

Synergistic Effect of Graphene Oxide/Halloysite in Anticorrosion Performance and Flame Retardancy Properties of Epoxy Nanocomposite Coating

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Synergistic effect composed of graphene oxide (GO) and halloysite (HNT) to serve as a promising anticorrosion performance and to enhance flame retardant (FR) properties of epoxy nanocomposite coating (NC) is studied. Using an epoxy as the matrix, GO/epoxy, HNT/epoxy, and hybrid GO/HNT/epoxy samples are prepared and the performance is characterized. The hybridization of GO and HNT leads to improve the barrier properties with EGO0.6H0.3 hybrid sample endows optimum synergistic effect. This is due to the improved state of nanofiller dispersion as well as better interfacial adhesion between the nanofillers and matrix which was confirmed by Transmission Electron microscopy (TEM) images. The Salt Spray test (SST) results corresponding to these effects reaffirmed that the corrosion resistance of the hybrid coatings improved with increasing the inorganic phase content. The thermal stability and flammability properties were investigated using Thermogravimetric Analysis (TGA) and Limiting Oxygen Index (LOI). The results of the LOI test showed that the addition of nanofillers marginally increases the LOI value of the epoxy NC. These results manifestly demonstrated that the formation of an efficient hybrid network slightly enhanced the coating performance through the synergy effect of hybrid nanofillers.

1. Introduction

Progressive destruction due to corrosion significantly affects the economy evolution, casualties and interrupts the technological development as well as structural failures which have a very detrimental impact on human beings and nature surroundings. Several anticorrosion technologies such as corrosion inhibitor, cathodic protection, and surface coating were implemented to solve these issues. Among these, the surface coating is the most often method used to protect or slow down the corrosion process. In nature, epoxy materials are widely used in the field of oil and gas sector due to their superior combination of chemical and corrosion resistance, excellent scratch hardness, wear endurance as well as good adhesion to most metals and alloy (Barletta et al., 2007).

However, epoxy resin suffers from inferior thermal and weathering stabilities and insufficient recoating times (Bakhshandeh et al., 2014). The major drawback associated to epoxy resins is flammability especially for applications that require high FR (Tugnoli et al., 2013) and poor resistance to crack propagation that facilitates the transfer of water, oxygen, and ions to the substrates surface, thus accelerating substrates corrosion.

Modification is required to resolve this situation through the addition of inhibitive pigment because they can simultaneously improve the barrier performance and to yield FR properties of the polymer due to its excellent thermal stability and gas barrier behavior (Zhu et al., 2001). Previous works demonstrated that the incorporation of nanofillers such as clays (Zhu et al., 2001) and graphene (Kabeb et al., 2019) are grabbed much more attention of many researchers due to its low cost and ease availability with least deleterious environmental and health impacts, which have been restricted by the environmental regulations (Shaw, 2010).

Owing to the ease of processing and lack of need for any chemical modification, the HNT has emerged as a promising candidate for epoxy resin for enhancing the properties of the hybrid material. GO is used as a co-dispersion agent (Zuo et al., 2017) to improve the dispersibility of HNT in an epoxy matrix. The homogeneous dispersion of hybrids GO/HNT result from unique structure and properties of GO sheets, enhanced interaction between nanofillers and matrix, consequently exhibit high corrosion protection properties. The presence of GO/HNT hybrids may provide appropriate coating systems for the protection of metal substrates with outstanding characteristics.

There were some reports on the use of hybrid graphene/MMT/polyimide (Zuo et al., 2017), GO/MMT/poly(vinyl alcohol) (Raheel et al., 2015), GNP/CNT/epoxy (Yang et al., 2011). Nevertheless, to date, no effort has been put on a systematic examination of the effect of hybrid GO/HNT/epoxy to enhance anticorrosion properties and FR of epoxy coating has been reported. Studied by (Li et al., 2014) shows the effect of reduced GO decorated with HNT (HNTs-d-rGO) on FR properties of polyamide 6 (PA6). The result indicates, the FR activity of integrated HNTs-d-rGO is higher compared with that of either HNTs, or GO, or a mixture of HNTs and GO (HNTs-m-GO) used in PA6 matrix. This might be attributed to the combination of the stable silica layer created by HNT and the barrier effect of rGO.

