The parametric study on anti-corrosion properties produced by electrochemically exfoliated

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Abstract. Graphene nanocomposite coatings has arisen topic of vast scientific interest due to the superior properties of graphene. In this study, we used electrochemically exfoliated graphene (EC-G) as a filler of polystyrene paints. Using solution blending method, a fine dispersion of polystyrene graphene (PS/G) paints could be attained. The anti-corrosion properties were proven by potentiodynamic polarization curves. The PS/G paints could boost the anti-corrosion properties with the loading of 0.5 wt% ECG, in which the corrosion rate decrease two degree levels from $2.37 \times 10^{-3}$ to $2.32 \times 10^{-5}$ mm/yr.

Keywords: polystyrene, electrochemically exfoliated graphene, coating, corrosion

1. Introduction

Nanocomposite coatings become massive potential for industrial coating applications recently. Creating and improving the novel structure and properties of material, flatters to be the fastest-growing area research of interest. Nanocomposite coatings can enhance durability and performance through smart coatings at lower cost [1-3]. Nanocomposite coatings introduce nanofillers into organic polymers to get superior properties. Organic polymeric coatings prevent corrosion by forming a barrier to insulate the metal from the corrosive environment. Yet, polymeric coatings are permeable to the corrosive species [4]. Hence incorporating nanofillers can lessen the permeability and extend the lifetime of the composite coatings [5].

Graphene is a single atom thick sheet comprised of sp2-hybridized carbon atoms, exhibits unique physicochemical properties and exceptional mechanical properties [6]. Graphene also has good barrier properties and impermeable to all gases and liquids [7]. Due to this reason, graphene can be developed as an outstanding candidate for nanofiller of polymeric coatings. Polystyrene has an excellent colour and chemical stability which usually used for protective and decorative coatings. Yu, Y.H et al [8] were success making well-dispersed polystyrene (PS)/modified-GO for corrosion protection using in situ miniemulsion polymerisation. However, need complex steps for its preparation.

Some studies [9, 10] used electrochemically exfoliated graphene (ECG) as filler for their nanocomposite coatings and prepared it with simple method. They just prepared the suspension by solution blending and obtain outstanding anti-corrosion properties for their coatings. Thus, in this work,
we also try to employ ECG for filler in the polystyrene coatings, addressing the complex preparation issue.

2. Materials and Methods

2.1 Materials

Extra pure reagent of polystyrene was purchased from Nippon Shiyaku Kogyo K.K (Japan). The electrochemically exfoliated graphene (EC – graphene) was synthesized based on the previous research [11]. The as-prepared graphene was dried at 60°C in vacuum oven. As calculated in accordance with the amount of polystyrene, the graphene dispersion was balanced (0.5 g, 0.1 g, and 0.15 g for 0.25 wt%, 0.5 wt% and 075 wt%). Then dispersed in 10 mL THF (Sigma Aldrich) using tip sonication. The polystyrene pellets were also dispersed in 10 mL THF. Both suspensions then stirred together using magnetic stirring for a couple of minutes to get a well-dispersed nanocomposite suspension.

A copper specimen (Alfa Aesar) with an area of 1 cm² was polished and cleaned. Before the polystyrene – graphene (PS/G) suspension was coated on the specimens, it was sonicated in the bath sonication for 10 minutes to remove the air bubbles. After coating, the specimens were dried at room temperature. The prepared specimens were used as the working electrode of electrochemical measurement.

2.2 Electrochemical measurements

The anti – corrosion inhibition properties of the PS/G coating was examined by electrochemical tests (potentiodynamic polarization measurements) using an Autolab PGSTAT 302 N machine. Measurements were performed in a 0.1 M NaCl solution at room temperature. A three – electrode system was used with a Pt wire as a counter electrode and Ag/AgCl as reference electrode. The open circuit potential (OCP) was monitored for 1 h to confirm the stability. When a stable OCP was obtained, the linear sweep voltammetry was set to +100 and -100 mV relative to the OCP. The sweep rate was mV/s. The corrosion potential (Ecorr) and corrosion current (Icorr) were determined by Tafel extrapolation.

3. Results and Discussions

3.1. Physical properties of PS/G paint

Figure 1. The nanocomposite suspension in THF (a) pure polystyrene (b) PS/G – 0.25 wt% (c) PS/G – 0.5 wt% (d) PS/G – 0.75 wt%

An excellent dispersion quality of PS/G paint is shown in the Figure 1. EC-graphene can dissolve well without any agglomeration. The dispersion of paint is one of factor that influence the anti – corrosion performance. A good dispersion will enhance the interfacial material of filler and polymer [12]. The uniformity of PS/G paint also can be observed from the drawdown card which had been coated by it. As demonstrated in the Figure 2, the paint can spread well giving the smooth surfaces.
3.2. Anti-corrosion properties of PS/G paints

