

POLYVINYLIDENE FLUORIDE/GRAPHENE OXIDE NANOCOMPOSITE AS
ANTI-CORROSION COATING IN NATURAL GAS STEEL PIPELINES

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ANTI-CORROSION COATING IN NATURAL GAS STEEL PIPELINES

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*Specially dedicated to
my beloved father, Chiong Chiew Mee, my beloved mother, Kee Ying Kiong
and
those people who have guided and inspired me throughout my journey of education*

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ABSTRACT

Internal corrosion causes the mechanical strength of natural gas steel pipelines to be reduced, leading to cracking. Superior properties of polyvinylidene fluoride (PVDF) makes its as an excellent candidate for the anti-corrosion coating in natural gas steel pipelines. Nevertheless, further development of PVDF nanocomposite is necessary to enhance the properties of neat PVDF in terms of wettability, mechanical strength, anti-corrosion and impermeable property. In this research, monolayer 3-aminopropyltriethoxysilane-graphene oxide (APTES-GO) with a thickness of 0.58 nm was successfully synthesized through surface functionalization of graphene oxide (GO). APTES-GO was selected as the nanofiller to be incorporated into the PVDF matrix. This is because PVDF/APTES-GO nanocomposite displayed better anti-corrosion performance than GO. PVDF nanocomposites filled with various loadings of APTES-GO (0.1 to 0.5 wt%) were prepared using *N,N*-dimethylformamide as the solvent. The detailed anti-corrosion performance of PVDF/APTES-GO nanocomposites coated onto carbon steel plate was evaluated using Machu, salt spray and acid immersion tests. X-ray diffraction and Fourier transform infrared spectroscopy confirmed that the increment of APTES-GO from 0.1 to 0.5 wt% loading had transformed β - and γ - to α -phase crystal. Field emission scanning electron microscopy revealed that the PVDF nanocomposite films with a thickness of $73.0 \pm 3.61 \mu\text{m}$ exhibited features of the symmetric membranes. Atomic force microscopy analysis also showed that the surface roughness of PVDF nanocomposite films increased with the increase of APTES-GO loading. Besides that, PVDF nanocomposite filled with 0.4 wt% APTES-GO showed the highest water contact angle of 102° and $\sim 306\%$ increase in tensile modulus as compared to the neat PVDF. This nanocomposite layer ($66.67 \pm 4.0 \mu\text{m}$) was found to exhibit good adhesion property with the lowest corrosion rate of 6.65 mm/yr and highest corrosion protection efficiency of 51.16% in corrosive environments.

ABSTRAK

Kakisan dalaman telah menyebabkan saluran paip keluli gas asli mengalami kurang kekuatan mekanikal dan mengakibatkan berlakunya retakan. Sifat-sifat unggul polivinilidena fluorida (PVDF) telah menjadikan ia sesuai untuk digunakan sebagai salutan anti-karat dalam saluran paip gas asli. Namun, keupayaan PVDF komposit nano perlu dipertingkatkan untuk menambahbaik PVDF dari segi kebolehasahan, kekuatan mekanikal, anti-karat dan sifat ketakbolehtelapan. Dalam kajian ini, ekalapisan 3-aminopropiltriethoxysilana-grafen oksida (APTES-GO) dengan ketebalan 0.58 nm telah berjaya disintesis melalui pengubahsuaian grafen oksida (GO). APTES-GO telah dipilih sebagai pengisi nano untuk dimasukkan ke dalam matriks PVDF. Ini kerana PVDF/APTES-GO komposit nano mempunyai prestasi anti-karat yang lebih baik daripada PVDF/GO. PVDF/APTES-GO komposit nano pelbagai muatan APTES-GO (0.1 hingga 0.5 % berat) telah disediakan dengan menggunakan *N, N*-dimetilformamida sebagai pelarut. Prestasi anti-karat terperinci PVDF/APTES-GO komposit nano bersalut ke plat keluli karbon telah dinilai menggunakan ujian Machu, semburan garam dan ujian rendaman asid. Belauan sinar-x dan spektroskopi inframerah transformasi Fourier mengesahkan bahawa tambahan APTES-GO daripada 0.1 hingga 0.5 % berat telah mengubah fasa β - dan γ - kepada α -fasa kristal. Mikroskop elektron pengimbas pancaran medan mendedahkan bahawa lapisan PVDF komposit nano dengan ketebalan $73.0 \pm 3.61 \mu\text{m}$ mempamerkan ciri-ciri membran simetri. Mikroskop daya atomik juga mempamerkan bahawa kekasaran permukaan PVDF filem komposit nano meningkat dengan peningkatan muatan APTES-GO. Selain itu, PVDF/APTES-GO komposit nano dengan 0.4 % berat APTES-GO telah menunjukkan sudut sentuhan air tertinggi 102° dan $\sim 306\%$ peningkatan modulus tegangan berbanding dengan PVDF. Lapisan komposit nano tersebut ($66.67 \pm 4.0 \mu\text{m}$) didapati mempamerkan sifat lekatan yang baik dengan kadar kakisan terendah iaitu 6.65 mm/tahun dan kecekapan perlindungan kakisan yang tertinggi sebanyak 51.16% dalam persekitaan yang mengkakis.