This work scrutinizes how additions of hybrid nanofillers into an epoxy matrix synergistically influence the anticorrosion performance and FR properties of epoxy NC. Determination of thermal stability and analysis of the microstructure of the coatings are also carried out in order to provide information and understanding of the overall influence of nanofillers addition in the epoxy matrix.

2. Methodology

2.1 Materials

Diglycidyl ether of bisphenol A (DGEBA) epoxy resin (BE-188), polyamine hardener (H2310 polyamine amide) were purchased from by Mc-Growth Chem. Graphene was bought from XG Science Inc., East Lansing, USA.

2.2 Preparation of nanocomposites

In this study, the properties of GO/epoxy (EGO), HNT/epoxy (EH), and hybrid GO/HNT/epoxy (EGOH) coating were characterized. Initially, nanofillers were dispersed in ethanol (1:250 mL solvent) with sonicator ultrasonic treatment for 15 min directly added to epoxy resin (E) and slowly stirred for another 15 min at ~200 rpm by a mechanical stirrer. A stoichiometric amount of hardener (2:1) was then added and the mixture was continuously stirred until uniformly mixed (Table 1). Finally, the prepared coatings were coated onto mild steel plates to form ~0.25 mm thickness of coating samples using a doctor blade film applicator. The coatings were cured at room temperature for about 24 h.

Table 1: Formulation of the epoxy nanocomposite coatings

Sample	Composition (wt%)			
	BE188	Hardener	GO	HNT
E0	66.7	33.3	-	-
EGO0.6	66.7	33.3	0.6	-
EH0.5	66.7	33.3	-	0.5
EGO0.6H0.2	66.7	33.3	0.6	0.2
EGO0.6H0.3	66.7	33.3	0.6	0.3
EGO0.6H0.4	66.7	33.3	0.6	0.4

2.3 Characterization and property measurements

Salt spray test (SST) was conducted on scratched coated plates with dimensions of 100 mm × 100 mm × 1.5 mm² for 200 and 500 h exposure in Q-FOG® cyclic corrosion chambers as specified in ASTM B117.

Limiting Oxygen Index (LOI) was carried out according to ASTM D 2863 Oxygen Test Method, Dynisco Instruments, the USA using a test specimen bar of 80 mm × 10 mm × 3 mm².

The thermal gravimetric analysis (TGA) measurement was conducted by the aid of a Perkin Elmer TGA/DSC at a thermal rate of 20 °C/min in the range of 20 - 500 °C. About 4-10 mg of the samples were heated from room temperature to 900 °C at a heating rate 10 °C/min under air temperature.

The morphology and dispersion state of nanofillers in the epoxy matrix was investigated by Hitachi, HRTEM 120 KV (HT7700) Instruments. TEM specimens with a thickness of around 60 nm were prepared by thin sectioning using Leica ultracut UCT ultramicrotome with a diamond cutter.

3. Results and discussion

The SST is an accelerated aging test method to evaluate the performance of the coating samples under extended exposure to a salted spray chamber. The visual comparison of the coating samples after exposure to 5.0 wt% NaCl solution up to 500 h are presented in Figure 1. Sufficient corrosion products and coating delamination generated at the scratch area after 200 h exposure for the coating embedded with single nanofiller compare to hybrid NCs. As the exposure time elapsed the corroded area progressed under the coating outside the scratch area, signifying poor anticorrosion performance of this sample. Black spots under the coating surface showed the delamination part of coating particularly for E0 and EH0.5 coatings (Figure 1a and 1c). Neat epoxy coating sample underwent severe corrosion with the dense frequency of blisters (ASTM D714-02). From the SST result, it is notably that the inclusion of GO/HNT resulted in better corrosion protection performance, the lesser the blister and rusted area (Table 2). Hybrid nanofillers provide an extra barrier layer to hinder electrolyte penetration therefore remarkably prohibited the underlying metal from corrosion attack particularly for hybrid coating with 0.6 phr of GO and 0.3 phr of HNT. A strong synergistic effect of hybrid nanofillers resulting in stronger interfacial interaction, providing good dispersibility, thus creating a more tortuous path and retarding the water or gas molecules passing through the polymeric matrix. The beneficial effect of hybrid clay/zirconia on the enhancement of the anticorrosion performance of epoxy coating has been reported by Behzadnasab et al. (2013).

