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Exploring the Effects of Nanofillers of Epoxy Nanocomposite Coating for Sustainable Corrosion Protection

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Development of coating durability and sustainability for industry to facilitate the corrosion potential minimization attract much attention in recent year. The selection of appropriate coating material is necessities to improve corrosion protection of metal. Epoxy nanocomposite coatings filled with different amount of graphene nanoplateles (GNP) and montmorillonite (MMT) was prepared via mechanical agitation process to enhance the flame retardancy and anticorrosion performance of mild steel substrates. Salt fog test, limiting oxygen index (LOI) and water absorption result reveal that embedding a small amount of filler remarkably improved anticorrosion performance and flame retardancy of epoxy nanocomposite coatings. Present study suggests a development of nanocomposite coating with superior mechanical properties which was evaluated by adhesion tape test.

1. Introduction

Sustainable development strategies on corrosion protection have been considered as a crucial element that should be highlighted simultaneously and holistically in the development process. Deterioration due to corrosion cannot be fully prevented, and thus, corrosion control strategies focus on slowing the kinetics and/or altering its mechanism. Good corrosion protection such as by utilization of polymer coating could possibly contribute to realization of sustainability and environmental stewardship.

Epoxy materials are widely used due to their excellent scratch hardness, good adhesion strength and wear endurance (Barletta et al., 2007). Despite significant improvements in coating technologies, problems continue in the long-term protection of metal from aggressive environments (Radhakrishnan et al., 2009). Continuous effort has been carried out to further enhance and prolonged the service of epoxy coating. Furthermore, flammability is the major limitation of epoxy coating particularly for applications that require high flame retardancy for instance in oil and gas industry (Tugnoli et al., 2013). Previous studies have shown that the barrier performance of epoxy coatings was enhanced by the incorporation of a second phase i.e. inhibitive pigment that is miscible with the epoxy polymer, by decreasing the porosity and zigzagging the diffusion path for deleterious species (Li et al., 2017) due to their effectiveness and appropriateness.

The inclusion of nanofiller in polymeric coatings such as layered silicate can greatly improve their corrosion resistance, thermal stability, flame retardancy, transparency, colour purity, resistance to organic solvents and reduce the tendency for the coating to blister or delaminate (Nazari and Shi, 2016). Moreover, nanocomposite coating has attracted a lot of attention as a simple and cost effective method of enhancing coating properties by the addition of a small amount of properly designed and dispersed nanoparticle fillers (Wang et al., 2006).

Previous studies focused on the anticorrosion properties of epoxy nanocomposite coating filled GNP (Shuan, 2016) and MMT (Tomić et al., 2014) have been reported. One related work studied by Nematollahi et al. (2010) shows the effect of nanoglass flake (GF) and MMT on anticorrosion performance of epoxy coating. They revealed that epoxy nanocomposite filled with GF showed a greater barrier property and great improvement of adhesion to substrate as the nanoparticles loading is increased up to 3 wt% compared to MMT filled ones and

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neat epoxy. In other relevant research, Wang et al. (2012) has reported the effect of different contents of nano-sized mesoporous silica MCM-41 and MMT on corrosion properties of epoxy coating. The results of salt fog test showed that at same filler loading, the incorporation of MCM-41 gave rise to a much better enhanced effects than epoxy filled MMT nanoparticles coating.
So far, no systematic study comparing the effect of GNP and MMT to enhance anticorrosion properties and flame retardancy of epoxy coating has been reported. The objective of this paper is to compare the effect of two different types of nanofillers; GNP and MMT on flame retardancy and anticorrosion performance of epoxy nanocomposite coatings used in protecting and providing long-term durability to mild steel plate. The flame retardancy was investigated by limiting oxygen index (LOI) while anticorrosion performance was examined via salt fog tests.

2. Methodology

2.1 Materials

Diglycidyl ether of bisphenol A (DGEBA) epoxy resin (BE-188), polyamine hardener (H2310 polyamine amide) were bought from by Mc-Growth Chem. Graphene was purchased from XG Science Inc., East Lansing, USA. 50 mm × 50 mm × 1.5 mm dimensions of mild steel plates were used for EIS and Tafel Polarization test.