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LIST OF ABBREVIATIONS

A	-	area of the specimen
ABF-G	-	aminobenzoyl group-functionalized graphene
ACME	-	anode, cathode, metallic, electrolyte
AFM	-	atomic force morphology
APTES	-	(3-aminopropyl) triethoxysilane
APTMS	-	3-aminopropyltrimethoxysilane
ASTM	-	American Society for Testing and Materials
CA	-	contact angle
CAPEX	-	capital expenditure
CI	-	corrosion inhibitor
CNTs	-	carbon nanotubes
CR	-	corrosion rate
CR _{uncoated}	-	corrosion rate of the bare carbon steel plates
CR _{coated}	-	corrosion rate of the carbon steel plates with coatings (mm/yr)
CRAs	-	corrosion resistant alloys
CS	-	carbon steel
D	-	density of specimen
DNA	-	deoxyribonucleic acid
DMF	-	dimethylformamide
EPD	-	cathodic electrophoretic deposition
FESEM	-	field emission scanning electron microscopy
FTIR	-	Fourier transform infrared spectroscopy
GO	-	graphene oxide
HBUA	-	hyperbranched urethane alkyd
HDPE	-	high density polyethylene
HIC	-	hydrogen induced cracking
K	-	constant (87.6)

M	-	mass loss
MIC	-	microbiologically influenced corrosion
PANI	-	polyaniline
p-GO	-	p-phenylenediamine/4-vinylbenzoic acid-modified graphene oxide
PGU	-	Peninsular Gas Utilization
MPTMS	-	3-mercaptopropyl trimethoxysilane
MWCNTs	-	multi-walled carbon nanotubes
rGO	-	reduced graphene oxide
SCC	-	stress-corrosion cracking
SWCNTs	-	single-walled carbon nanotubes
PIHA	-	polymeric isocyanate crosslinked with hydroxyl functional acrylic
PP	-	polypropylene
PS	-	polystyrene
PVDF	-	polyvinylidene fluoride
OTS	-	octadecyltrichlorosilane
STEM	-	scanning transmission electron microscopy
T	-	time of exposure
TGA	-	thermal gravimetric analysis
TLC	-	top-of-the-line corrosion
TTM	-	Trans Thailand-Malaysia
UV	-	ultraviolet
XRD	-	x-ray diffraction

LIST OF SYMBOLS

%	-	percent
°C	-	degree celsius
±	-	within the range
wt	-	weight
e^-	-	electron
°	-	degree
~	-	approximately equal
μ	-	micro
λ	-	lambda
Å	-	angstrom

CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Up to date, natural gas is continuous to remain as an important energy resource than other fuels. In 2012, about 21 percent of fuel share is natural gas, which is equivalent to almost 2000 billion barrels of oil equivalent. When reaching 2030, it is expected that the universal need for natural gas would be nearly 23-38 trillion barrels of oil every year (Papavinasam, 2013). This phenomenon has urged oil and gas industries such as Shell and ExxonMobil to be involved actively in exploration activities to allocate the new gas fields. However, natural gas steel pipelines require the advanced coating that can endure corrosive environments in order to transport raw natural gas from the gas fields to production facilities (Ajayi and Lyon, 2014).

In Malaysia, about 2 billion cubic feet (Bcf/d) natural gas are transported for each day through 2500 km long pipeline systems. In the north, about 614 km Trans Thailand-Malaysia (TTM) Gas Pipeline network is connected to the Peninsular Gas Utilization Pipeline System (PGU). In 2020, it is expected that natural gas can be transported from the East Natuna gas field, China to Kerteh, Malaysia through the Trans-ASEAN Gas Pipeline (*Malaysia International Energy Data and Analysis*, 2014). Meanwhile, it has been discovered that the concentration of hydrogen sulfide (H₂S) and carbon dioxide (CO₂) in the gas fields in Malaysia are very high. These corrosive agents encourage corrosion to occur in the natural gas gathering and transmission

pipelines (Sass et al., 2005). About \$600 million was spent annually for the replacement and maintenance of corroded pipelines due to corrosion in oil and gas industry. Without proper mitigation, corrosion can cause giant economic costs and enormous damage to health, safety and environment (Yuan et al., 2016).

Even though cathodic protection is effective to protect the external surface of the natural gas steel pipelines from corrosion, it cannot prevent internal corrosion in pipelines. 16 years ago somewhere in August 2000, 12 people had been killed and property loss worth about USD 1 million due to an incident of natural gas transmission pipeline rupturing in Carlsbad, New Mexico (Sass et al., 2005) and (Ali et al., 2012). Moreover, pipelines cracking is one of the consequences that caused by the high severity of internal natural gas steel pipelines corrosion. Subsequently, methane will be leaked and emitted into the environment. Methane, which is one of the greenhouse gases can cause critical global warming. The negative impact of methane is 86 times higher than carbon dioxide (CO₂) (Jackson et al., 2014).

Currently, corrosion inhibitors, biocides, cathodic protection and process optimization have been utilized in oil and gas industry to cope with the internal pipelines corrosion (Papavinasam, 2013). In order to further improve the performance of existing technologies for corrosion mitigation, the consideration for coating with superior properties is crucial. The selected material should have high mechanical strength, anti-microbial and anti-corrosion (Bickerstaff et al., 2002). On the other hand, high corrosion-resistant alloys (CRAs) such as duplex stainless steel are not ideal as the material for natural gas steel pipelines due to the extremely high capital expenditure (CAPEX). On the other hand, corrosion inhibitors are sensitive to thermal degradation, difficult to monitor and non-environmentally friendly (Finšgar and Jackson, 2014).

So far, the polymer coating is one of the most commonly used approaches to reduce the corrosion rate by preventing direct contact between the inner surface of the pipelines and the corrosive environment. However, traditional polymeric coatings such as epoxy and polyethylene are still permeable to

corrosive ions and water (Bayram et al., 2015). Recently, the development of polymer nanocomposites has represented a new paradigm shift in material science to address the corrosion issue (Chang, 2013). Many researches have been carried out to incorporate novel nanofillers into polymer matrices, which may introduce new ways to develop the state-of-the-art coatings to improve the anti-corrosion performance by decreasing the permeability rate of water and corrosive species. Polyvinylidene fluoride (PVDF) is one of the high-performance polymers due to its extraordinary properties such as high mechanical strength, remarkable chemical corrosion resistance (acids and bases), low coefficient of friction, good resistance to stress cracking, good fatigue resistance, excellent electrochemical and thermal stability (Maccone et al., 2000).