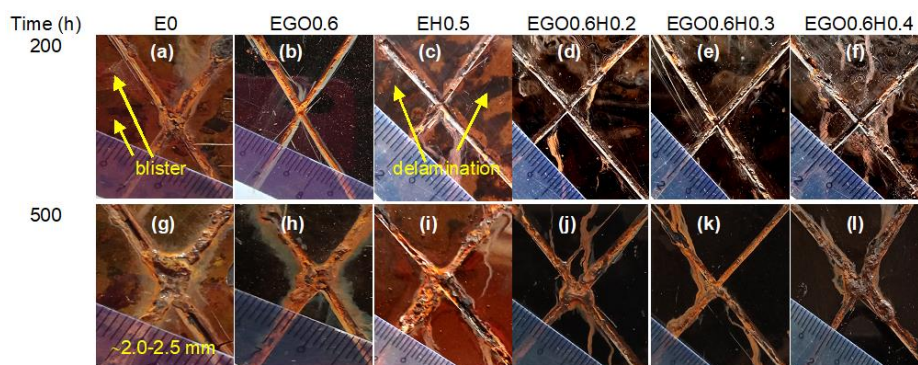


Figure 1: Visual appearance of mild steel plate after 200 h of exposure for (a) E0, (b) EGO0.6, (c) EH0.5, (d) EGO0.6H0.2, (e) EGO0.6H0.3, (f) EGO0.6H0.4; after 500 h of exposure for (g) E0, (h) EGO0.6, (i) EH0.5, (j) EGO0.6H0.2, (k) EGO0.6H0.3, (l) EGO0.6H0.4 in a salt fog chamber

After 500 h of exposure, the rusted area progressed under the coating and outermost the scribe line. The greater density of blisters (no. 6 medium pitches) appeared on the single nanofillers and neat epoxy coating samples suggesting the amelioration of water, oxygen, and corrosion ions at the coating-substrate interface, leading to the initiation and growth of coatings delamination. Contrarily, no apparent blisters were seen even after 500 h of exposure for hybrid coatings samples. These results can be ascribed to the fact that the addition of an appropriate amount of hybrid GO/HNT coating can block the paths of water and oxygen to the extent that they barely penetrate through to the metal substrate therefore effectively prevent the epoxy coating from blistering and delamination.

Table 2: Anticorrosion performance of nanocomposite coating after 500 h exposure to NaCl solution

Sample	Blistering		Rust grades
	Size	Frequency	
E0	6	Dense	2
EGO0.6	6	Medium	6
EH0.5	6	Medium	5
EGO0.6H0.2	8	Few	8
EGO0.6H0.3	8	Few	8
EGO0.6H0.4	8	Few	7

One possible explanation for this observation is the role of GO as a co-dispersing agent on HNT nanofiller dispersion enhancement, leading to further enhancement of the coating barrier properties against electrolytes diffusion. Notably, the rod-like geometry structure of HNT and low hydroxyl density on the surface, makes

them readily dispersed in a polymer matrix (Liu et al., 2007). Incorporation of GO and MMT particles functionalized with aminosilane and 1,4-butanediol diglycidyl ether (BDDE) molecule into epoxy coating resulted in significant improvement of corrosion resistance compared to neat particles (Sari et al., 2017). Hybridization of two geometrically dissimilar fillers of MWCNT and GNP has been used to improve the properties of polyetherimide composite that they formed a co-supporting network of both fillers (Kumar et al., 2010). However, an excessive amount of nanofiller loading (EGO0.6H0.4) marginally reduce the barrier properties (Figure 1f and 1l) which might be ascribed to inhomogeneous dispersion and particle agglomeration that rigorously affects the transport properties of the hybrid NCs and become the root cause for the barrier performance reduction.

