three different reaction times starting from 30 minutes, 60 minutes, and lastly 90 minutes. The optimum formulation is found at 60 minutes time reaction by using sonication method. This is due to dynamic features of sonicator that have good quality for dispersion of the graphene into the polymer matrix. Prog. Color Colorants Coat. 12 (2019), 211-218© Institute for Color Science and Technology.

1. Introduction

Corrosion is the affinity of metal to alter into its oxide form. The performance and properties of the metal could be a failure due to the alteration of oxides [1]. Therefore, in order to protect the metal from corrosion, the most viable and popular method is by application of protective primer coatings. The most commonly used primer are polyurethane, epoxy, and polyester resin. This research was developing the polyester as a primer coating.

Polyester (PE) resin is a thermosetting polymer which is widely used in various industries such as coating, construction, transportation, storage tanks, and piping. PE is very economic, chemically resistant, has high dimensional stability and low moisture absorption. The drawbacks of PE are that they show significantly higher cure shrinkage, low tensile strength, and stiffness. To get improved properties in the PE resin composites, different fillers like clay, layered silicates, carbon fiber, and CNTs have been used [2].

Graphene (GR) was first prepared in 2004 and has a single atom layer crystal with a carbon atom bound by sp2 [3]. Graphene has excellent chemical stability, high conductivity; outstanding mechanical properties and corrosion resistance [4, 5] have broad application prospects in the field of corrosion protection coatings.

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Graphene is an excellent protective coating material as it has a stable physical barrier between the base metal and the active medium to prevent diffusion and permeation of electrolytes [6]. Hence, the graphene was added as the reinforcement filler in the polyester resin based primer coatings.

The mixing technique is very crucial to determine the properties of the primer coatings, as dispersion is the vital factor in obtaining excellent mechanical, thermal and corrosive properties in polymeric coatings. A variety of methods to promote dispersion have been reported, using mechanical techniques including high shear mixing, tip sonication, milling, injection moulding, melt blending and many more [7, 8].

In this paper, polyester filled graphene was proposed using sonication and mechanical method with various reactions times from 30-90 minutes. The sonication method and mechanical stirring were being chosen in this research because sonication is the main technology for mixing nanoparticles with the polymer matrix. Sonication also provides a uniform dispersion of nanoparticles, destroys the aggregate of nanoparticles and degassing polymer matrix [9]. Whilst, mechanical stirring is the old ways of mixing method that has been widely used until today. Therefore, this research was proposed to investigate the difference of sonication technique and mechanical stirring method as well as to estimate how the time reactions are effected on the corrosive properties of primer coatings. Apart from that, new knowledge regarding different mixing techniques also can be gained. The corrosive properties of the primer coatings were evaluated using Tafel measurement test and immersion test in 3.5% NaCl solution for 9 days.

The significance creation of this research paper was about the interaction of graphene with polyester resin by using different mixing techniques to improve the dispersion of graphene. Besides that, as compared with studies from previous research, this research was focusing on the dispersion of graphene into the polyester resin by using sonication method and mechanical stirring which affects the corrosive properties of the primer coatings regardless of the mixing techniques. Moreover, from previous research, there were limited papers regarding the effect of time that was studied in the determination of the optimum reaction time for dispersion of graphene into polyester resin. That is why this research was proposed.

2. Experimental

2.1. Materials and equipments

The chemicals used in this research were purchased from Fluka and used without further purification. The chemicals used were ethanol, sodium chloride (NaCl), polyester resin (SYNOLAC 9605S65 MY), methyl ethyl ketone peroxide (MEKP), graphene powder (900561 ALDRICH) and acetone. The equipments and instruments that used in this research were carbon steel plate (15 cm × 10 cm × 0.2 cm), hand brushes, ultrasonic bath or Cress ultrasonic model 4HT-1014-6 or sonicator, mechanical stirrer (WiseStir), Autolab PGSTAT240, and ATR-FTIR of Perkin Elmer Spectrum RX1 Fourier-transform infrared spectrometer.

2.2. Preparation of Polyester-Graphene (PE-GR) mixture

2% of GR equivalent to 1 g was dispersed in a minimum amount of ethanol at 5 mL by sonication (40 kHz, 27 °C) and mechanical stirring (1000rpm) for 1 h at 27 °C. Then required the amount of PE resin (5 mL) was introduced into the above dispersion and mixed for different reaction time which 30, 60 and 90 minutes. After that, 0.3 mL of the curing agent (MEKP) was added into the mixture and stirred [10].

