SYNTHESIS AND CHARACTERIZATION OF WATERBORNE POLYURETHANE DISPERSION FOR ANTIFOULING PAINT

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FACULTY OF ENGINEERING
UNIVERSITI MALAYSIA SABAH
2019

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THESIS SUBMITTED IN FULFILLMENT FOR THE DEGREE OF MASTER OF ENGINEERING

FACULTY OF ENGINEERING
UNIVERSITI MALAYSIA SABAH
2019

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS

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DATE OF VIVA	:	**30th AUGUST 2019**

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ACKNOWLEDGEMENT

First of all, I would like to express my deepest gratitude to my research supervisor Prof. Dr. Coswald Stephen Sipaut @ Mohd Nasri for his continuous guidance, supervision, and motivation throughout this research. Without his continuous help and guidance in the experimental works, paper publication, and thesis writing, I would not be able to complete my study.

I would also like to express my gratitude to all laboratory assistants of Faculty of Engineering and Faculty of Natural Science and Resources, Universiti Malaysia Sabah, especially, Mdm. Noridah Abbas, Mr Raysius, Mr Abdullah Tarikim, and Mr Taipin Gadoit for their full cooperation in providing assistance during the operation of analytical instruments.

Next, I would like to acknowledge the Ministry of Higher Education Malaysia and Universiti Malaysia Sabah for the research funding under PRGS008-TK-2/2015 and GUG0162-2/2017.

Last but not least, I would like to express my deepest and warmest appreciation to my parents, family, and friends for their continuous support, motivation, and encouragement during my study. Without their encouragements and supports, I would not have the confidence in completing my study with an excellent performance.

ANGEL KUOK MEI ERH

18th September 2019

ABSTRACT

The continuous accumulation of marine fouling on the submerged marine structures has caused significant impacts to the maritime industries. This led to the development of more effective anti-fouling paints. To date, toxic to green biocides were still widely used in anti-fouling paints to remove fouling. Recent studies showed that polyurethane coatings can exhibit anti-fouling activity without using biocide. However, they had low anti-fouling efficiency. In this study, the biocide-free, and waterborne polyurethane dispersion (PUD) was synthesised using a prepolymer mixing process. The main ingredients were isophorone diisocyanate (IPDI), polyethylene glycol (PEG), dimethylolpropionic acid (DMPA), 1,4-butanediol (BD), and water. The effects of the molar ratio of diisocyanate to PEG (NCO/OH_{PEG}), and DMPA content were investigated on the particle size and distribution, zeta potential, thermal stability, adhesion strength, and solubility rate of PUD coating in seawater and distilled water. The stable PUD at NCO/OH_{PEG} (9 – 11) and DMPA content (7 – 11 wt%) exhibited small particle size (around 48 – 166 nm), high zeta potential (around -50 to -66 mV), and can form dry PUD coatings. The presence of urethane groups in the PUD was ascertained via Fourier Transform Infra-red (FT-IR) spectroscopy. The PUD coatings exhibited adhesion strength of more than 2 MPa on stainless steel substrates and did not detach in seawater. However, they detached in distilled water. (3-aminopropyl)triethoxysilane (APTES) was added to improve the coating stability in distilled water. APTES-modified (APUD) sample was produced using two methods either APTES addition at either (a) before, or (b) after the reaction with BD in the PUD synthesis. The APTES content of 10 mol% was just sufficient to form stable APUD and APUD coatings. APUD coatings produced from method (a) detached in distilled water but not for the APUD coating from method (b). APUD coating from method (b) exhibited the highest adhesion strength on stainless steel (3.303 MPa), followed by carbon steel (2.537 MPa), and the lowest on aluminium (2.280 MPa). This coating was found not suitable to be coated on carbon steel as heavy blisters, scratches, and white spots formed when immersed in seawater and distilled water. The solubility of this APUD coating on stainless steel and aluminium ranged from 0.161 to 0.237 %/day in seawater and 0.468 to 0.550 %/day in distilled water. In overall, this research showed that APUD coating had the potential to work as an anti-fouling paint in the maritime industries.