2.2 Preparation of nanocomposites

In this research, the properties of epoxy nanocomposite coating filled with different types of filler i.e. GNP and MMT were considered. Nanofillers were dispersed in ethanol (1:250 mL solvent) with sonicator ultrasonic treatment for 15 min to prepare nanofillers suspension which was then put in the fume hood to evaporate the ethanol and therefore it can reduce the formation of an air bubble in the mixture. The nanofiller suspension was directly added to epoxy resin (E) and slowly stirred at ~200 rpm by mechanical stirrer for 15 min. Finally, stoichiometric amount of hardener with a weight ratio 2:1 was added into the mixture and continuously stirred until uniformly mixed (Table 1). The composition of GNP and MMT is not standardized because the amount of effective fillers are in the different range i.e. 0.6 to 1.0 for GNP and 0.5 to 2.0 wt% for MMT. The prepared coatings were then coated onto mild steel plates to form ~0.25 mm thickness of coating samples using a doctor blade film applicator. The coatings were left at room temperature for 24 h in the fume cupboard for curing process.

Table 1: Formulation of the nanocomposite coatings filled GNP and MMT

Sample	Composition (wt%)			
	BE188	Hardener	GNP	MMT
E0	66.7	33.3	-	-
EG0.6	66.7	33.3	0.6	-
EG0.8	66.7	33.3	0.8	-
EG1.0	66.7	33.3	1.0	-
EM0.5	66.7	33.3	-	0.5
EM1.0	66.7	33.3	-	1.0
EM1.5	66.7	33.3	-	1.5
EM2.0	66.7	33.3	-	2.0

2.3 Characterization and property measurements

Limiting Oxygen Index (LOI) was measured using Dynisco Instruments, USA according to ASTM D 2863 with dimensions of 80 mm × 10 mm × 3 mm^2.
Salt fog test was performed on scratched coated plates with dimensions of 100 mm × 100 mm × 1.5 mm^2 for 200 and 500 h exposure to accelerate corrosive environment in salt fog chamber according to ASTM B117 standard.
The adhesion of epoxy filled GNP and MMT coatings on mild steel plate substrates were examined according to ASTM D3359 standard.
A static immersion test was conducted to evaluate water resistance of films according to ASTM D570-98 standard. 50 mm × 50 mm × 1.5 mm samples were immersed in distilled water and the water uptake (M_t) of the specimens at specific time interval was expressed as a function of time in Eq(1):

$$M_t = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

M_t is the percent of water uptake, W_t denotes the weight of the films at different times and W_0 is the initial was characterized.
The dispersion of nanofillers in epoxy coatings were evaluated by HRTEM 120 KV Hi-Tech Instruments.

3. Result and discussion

Figure 1 shows the LOI value for EG and EM nanocomposite coatings. It can be seen that all samples including neat epoxy represents more than 21 % LOI values which indicated they are unlikely to support burning and provide an excellent flammability resistance. Nanofillers can acts as a barrier and reluctant the heat released and hinder the transfer of the combustion of gases to the flame zone (Lewin, 2003). LOI value increase with the continuously increasing content of GNP and MMT with 1.0 wt% GNP demonstrated the highest LOI value of 24. The results are in agreement with previous work by Huang et al. (2012). A studied showed the linear relationship of LOI values with graphene contents fitted well with trend for char formation i.e. increasing graphene content corresponded to the increment of char residual. Well dispersed filler adequate of forming a continuous network, which act as a heat shield (Bhattacharya, 2016). LOI maintained at constant level of 23.5 % indicating an optimum MMT filler loading is about 1.5 wt%. EG was found exhibits much greater flame retardancy properties than EM. The results are in agreement with previous work by Huang et al. (2012) which revealed that, graphene possess a stronger effect as flame retardancy in PVA matrix than MMT and MWNTs.