2.3. Preparation of wet paint to coat the carbon plate

The prepared coatings was applied to the surface of carbon steel plates by using a hand brush to coat them for 3 layers and left to cure for 7 days at room temperature.

2.4. Characterization of Primer Coatings Produced

The produced primer coatings were undergone Fourier Transformed Characterization (FT-IR) for functional groups present determination. The spectra were evaluated on samples from a frequency range of 600 cm^{-1} to 4,000 cm^{-1}.

2.5. Autolab PGSTAT204 (potentiostat/galvanostat)

The spectra were evaluated on samples from a frequency range of 600 cm^{-1} to 4,000 cm^{-1}. 2.5 Autolab PGSTAT204 (potentiostat/galvanostat). The coated steel plate was immersed into the 3.5% NaCl solution that placed in the beaker together with platinum foil and a saturated calomel electrode which act as a counter electrode and a reference electrode, respectively using an Autolab PGSTAT204.

2.6. 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 sea water and salt solution (3.5% of NaCl) for 9 days at room temperature and observed visually.

3. Results and Discussion

3.1. FT-IR analysis

The FT-IR spectrum of GR (Figure 1), the spectrum of pristine graphene, showed the peaks of aromatic C-H stretching at 3532.60 cm^{-1}, while the peaks of aromatic C=C has appeared at 1710.35 cm^{-1}. Upon the association of graphene with unsaturated polyester resin, the C-H stretching peak of graphene showed that the shifted of the peaks to 3596.80 cm^{-1} which indicates that the OH groups in the unsaturated polyester resin. This finding was in line with the findings by Bora et al. [2] in their previous research. The new peaks were found in the spectrum of graphene associated with unsaturated polyester at 2950 cm^{-1} and 2830.43 cm^{-1} which is highlighted in the green box in Figure 1. These peaks indicated that the C-H stretching of polyester resin which was shifted from the graphene. Besides that, in the turquoise box, the new peaks appeared at 1788.19 cm^{-1} which indicates that the C=O of the ester group of polyester resin. The aromatic C=C stretching of polyester resin was shifted from 1710.35 cm^{-1} to 1679.20 cm^{-1}. The peaks at 1079.85 cm^{-1} and 1231.35 cm^{-1} bands appear for C-O-C stretching vibrations attached with aliphatic and aromatic moiety. These peaks indicated that the graphene filler was successfully grafted onto the unsaturated polyester resin. Previous research by Swain [11] found that PE-GR forms C-O-C groups at 1045-1095 cm^{-1} that confirms that PE reacts with carboxyl over the GR to form the composite.

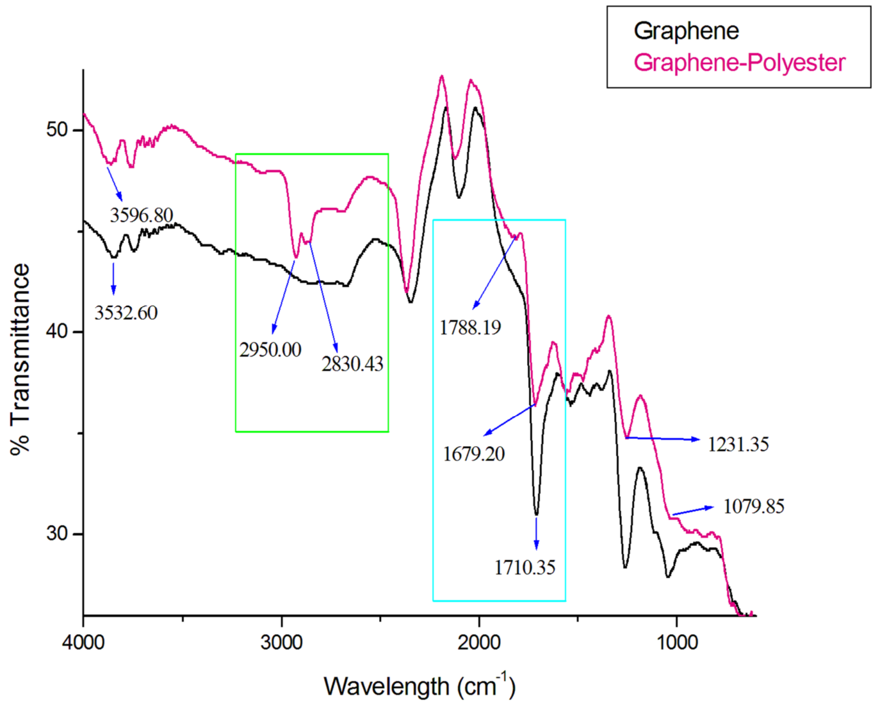


Figure 1: FT-IR spectrum of graphene and graphene-polyester.

