CHARACTERIZATION OF GRAPHENE OXIDE PICKERING EMULSION AND SILICA NANOPARTICLES FOR WATERBORNE EPOXY COATING

BY

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A thesis submitted in fulfilment of the requirement for the degree of Master of Science (Materials Engineering)

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ABSTRACT

The application of epoxy resins as the anticorrosion coating has obtained widespread application because of their superior adhesion to various substrate and excellent chemical inertness. However, epoxy resin tends to form microcracks and the VOCs released during the drying process is harmful. Although the waterborne epoxy coatings are a much safer alternative, they are prone to swell caused by water absorption. With the consideration for the environment and human health in mind, this research aimed at developing a new and improved waterborne coating that employed graphene oxide (GO) encapsulated linseed oil and silica nanoparticles (SiO_2) as healing microcapsules and anticorrosion agent respectively. This research was divided into three main phases; phase (A), synthesis of graphene oxide microcapsules (GOMs) via Pickering emulsion method, phase (B), synthesis of amine-stitched graphene oxide microcapsules (Amine-stitched GOMs), and phase (C), preparation of coating sample. GO was selected as the microcapsule's shell due to its flexibility and excellent barrier properties, while the linseed oil core is able to polymerize when in contact with the atmosphere to form a hydrophobic film. SiO_2 was used to increase the density and adhesion between the coating and the substrate. This coating was formulated through the copolymerization of waterborne epoxy resin with the incorporation of GOMs and SiO_2 nanoparticles. Waterborne epoxy acted as a matrix while GOMs and SiO_2 nanoparticles act as a guest component. The coating was directly applied on carbon steel type S50C as the substrate. The test of adhesion, immersion, and salt spray was conducted in accordance with ASTM D3359, B895, and B117-94 respectively. The POM, TGA, and TEM showed that the GOMs were successfully synthesized, having a size ranging from 5.39 µm to 20.45 µm, coefficient of variation (Cv) of 0.34, shell thickness around 140 to 160 nm, and 94% loading capacity. Based on the physical analysis and corrosion test, the addition of GOMs and SiO_2 nanoparticles reduced the swelling degree and corrosion rate of a waterborne epoxy coating by 54.1% and 62.7% respectively. The novel formulated coating also demonstrated good adhesion to the metal substrate and possess the ability to perform as a self-healing coating. Incorporation of 10 wt% GOMs and 1 wt% of SiO_2 nanoparticles were identified as the best composition for waterborne epoxy coating in improving waterborne coating properties.

خلاصة البحث

قد حصلت مادة الإيبوكسي التي تستخدم كطلاء لمنع التآكل على إستعمال واسع بسبب قوة إلتصاقها المتفوق لمختلف المواد المتفاعلة والمواد الخاملة كيميائيا. ومع ذلك,مادة الإيبوكسي تميل إلى تشكيل شقوق صغيرة والمركبات العضوية المتطايرة المنبعثة أثناء عملية التجفيف تكون مضرة. ورغم أن طلاءات الإيبوكسي المائية تعتبر بديلًا أكثر أماناً, ولكنها أكثر عرضة للتضخم بسبب إمتصاص الماء. يهدف هذا البحث في تطوير الطلاء المائي بشكل جديد ومحسن مع الأخذ بعين الإعتبار البيئة المحيطة وصحة الإنسان, والذي يستخدم أكسيد الجرافين (GO) المغلف بزيت بذر الكتان وجزيئات السيليكون (SiO_2) ككبسولات شفاء وعامل مضاد للتآكل. وينقسم هذا البحث إلى ثلاثة مراحل; المرحلة الأولى (A), توليف كبسولات أكسيد الجرافين (GOMs) على طريقة مستحلب بيكرينغ. المرحلة الثانية (B), توليف كبسولات أكسيد الجرافين المخيطة بالأمين (Amine-stitched GOMs). وأما المرحلة الثالثة (C), هي تجهيز عينات الطلاء. وتم اختيار أكسيد الجرافين كغلاف للكبسولات بسبب مرونتها ومناعتها الممتازة, بينما نواة بذرة الكتان قادرة على التبلمر عندما تتصل بالغلاف الجوي لتشكيل غشاء الهيدروفوبيك. كان يستخدم ثاني أكسيد السيليكون لزيادة شدة وقوة التصاق بين الطلاء والمادة المتفاعلة. هذا الطلاء قد صيغ عن طريق البلمرة من مادة الإيبوكسي المائي ودمجه مع كبسولات أكسيد الجرافين ونانويات ثاني أكسيد السيليكون. ويعمل الإيبوكسي المائي كنسيج غشائي, بينما كبسولات أكسيد الجرافين ونانويات ثاني أكسيد السيليكون يعملون كعنصر مضيف. ويستعمل الطلاء مباشرة على الكربون الصلب من نوع S50C كمادة متفاعلة. تم إختبار سلوك كلّ من الإلتصاق, الإنغمار ورذاذ الملح وفقاً لـ ASTM D3359, B895, و B11794 بالتوالي. أظهرت الـ POM, TGA, و TEM أن كبسولات أكسيد الجرافين قد تم توليفها بنجاح, مع وجود أحجام تتراوح ما بين 5.39 ميكرومتر. و 0.34 من معامل الإختلاف. وسماكة القشرة تتراوح ما بين 140 إلى 160 نانومتر , و 94 بالمئة من قدرة التحميل. وبناء على التحليل الفيزيائي واختبار التآكل, الزياة في كبسولات أكسيد الجرافين وثاني أكسيد السيليكون قلصت درجة الإنتفاخ ونسبة تآكل طلاء الإيبوكسي المائي, بنسبة 54.1 بالمئة و 62.7 بالمئة على التوالي. الطلاء المطور حديثا قد برهن خصائص إلتصاق جيد على الركيزة المعدنية وامتلاكه القدرة على الإستشفاء الذاتي. طلاء الإيبوكسي المائي المكون من 10 بالمئة من سمك حائط كبسولات أكسيد الجرافين و 1 بالمئة من سمك حائط نانويات ثاني أكسيد السيليكون يعتبر أفضل تركيب لطلاء الإيبوكسي المائي في مجال تطوير الطلاءات المائية.