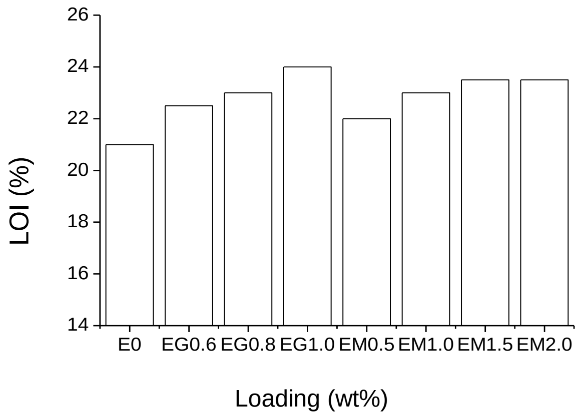

Figure 1: LOI values of EP and EM nanocomposite coatings

The anticorrosion performance of EG and EM nanocomposite coatings after 200 and 500 h exposing to 5.0 wt% NaCl solution is visually inspected as shown in Figure 2 while the blistering grade is tabulated in Table 2. Mild steel plate coated with neat epoxy system underwent severe corrosion compared to nanocomposite filled with GNP and MMT coatings. Medium size of blisters were seen near the scratches area and over the whole coated surface in the neat epoxy coating sample with a brown adherent corrosion product (Figure 2a). Few blisters and rust are present on surface of other coated plates of EG0.6, EG0.8, EM0.5 and EM1.0 coating surface after 200 hours of exposure. Meanwhile, no blister was seen on surface of EG1.0, EM1.5 and EM2.0 samples that suggest an indication that no apparent localized corrosion attack after 200 hours of exposure time in salt fog chamber. At the same nanofillers loading (1 wt%), EG coatings perform better anticorrosion performance than EM. Nanocomposite coatings consist of plate-like filler with high aspect ratio and hydrophobic characteristic offer by GNP have particularly interest as barrier materials (Feller et al., 2015). The well-dispersed graphene blocking the pores/defect and attenuated the electrolyte diffusion (Liu et al., 2016) toward the substrate. Previous study has proved that the use of MMT are effective in increasing the anticorrosion performance of coatings and decreasing the degradation and blister density of coatings samples (Bagherzadeh and Mahdavi, 2007) through the formation of a nano-network composite (Wang et al., 2012). The large surface area and stronger attractive interactions as a result of exfoliation attributes to high performance polymer/layered silicate nanocomposite (Vaia et al., 1999).
The results from the visual examination of the exposed coated mild steel plate to salt fog test after 500 h clearly suggest that the incorporation of GNP and MMT enhanced the anticorrosion performance of epoxy coating. Results disclosed that, the rust width after 500 h exposure in salt fog chamber for EG and EM nanocomposite coatings were less than neat epoxy coating (more than 2.5 mm compare to EG and EM i.e. between 2.0-2.5 mm). This result enables us to conclude that particularly GNP and MMT efficiently enhances anticorrosion performance of the epoxy coating especially at 1.5 wt% MMT content. Therefore, this study is coincide with

previous result by Tomić et al. (2014). However, they reported that, the best corrosion protection performance of epoxy/clay nanocomposite was at 1.0 wt% clay loadings, due to enhanced clay dispersion in epoxy coatings. Present study indicates, when the fillers content are high (more than 1.5 wt% MMT) the barrier performance start to decrease. Low compatibility of clay particles with epoxy coating causing particles aggregation therefore lead to poor adhesion to the polymer matrix and enabling electrolyte to penetrate into the interlayer space of platelets (Bhattacharya, 2016).