Even though PVDF is not a common polymer used for internal coating in natural gas steel pipelines, many researchers have validated it to be an exceptional matrix to investigate due to its extraordinary properties (Liu et al., 2011). However, PVDF suffers from several limitations due to the presence of free volumes in PVDF matrix. This makes PVDF exhibits membrane feature (selective barrier) (McCafferty, 2010). These undesired properties have resulted in easy penetration of the corroding agents for corrosion to take place (Das and Prusty, 2013). Nanofillers help to improve anti-corrosion properties in several ways. Nanofillers reduce the contact tension or wettability, minimize the penetration of water and corrosive species by increasing the tortuous pathway and lower the surface roughness for better water and oil repellence (Nazari and Shi, 2016).

Recently, the astounding properties of graphene-based nanomaterials due to their superior properties such as excellent mechanical strength and chemical stability, anti-microbial, anti-corrosion and impermeable features have paved the way for their applications in the field of anti-corrosion (Chang, 2013). Based on these superior properties, platelet formed of graphene-based nanomaterials can serve as the potential nanofillers for polymer nanocomposite coating, even at very low loading due to their larger surface area compared to carbon nanotubes (CNTs). Furthermore, graphene-based nanomaterials can reduce the total free volumes, increase the overall mechanical strength, lower the possibility of matrix defects and cracks, assist in bridging to link

more matrix molecules and increase the cross-linking density of the resulting polymer nanocomposite (Ammar et al., 2016). Thus, incorporation of graphene-based nanomaterials into the polymer matrix can become the promising solution for natural gas steel pipelines anti-corrosion coating (Kuilla et al., 2010).

In the current study, 3-aminopropyltriethoxysilane (APTES) was used as the precursor to functionalize graphene oxide (GO), which involved silane silanization and polycondensation in synthesizing monolayer of APTES-GO. The as-fabricated APTES-GO was characterized and the effects of the APTES-GO on the surface morphology, wettability and mechanical strength of PVDF/APTES-GO nanocomposite were investigated. Carbon steel (CS) plate, which has similar properties with commercial natural gas steel pipelines was used in the current study. The detailed anti-corrosion performance of the novel PVDF/APTES-GO nanocomposite coated onto CS plate was evaluated through Machu, salt spray and acid immersion tests to determine the potential to be implemented as the anti-corrosion coating in natural gas steel pipelines.

1.2 Problem Statement

In oil and gas industry, natural gas steel pipelines are made from low-CS that is low cost, readily available and easily fabricated. CS is a metal alloy containing iron and carbon. However, natural gas steel pipelines are vulnerable towards corrosion. Corrosion occurs when the atoms of the CS in natural gas steel pipelines lose electrons continuously in the corrosive environments. Many approaches have been implemented to protect the internal surface of natural gas steel pipelines. The industry has established different approaches for corrosion mitigation strategies such as the implementation of the conventional corrosion inhibitors and scale inhibitors. Nevertheless, these techniques are not effective to reduce the corrosion rate in natural gas steel pipelines. In light of this, the PVDF coating can be coated in the natural gas steel pipelines, which provides a physical barrier to reduce penetration of corrosive species onto the metal surface.

However, the neat PVDF coating suffers from several weaknesses due to the presence of free volumes in their matrixes that allow penetration of water and corrosive species, which can reduce the corrosion protection ability of the polymer due to hydrolytic degradation. Besides that, poor crack propagation resistance and vulnerability to comprise pinholes tend to decrease the adhesion strength of the resulting PVDF coating-metal interface. Reduction of oxygen at the interface could result in delamination of the polymer coating from the metal surface. This phenomenon is referring to the electrochemically driven process whereby the bonds at the PVDF coating-metal interface are damaged by radicals (Ammar et al., 2016). Hence, GO can be incorporated into the PVDF matrix with the purpose of improving the corrosion protection and barrier properties.