3.2. Autolab PGSTAT204 (potentiostat/ galvanostat)

Results for Tafel plot polarization of polyester-graphene coatings have been presented in Table 1. Based on Table 1, the higher the reaction time from 30-60 minutes, the lowest (corrosion rate, corrosion current) and the highest the (polarization resistance, corrosion potential) for sonication and mechanical mixing method. This is indicated that the dispersion of the graphene into the polyester resin was achieved and no agglomerations occurred [12]. The graphene was well dispersed in the polyester resin which makes the coatings become protected from deterioration. However, the extension of the reaction time to 90 minutes for both mixing method, the enhancement in the graphene dispersion was very poor. Besides that, the agglomerations of the graphene in the polyester resin make it produced voids and hence allowed the electrolyte to pass through easily as well as reduced the corrosion inhibitor properties of the coatings. The agglomeration of graphene has occurred because the graphene particles were damaged and had defects in the structure during excessive energy provided to the dispersed particles, resulting in reagglomeration of broken particles [13]. In other words, once the graphene sheets were cut into pieces small enough during one hour sonication, they tended to restack together with the extension of sonication time [14]. This is proven by increasing in corrosion rate at 1.149 millimeter per year (mmpy), and 1.249 mmpy for sonication and mechanical method, respectively.

The optimum corrosion rate for the sonication method and mechanical method were at 60 minutes reaction time with readings of 0.375 mmpy and 0.536 mmpy, respectively. This is attributed to the good utilization of graphene into the polyester resin make it protected from electrolytes and free from corrosion. Also, the coating exhibits optimum barrier properties compared to the other reaction times (30 minutes and 90 minutes). This is proved by the highest polarization resistance, Rp at 88.974 Ω for sonication method, whilst, 78.941 Ω for mechanical stirring which indicates that the higher the value of Rp, the higher the resistance of the coating towards the corrosion [15, 16] The greater the corrosion potential, Ecorr towards positivity, the lowest the corrosion current, icorr, which reduced the potential of electrolyte from entering the substrate.

As compared between sonication and mechanical method, the sonication method was the optimum method. This is due to the quality of nanocomposites produced by mixing nanoparticles with liquid resin using mechanical stirring only is significantly less than the quality of mixing using the sonication method. The sonication is a treatment by ultrasonic waves going from a vibrating indenter as it helps to exfoliate graphene particles originally consisting of several layers. During sonication, the local temperature and pressure used can lead to splitting macromolecules, changes in the structure of macromolecules to more grafted one, and creation of free radicals. Sonication provides a uniform dispersion of nanoparticles, destroys aggregate of nanoparticles and many more [9, 17]. Therefore, sonication was much better quality than the mechanical stirring method.

Table 1: Results for Tafel plot polarization of polyester- graphene coatings.

Mixing method/time	Corrosion potential, E_{corr} (mv)	Corrosion current, i_{corr} (μA/cm^2)	Corrosion rate (mmpy)	Polarization resistance (Ω)
Sonication/30 min	-332.220	45.6780	0.498	65.880
Sonication/60 min	-243.880	32.2920	0.375	88.974
Sonication/90 min	-412.650	56.7450	1.149	43.298
Mechanical/30 min	-368.980	52.4530	0.678	50.264
Mechanical/60 min	-347.260	48.7780	0.536	78.941
Mechanical/90 min	-436.700	63.6850	1.249	29.658

3.3. Immersion test

The results of immersion testing in seawater and salt solution follows the same trend with Tafel polarization measurements which are the higher the reaction times from 30-60 minutes, the lowest the corrosion occur on a steel plate for sonication and mechanical stirring techniques of coatings. The utilization of graphene in the coatings makes the corrosion protection increased, and the steel plate last longer.

The optimum result that gives the good barrier property was at 60 minutes reaction times with the sonication method. It gives no contact between the metal substrate and electrolyte as they cannot pass through the coating surfaces. It also shows the optimum result for corrosion as it only shows small flacking without the corrosion at “X” scratched after 9 days of immersion. The highest corrosive resistance of coating for the mechanical stirring method was at 60 minutes of reaction time as the plate was not corroded at all as well as the blistering and flaking have not occurred. This is due to the well dispersion of graphene into the polyester resin and the mixture became homogeneous and hence, inhibits the corrosion to occur. The dispersion of graphene in the coating gives no agglomerations occurred and inhibits the contact between the electrolyte and the metal substrate as well as the coating exhibits better barrier property than the other reaction times [12, 16]

Table 2: Immersion test for polyester-graphene coatings via sonication and mehanical method in seawater and salt solution after 9 days.