The embedment of hybrid nanofillers being an innovative approach to achieve multi-functionality properties of epoxy composites by considering regulatory fire safety order (Hesami et al., 2014). Combination of GO/HNT gaining interaction between each other's owing to reasonable enhancements of FR performance as shown in Table 3. These results clearly demonstrated that hybrid GO/HNT in the ratio of 0.6:0.4 phr offered the best FR performance (25.0 %). The present of HNT attached to the surface of GO sheets can occupy the leakage or defect pathways on GO sheets derived from the chemical oxidation process, improving the oxygen barrier properties. The synergistic FR role of GO and MMT on the polyimide composite aerogels have been previously reported (Zuo et al., 2017). The formation of hybrid GO/MMT is due to the hydrogen bonding and crosslinking effects between GO sheets and MMT platelets which exhibit excellent thermal stability and gas barrier behavior. Li et al. (2014) revealed that the FR performance of PA6 was further improved with the addition of reduced GO decorated with HNT nanotubes (HNTs-d-rGO) hybrid composite. HNT can produce a thermal insulation barrier on the char surface of PA6, which reinforces the barrier effect of GO (Marney et al., 2008). Based on the aforementioned discussion, it can be concluded that the mechanism of FR in this study may be very similar to previous research (Ávila et al., 2010). Formation of a dense continuous char on the surface during burning shields the underlying material and slows the mass loss rate of decomposition products.

Table 3: LOI value of hybrid nanocomposite coatings

Sample	LOI (%)
E0	21.0
EGO0.6	23.0
EH0.5	21.5
EGO0.6H0.2	24.0
EGO0.6H0.3	24.0
EGO0.6H0.4	25.0

TGA curves for epoxy NC are shown in Figure 2 and a summary of the TGA results is given in Table 4.

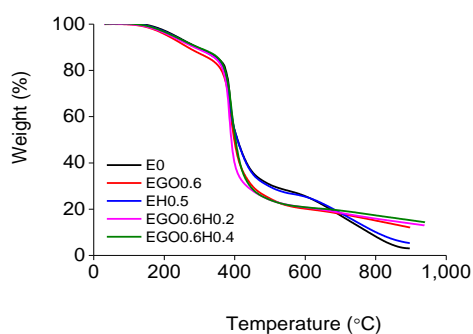


Figure 2: TGA curve of epoxy nanocomposite coatings

The thermograph for all of the coatings displayed a single step decomposition behavior. Clearly, the presence of hybrid nanofillers accelerated the thermal degradation of epoxy NCs, produces more char residue and inflammable gases, resulting to an enhancement of FR of epoxy NC stability compared with the neat and single nanofillers coatings. This enhancement can be attributed to the barrier effect of clay nanofillers which decreased the diffusion of degradation products into the polymer matrix (Hesami et al., 2014). Graphene deliberated as perfect scavengers of free radicals because of their high electron affinity (Rybiński et al., 2017). Therefore, it acts as a reactive spot for trapping the free radicals within the nanofiller network causing resistive

mobility, improving epoxy composite performance including its thermal stability (Hesami et al., 2014). A slight delay of the thermo-degradation of hybrid coatings under the influence of hybridization of nanofillers is accompanied by the reduction in their flammability as above discussed. The T_m occurred in the of range 386.00–391.00 °C that was related to the breaking down the polymer chains into volatile fragment or degradation of the epoxy composite. The rate of char formation increased in hybrid coatings with EGO0.6H0.4 being the highest.