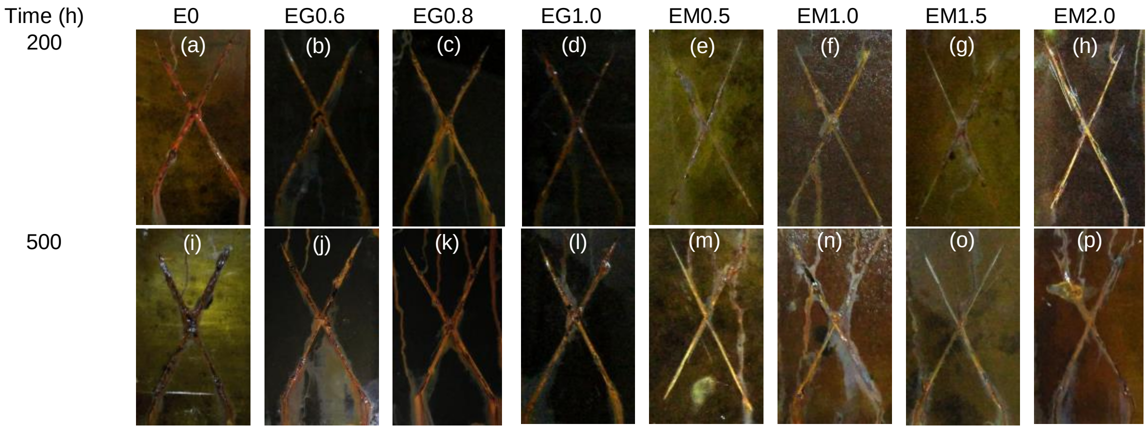

Figure 2: Visual appearance of mild steel plate coated with neat (E0), EG and EM coatings after 200 and 500 h of exposure in salt fog chamber

The results of adhesion test for coated mild steel plate before and after 200 h immersion in 5.0 wt% NaCl solution are depicted in Table 2. Before the plates are exposure to salt solution, epoxy filled GNP and MMT coatings possess an excellent adhesion and the adhesion strength values are similar for all samples. The enhancement in coating adhesion presumably is due to the interaction between the epoxy matrix and nanofillers. However, after 200 h exposure in the salt solution, the coating adhesion for neat epoxy dropped significantly from 5 B to 0 B, while sample with 0.8 wt% GNP exhibited an optimum adhesion strength. When the content of nanofiller loading was higher than the optimum, GNP tend to restack (Figure 3a). Corrosive solution easily found their way to penetrate through the coating pores and reach the metal substrates, initiating of electrochemical processes on the metal surface (Hosseini et al., 2009).

Table 2: Adhesion test results and blistering grade after expose to 5.0 wt% NaCl solution

Sample	Adhesion strength		Blistering grade after exposing	
	Before exposure	After 200 h exposure	200 h	500 h
E0	5B	0B	Medium	Medium
EG0.6	5B	2B	Few	Few
EG0.8	5B	3B	Few	Few
EG1.0	5B	2B	None	Few
EM0.5	5B	1B	Few	Few
EM1.0	5B	2B	Few	Few
EM1.5	5B	2-3B	None	None
EM2.0	5B	2B	None	Few

Incorporation of platelet and silicate layers attenuated the penetration of electrolyte solution through the coatings and this reduction is more notably for 1.5 wt% MMT samples. Adhesion strength start to decrease after 1.5 wt% MMT content probably due to poor dispersion and agglomeration of the nanofiller (Figure 3b). The adhesion test results coincided with the results of salt fog test. Adhesion bonds destruction is relatively increase of coating delamination from the substrate thus enables the corrosive agent passed through the metal. The nanoparticles occupy the voids, crevices and of the polymer and substrates and improve coating adhesion to substrates (Nematollahi et al., 2010). Wang et al. (2012) showed that MCM-41 and MMT favour to fill small holes defects formed from local shrinkage during curing of the epoxy resin and acted as a bridge interconnecting more molecules.

(a) (b)