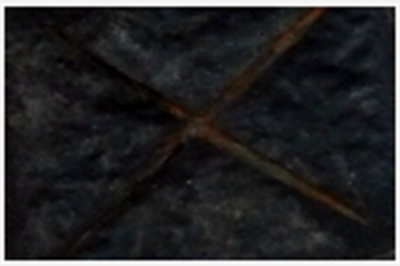
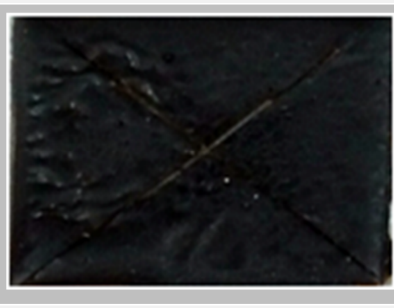
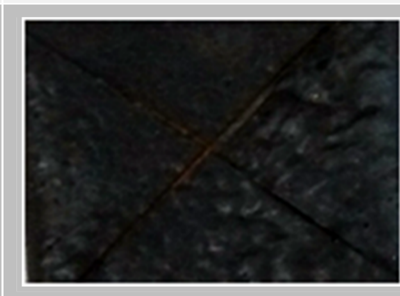
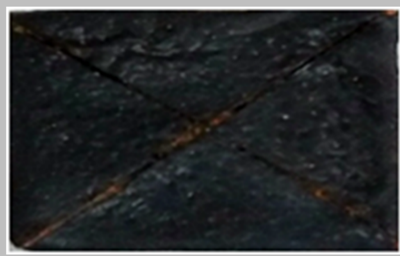
Mixing method/time	Seawater	Salt solution
Sonication/30 minutes		
Sonication/60 minutes		
Sonication/90 minutes		

Table 2: Continue

Mixing method/time	Seawater	Salt solution
Mechanical/30 minutes		
Mechanical/60 minutes		
Mechanical/90 minutes		

The particle size gradually decreased as the dispersion time increased, and reached the primary particle size, indicating that the graphene was dispersed into polyester resin. However, at 90 minutes reaction time for both mixing method, the steel plate was corroded a little. This is due to the agglomeration that occurred as the graphene particles were damaged and broken during excessive energy was provided to the dispersed nanoparticles, resulting in reagglomeration of broken particles [13] and dispersion of graphene into the polyester resin was not achieved well.

The immersion test results by using 3.5% of NaCl solution as a medium solution shows the higher rate of corrosion when compared to the immersion in seawater as the salt solution was more aggressive towards carbon steel plate than seawater [18]. For this testing, the trends were similar as the sea water immersion testing whereas the optimum reaction times for sonication method was at 60 minutes which suitable enough for dispersion of graphene and enhanced the inhibition properties of the coatings from corrosion to occur. It shows that no corrosion and blister occurred at the “X” scratched. This is also in line with the mechanical stirring method which the optimum corrosive resistance properties of the coating were at 60 minutes reaction time. According to Hao et al. [19] in his research, filler functions to inhibit the corrosive medium to pass through the coating. It means that the contact between electrolyte and metal substrate was not occurred which resulting in no corrosion occurred.

In comparison, of the mixing techniques, the sonication method was better than mechanical stirring. It is the same trend with the Tafel polarization test, which the graphene was dispersed well and become homogeneous with the polyester resin as the sonication method is a way good quality compared to mechanical stirring method [16]. This is due to the sonication is a treatment by ultrasonic waves going from a vibrating indenter as it helps to exfoliate graphene particles originally consisting of several layers. During sonication, the local temperature and pressure used can lead to splitting macromolecules, changes in the structure of macromolecules to more grafted one, and creation of free radicals. Sonication provides a uniform dispersion of nanoparticles, destroys aggregate of nanoparticles and many more [9, 17].

4. Conclusions

It was observed that the dispersion of graphene in a polyester resin via sonication and mechanical stirring at different reaction time from 30-90 minutes have an effect on the corrosive behavior of the primer coatings. The FT-IR analysis was done to determine the functional group involved and to ensure that the graphene has been grafted onto the polyester resin. The Tafel testing and immersion testing was done successfully and the results showed that the optimum reaction time for both mixing techniques was at 60 minutes. This is proved that the graphene was dispersed well in the polyester resin and become homogeneous to inhibit the corrosion. However, the best mixing technique was the sonication method as it has a good quality compared to mechanical stirring. This is supported by the results obtained from Tafel testing and immersion test, which indicates that the results obtained for sonication were much better than mechanical stirring.

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