APPROVAL PAGE

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DECLARATION

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LIST OF SYMBOLS

%	percentage
~	approximate
≤	less than or equal to
≥	more than or equal to
°	degree
° C	degree celcius
$	dollar
λ	wavelength
μm	micrometer
Ca	capillary action
cm	centimeter
cm^{-1}	reciprocal centimeter
cm^{2}	squared centimeter
C_v	coefficient of variation
g	gram
g^{-1}	reciprocal gram
GPa	gigapascal
g/L	gram per liter
Hg	hectogram
hr	hour
K^{-1}	reciprocal Kelvin
m^{-1}	reciprocal meter

mg	milligram
mg/ml	milligram per milliliter
min	minute
min^{-1}	reciprocal minute
ml	milliliter
mm	millimeter
nm	nanometer
rpm	rotation per minute
s	second
Tg	glass transition temperature
TPa	terapascal
V	volt
wt %	weight percentage
W	watt
θ	theta
θ_w	contact angle

LIST OF EQUATIONS

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LIST OF ABBREVIATIONS

2D	two dimensional
Al_2O_3	aluminum (ii) oxide
ALA	α-linolenic acid
APTES	(3-aminopropyl)triethoxysilane
ASTM	american society of testing and materials
BTA	benzotriazole
C	carbon
C=C	compound containing alkene group
CAGR	compound annual growth rate
CNT	carbon nanotube
Cr	chromium
C-OH	compound containing aldehyde group
–COOH	compound containing carboxyl group
D-2000	poly(propylene glycol) bis(2-aminopropyl ether)
DCPD	dicyclopentadiene
DMF	dimethylformamide
e^-	electrons
EC	ethyl cellulose
EI	emulsion index
EIS	electrochemical impedance spectroscopy
EN	electrochemical noise
*f*GO	functionalized graphene oxide

fSiO_2	functionalized silica
Fe	iron
$Fe(OH)_2$	iron hydroxide
Fe^{2+}	iron ion lack of 2 electrons
$Fe_2O_3.H_2O$	hydrated iron hydroxide
Fe_3O_4	iron (iii) oxide
FT-IR	fourier transform infrared
GDP	gross domestic product
GO	graphene oxide
GOMs	graphene oxide microcapsules
GONs	graphene oxide nanosheets
H_2O	water
HMIM	1-hexyl-3-methylimidazolium chloride
HNTs	halloysite clay nanotubes
ICP-MS	inductively coupled plasma mass spectrometry
IMPACT	international measures of prevention, application, and economics of corrosion technologies
LbL	layer-by-layer
LDPE	low-density polyethylene
M_n	molecular number
Mn	manganese
MSNs	mesoporous silica nanoparticles
NACE	national association of corrosion engineers
NaCl	sodium chloride

NMP	n-methylpyrrolidone
NPS	nanoparticles
NS	nanosheet
O/W	oil-in-water
O_2	oxygen gas
OH	hydroxide
OH^-	hydroxide ion
P	phosphorus
PANI	polyaniline
PBAR	plant-based alkyd resin
PEI	polyethyleneimine
PEO	plasma electrolytic oxidation
PET	polyethylene terephthalate
PI	polyimides
PMMA	polymethyl methacrylate
POM	polarized optical microscope
PSA	particle size analyzer
PSS	polystyrene sulfonate
PU	polyurethane
PUF	poly(urea-formaldehyde)
PVA	poly-vinyl alcohol
rGO	reduced graphene oxide
RGONs	reduced graphene oxide nanosheets
S	sulfur

SAC	sulfanilic acid azocromotrop
SB	solvent-based
SEM	scanning electron microscope
Si	silicon
SiO_2	silica / silicon dioxide
TEM	transmission electron microscope
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TiO2	titania/titanium dioxide
TNTs	titanium dioxide nanotubes
TRGO	thermally reduced graphene oxide
UF	urea-formaldehyde
W/O	water-in-oil
WB	waterborne
XRD	x-ray diffractometer
ZnO	zinc oxide
ZrO	zirconium oxide

CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Corrosion is always being the major reason for energy and material loss. Many researchers are still bewildered on how to overcome the corrosion in steel structure, especially in oil and gas industries where the metal structure is exposed to the moist and aggressive environment. The behaviors of materials in such environment have urged both researchers and scientists to find a good solution to solve this problem. Hence, a layer of corrosion-resistant coating is the most effective way, as the coating act as the intermediate surface between the metal substrate and the environment, protecting against erosion and corrosion (Metal Coatings Corporation, 2016). But, the conventional coatings only give a slight improvement in the properties of the substrate as they are made up of micron-scale substances. Solidification of conventional coating also leads to a few defects such as micro-pores and bubbling (He et al., 2015). Also, they are easy to crack (Cotting & Aoki, 2015). Besides the infamous nanocoating, which possesses excellent physical, mechanical, thermal, and chemical properties, the utilization of smart coating is another great alternative.

Smart coating is a new generation coating transcending the conventional coating and other functional materials. Rather than act as a rigid barrier between the substrate and the environment, which is what conventional coatings did, smart coatings are designed to respond to the environment and, through that response, enhance the coating's service life and functionality (I. S. Cole, 2014). It is also frequently used interchangeably with self-healing coating (Hughes et al., 2016).