Table 1: Potentiodynamic polarization parameters for copper coated PS/G paints

| Sample         | $E_{corr}$ (V) | $I_{corr}$ (µA.cm$^{-2}$) | $\beta_a$ (mV) | $\beta_c$ (mV) | CR (mm/yr) |
|----------------|----------------|--------------------------|----------------|----------------|-------------|
| Bare           | 0.048          | $5 \times 10^{-1}$       | 82.5           | 111.4          | $1.17 \times 10^{-2}$ |
| PS             | 0.019          | $1 \times 10^{-1}$       | 79             | 75.6           | $2.37 \times 10^{-3}$ |
| PS/G 0.25 wt%  | -0.062         | $5 \times 10^{-3}$       | 65.8           | 57             | $1.16 \times 10^{-4}$ |
| PS/G 0.5 wt%   | 0.004          | $1 \times 10^{-3}$       | 22.8           | 29.2           | $2.32 \times 10^{-5}$ |
| PS/G 0.75 wt%  | 0.096          | $2 \times 10^{-2}$       | 28.8           | 28.3           | $3.94 \times 10^{-4}$ |
The potentiodynamic polarization curve of log I versus E were constructed for a potential range of -100 to +100 mV relative to \( E_{OCP} \). The electrochemistry parameters were obtained from extrapolating the cathodic and anodic plot from potentiodynamic polarization curve. All parameters are listed in Table 1.

Figure 1 shows that the \( E_{corr} \) of sample coated pure polystyrene (0.019 V) is shifted to the left site compared to the \( E_{corr} \) of bare Cu (0.048 V). Polystyrene is the type of non-conjugated polymer which provide the corrosion protection on metal by forming gas barrier [8]. The \( \beta_c \) value of sample PS is larger than the \( \beta_a \), indicates that the formed gas barrier may cannot sustain the diffusion of corrosive agent (\( O_2 \) and \( H_2O \) gasses). Therefore, the protection is from the passive film which created by anodic reaction in anodic side. Incorporating 0.25 wt% and 0.5 wt% of graphene shifted the \( E_{corr} \) more to the negative value, while for 0.75 wt% graphene loaded in composite cause \( E_{corr} \) shifted to the positive value. EC-graphene protects the coated metal from both anodic and cathodic site.

Moreover, the corrosion current density decreased with the increase of graphene loading until reaching the maximum value (Table 1). The lowest current density value was achieved within the graphene loading of 0.5 wt%. It implies that the optimum protection of PS/G paints was occurred at that condition. Suggesting that EC-graphene act as excellent filler. The optimum corrosion rate exhibited two degrees reduction compared with pure PS coating (2.37 \( \times \) 10^{-3} to 2.32 \( \times \) 10^{-5} mm/yr).The results of this study shows the some mechanism trend with our previous study [10], that EC-graphene could provide the long diffusion pathway than pure polymer.

4. Conclusion
Incorporating EC-graphene could improve the anti-corrosion properties of polystyrene. The loaded EC-graphene at 0.5 wt% reduced the corrosion rate up to 2.32 \( \times \) 10^{-5} mm/yr which is two degrees lower than the corrosion rate of pure polystyrene. The excellent PS/G nanopaints were prepared only using a simple mixing method. And could the good dispersion of the paints.

References
[1] Silverman, J.B.E., Challenges and opportunites in multifunctional nanocomposite structures for aerospaces applications. MRS Bull, 2007. 32(04): p. 1415-1423
[2] Liu, K., Y. Tian, and L. Jiang, Bio-inspired superoleophobic and smart materials: design, fabrication, and application. Progress in Materials Science, 2013. 58(4): p. 503-564.
[3] Kim, H., A.A. Abdala, and C.W. Macosko, Graphene/Polymer Nanocomposites. Macromolecules, 2010. 43(16): p. 6515-6530.
[4] Abu-Thabit, N.Y. and A.S.H. Makhlouf, Recent Advances in Nanocomposite Coatings for Corrosion Protection Applications, in Handbook of nanoceramic and nanocomposite coating and materials. 2015, Elsevier Ltd. p. 515-549.
[5] Gopakumar, T., N. Patel, and M. Xanthos, Effect of nanofillers on the properties of flexible protective polymer coatings. Polym. Compos, 2006. 27(4): p. 368-380.
[6] Geim, A.K. and K.S. Novoselov, The rise of graphene. Nature Materials, 2007. 6(3): p. 183-191.
[7] Bunch, J.S., et al., Impermeable atomic membranes from graphene sheets. Nano Letters, 2008. 8(8): p. 2458-2462.
[8] Yu, Y.H., et al., High-performance polystyrene/graphene-based nanocomposites with excellent anti-corrosion properties. Polymer Chemistry, 2014. 5(2): p. 16.
[9] Wang, P., et al., A cost-effective method for preparing mechanically stable anti-corrosive superhydrophobic coating based on electrochemical exfoliated graphene. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2016(COLSUA-21138): p. 6.
[10] Dutta, D., et al., Revisiting graphene-polymer nanocomposite for enhancing anticorrosion performance: a new insight into interface chemistry and diffusion model. Nanoscale, 2018. 10(26): p. 12612-12624.
[11] Su, C.Y., et al., *High-Quality Thin Graphene Films from Fast Electrochemical Exfoliation*. Acs Nano, 2011. **5**(3): p. 2332-2339.

[12] Sung, F.a., *Nanotechnology Applications in Coatings*. ACS Symposium Series, 2009.