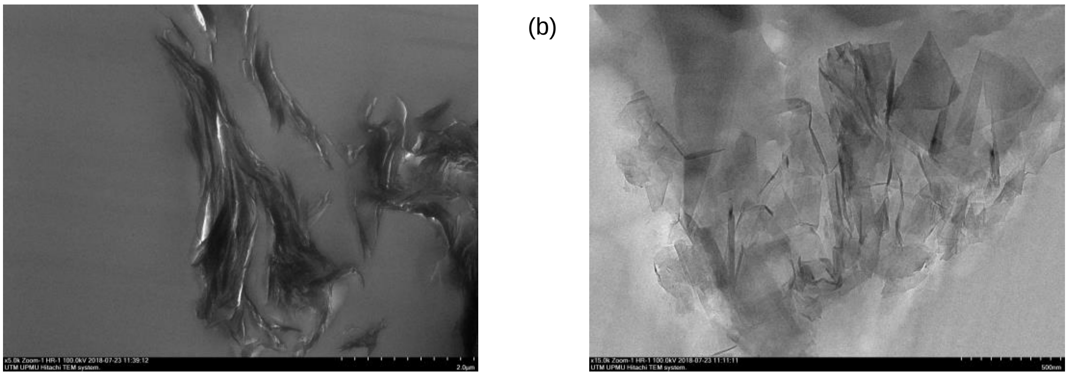

Figure 3: TEM images (a) 1.0 wt% GNP (b) 2.0 wt% MMT

The inclusion of nanofillers essentially diminished water absorption rate (Prolongo et al., 2014) that might be presumably due to the interaction between the epoxy matrix and nanofillers. Well-oriented nanofillers hindering the amelioration of water molecules and force them to follow a more tortuous path. Beneficial effect of nanofillers as efficient barriers against transport of water through the polymer coating is resulting from the increased path length for molecules diffusing through the material (Šupová et al., 2010). Hydrophilic nature of neat epoxy resin in contrast to GNP which presents hydrophobic behaviour is a factor affecting correlation of water uptake (Figure 4). Nevertheless, at higher loading, the reduction in water absorption is restricted due to the poor nanofillers–epoxy interface, which generates the presence of voids. Nanoparticle fillers can promote the creation of pores that favour the penetration of water molecules through coating and consequently have a negative influence on durability. Result demonstrates GNP exhibited better water resistance properties compare to MMT at the same nanofillers loading of 1 wt%. Water absorption behaviour of coatings containing Na^+-MMT could be due to the hydrophilic properties of Na^+-MMT(Bagherzadeh and Mousavinejad, 2012).

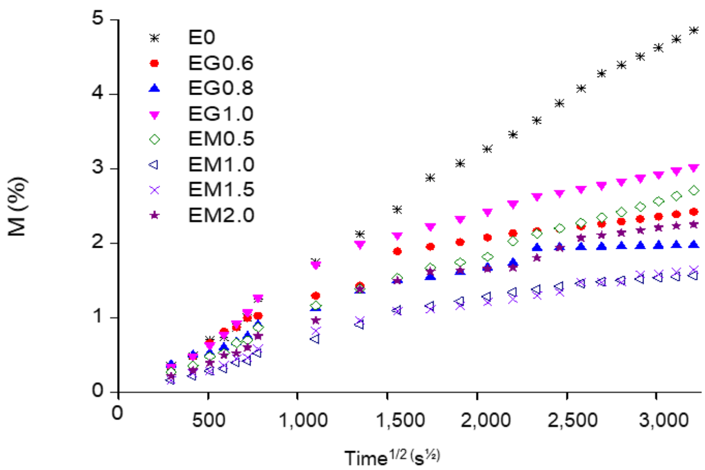

Figure 4: Water uptake of neat epoxy, EG and EM nanocomposite coatings

4. Conclusions

It was concluded that epoxy nanocomposite coating filled GNP and MMT exhibited significant improvement in anticorrosion performance and flame retardancy in comparison with neat epoxy coating sample. EG and EM samples showed a good barrier and flame retardancy property, and this property is exaggerated as the nanofillers content increased. GNP and MMT with 1.0 and 1.5 wt% are chosen as a sufficient GNP and MMT content with the best anticorrosion and flame retardancy performance. It is worthy to note that increasing nanofiller beyond an optimum loading, may attenuated the barrier properties and adhesion to substrates due to stacking and aggregation of nanofillers as well as reduction of the interface area. Altogether, the inclusion of nanofillers can contribute to more sustainable materials with increased long-term serviceability particularly at extreme conditions. As a continuation of this research, the effect of hybrid nanofillers on anticorrosion performance and flame retardancy of epoxy nanocomposite coatings, will be treated in a future publication.

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