Table 4: Summary of TGA results

Sample	$T_{10\%}$ (°C) ^a	T_m (°C) ^b	Residue char at 800 °C (wt%)
E0	268.21	388.78	15.06
EGO0.6	266.19	386.67	13.98
EH0.5	297.86	386.67	10.02
EGO0.6H0.2	287.62	386.54	15.05
EGO0.6H0.4	294.16	391.00	15.90

^a $T_{10\%}$ is defined as the temperature at 10 % weight loss occurred

^b T_m defined as the temperature at a maximum mass loss from the TGA curve

TEM images were depicted in Figure 3 to further explore and compare the structure and morphology of single and hybrid GO/HNT coatings. The TEM image of hybrid GO/HNT (Figure 3c) shows that the individual GO and HNT platelets were bound together, generating mixed filler. Some aggregates of the HNT nanofillers are still in the registry of about ~26.5 nm spacing, and some GO nanofillers have penetrated inside the gallery. Hydrogen bonding between GO and HNT can hold them together as a single unit after they were well mixed with sonicator and stirred for a long time (Raheel et al., 2015). GO and HNT surfaces could become charged and Na⁺ ion acts as a linker between them, resulting in a high contact area between the GO/HNT structures and the polymer matrix (Zhang et al., 2011). Synergistic improvement in coating properties may attribute to prolonged the diffusion pathway of corrosive media to the metal substrate as aforesaid in SST result. Yue et al. (2014) revealed that composite with the hybrid GNP/CNT filler system shows superior dispersion of the CNT in the matrix with no rich CNT domains appeared on the surface. The well-dispersed CNT enable to prevent stacking of the GNP sheets, thwarting void or holes formation. The dispersion becomes even more challenging with the increase in nanofiller content. This reason can be used to describe the limitation in the improvement of barrier and FR properties of the epoxy coating with an increase in nanofiller content. GO is much more hydrophilic because it possesses a large number of oxygen-containing groups on its surface compared to HNT. So it was expected that the dispersed state of GO in the epoxy matrix is much better than HNT (Figure 3a). Some of the HNT restack and forming several layers, indicating that they were not fully exfoliated to the single layer (Figure 3b).

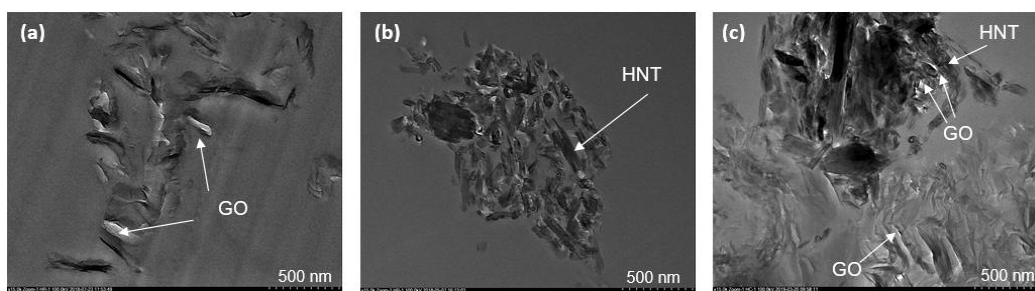


Figure 3: TEM micrographs of hybrid (a) GO (b) HNT (b) GO/HNT coatings

4. Conclusions

The combination of GO/HNT was observed to synergistically enhance the anticorrosion performance of epoxy NC where 0.6GO:0.3HNT proved to be more effective than neat and single nanofiller coatings. It is most likely due to stronger interfacial interaction, providing better-quality of GO dispersion in the presence of HNT. A well-dispersed GO and HNT exhibited steady improvement in FR properties and thermal stability of epoxy coatings and this property is exaggerated as the nanofillers content increased. In the future, minimizing the stacking effect and aggregation of nanofillers particularly at higher nanofillers loading would expect to further improve the NC performance hence raising the bar for materials sustainability.

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