In addition, hydrophilicity nature of GO does not possess good corrosive solution-repellency feature. In other words, adsorption of water molecules and corrosive ions are likely to occur in the resulting PVDF/GO nanocomposite, which can increase the rate of corrosion. So, GO is functionalized with hydrophobic APTES functional groups to increase its hydrophobicity before incorporating into the PVDF matrix. The presence of numerous reactive sites on the surface of GO enables surface modification or covalent functionalization to fabricate hydrophobic GO that can repel and impermeable to corrosive solutions. This can delay the penetration of electrolyte containing corrosive ions and water to an underlying metal surface and reduce the corrosion rate.

1.3 Objective of Study

The objectives of this study are:

- a) To synthesize and characterize monolayer APTES functionalized GO.
- b) To fabricate and characterize hydrophobic PVDF/APTES-GO nanocomposite.
- c) To evaluate the anti-corrosion performance of APTES-GO nanocomposite as the coating layer for natural gas steel pipelines.

1.4 Scope of Study

To achieve the above-mentioned objections, the scope of the study is outlined as below:

- a) Synthesize GO through modified Hummer's method, which involves oxidation of graphite.
- b) Modify GO with hydrophobic APTES functional group.
- c) Characterize GO and APTES-GO using x-ray diffractometer (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), atomic force morphology (AFM) and scanning transmission electron microscopy (STEM).
- d) Incorporate hydrophobic APTES-GO into PVDF matrix to fabricate PVDF/APTES-GO nanocomposite using solvent casting approach.
- e) Study the effect of APTES-GO loadings from 0.1 to 0.5 wt% towards the properties of the resulting PVDF nanocomposites.
- f) Study the surface morphologies, crystal structure, thermal stability, surface roughness and infrared spectra of PVDF/APTES-GO nanocomposites using Field Emission Scanning Electron Microscopy (FESEM), XRD, TGA, AFM and FTIR respectively.
- g) Determine the wettability (water contact angle) and mechanical (tensile modulus and tensile strength) behaviors of PVDF/APTES-GO nanocomposites.
- h) Dip coat PVDF/APTES-GO nanocomposites onto CS plate, which has similar properties as commercial carbon steel pipelines.
- i) Assess the anti-corrosion behavior of PVDF/APTES-GO nanocomposite coatings/carbon steel system using Machu, salt spray and acid immersion tests.
- j) Determine the optimized APTES-GO loading to be incorporated into PVDF matrix for anti-corrosion coating in natural gas steel pipelines.

- k) Investigate the adhesion of PVDF nanocomposite filled with optimized APTES-GO loading with neat PVDF using Machu test.

1.5 Significance of Study

The excellent properties of graphene have incited more research in this field. Up to now, the performance of polymer/graphene nanocomposites in applications such as supercapacitors, lithium-ion batteries, solar cells, electrochemical sensing and membrane-based separation applications are widely investigated. Presently, most of the research of PVDF/graphene nanocomposites is predominantly focusing on their electrical conductivity features in fuel cells, transistors and photocatalytic applications. So far, there is no research being reported on the incorporation of graphene-based nanomaterials as nanofillers in the fabrication of PVDF nanocomposites for anti-corrosion coating in natural gas steel pipelines up to date. Since many researches outcomes have revealed that graphene exhibited anti-corrosion properties, the present study would focus on the covalent functionalization of GO with hydrophobic silane molecules such as APTES to increase the hydrophobicity of GO (APTES-GO). This can, in turn, heighten the performance of GO as the coating material.

Moreover, the mechanism of formation of monolayer APTES-GO has not been reported so far. Most of the researches are focusing on the multilayer APTES-GO as a reinforcement agent in the polymer. Therefore, it is anticipated that the current research will provide insight into PVDF/APTES-GO nanocomposite, specifically in the field of anti-corrosion.

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