ABSTRAK

SINTESIS DAN PENCIRIAN DISPERSI POLIURETANA SEBAGAI CAT ANTI-TUMBUH

Pengotoran marin yang berterusan terhadap struktur-stuktur kapal marin yang separa tenggelam telah menjejaskan industri maritim. Ini membawa kepada pembangunan cat anti-tumbuh yang lebih efektif. Sehingga kini, biosida yang bersifat toksik dan biosida hijau digunakan secara meluas dalam cat anti-tumbuh. Kajian terkini menunjukkan bahan penyalut poliuretana dapat mempamerkan sifat sebagai cat anti-tumbuh tanpa penggunaan biosida. Walau bagaimanapun, kecekapannya masih di tahap yang rendah. Dalam kajian ini, dispersi poliuretana berbasis air (PUD) yang bebas biosida telah disintesis menggunakan proses "prepolymer mixing". Bahan-bahan utamanya terdiri daripada isophorone diisosianat, polietilen glikol (PEG), asid dimetilolpropionik (DMPA), 1,4-butanadiol (BD), dan air. Tujuan kajian ini dijalankan untuk menentukan kesan nisbah molar diisosianat kepada PEG (NCO/OH_{PEG}), dan kandungan DMPA ke atas saiz zarah dan taburannya, "zeta potential", kestabilan haba, kekuatan rekatan, dan kadar kelarutan bahan penyalut PUD dalam air laut dan air suling. Hasil kajian menunjukkan bahawa PUD yang stabil dengan nisbah NCO/OH_{PEG} (9 – 11), dan kandungan DMPA (7 – 11 wt%) mempamerkan saiz zarah yang kecil (sekitar 48 – 166 nm), "zeta potential" yang tinggi (sekitar -50 hingga -66 mV) dan boleh membentuk bahan penyalut yang kering setelah semua kandungan air di dalamnya telah disejatkan. Hasil analysis spektroskopi inframerah (FT-IR) menentukan kewujudan kumpulan berfungsi uretana di dalam PUD. Berdasarkan hasil kajian ini, didapati bahan penyalut PUD tersebut yang disalut atas substrat keluli tahan karat menunjukkan kekuatan rekatan yang tinggi iaitu melebihi 2 MPa dan tidak tertanggal apabila direndam di dalam air laut. Walau bagaimanapun, bahan penyalut ini tertanggal apabila direndam di dalam air suling. (3-aminopropil)triethoxysilane (APTES) telah ditambah untuk meningkatkan kestabilan bahan penyalut tersebut apabila direndam di dalam air suling. PUD yang diubahsuai dengan APTES (APUD) dihasilkan dengan dua cara, sama ada (a) penambahan APTES sebelum atau (b) selepas tindak balas kimia dengan BD dalam proses sintesis ini. Hasil kajian mendapati bahawa kandungan APTES sebanyak 10 mol% dapat membentuk APUD yang stabil dan bahan penyalut APUD yang kering. Walau bagaimanapun, bahan penyalut APUD yang dihasilkan daripada cara (a) tertanggal apabila direndam di dalam air suling tetapi bahan penyalut APUD yang dihasilkan daripada cara (b) tidak. Hasil kajian menunjukkan bahawa bahan penyalut APUD yang dihasilkan daripada cara (b) mempamerkan kekuatan rekatan yang tinggi atas substrat keluli tahan karat (3.303 MPa), diikuti oleh substrat keluli karbon (2.537 MPa), dan kekuatan rekatan yang terendah atas substrat aluminium (2.280 MPa). Hasil kajian juga mendapati bahawa bahan penyalut APUD ini tidak sesuai untuk disalut atas substrat keluli karbon kerana lepuh, calar, dan bintik putih boleh terbentuk apabila direndam di dalam air laut dan air suling. Kadar kelarutan bahan penyalut ini yang disalut atas substrat keluli tahan karat dan aluminium adalah dalam sekitar 0.161 hingga 0.237 %/hari dalam air laut dan 0.468 hingga 0.550 %/hari dalam air suling. Keseluruhannya, kajian ini menunjukkan bahawa bahan penyalut APUD ini mempunyai ciri-ciri yang baik dan boleh berfungsi sebagai cat anti-tumbuh dalam industri maritim.

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AF	-	Anti-fouling
APTES	-	(3-aminopropyl)triethoxysilane
APUD	-	PUD modified with APTES
BD	-	1,4-butanediol
DABCO	-	1,4-diazabicyclo[2.2.2]octane
DBTDL	-	Dibutyltin dilaurate
DMPA	-	Dimethylolpropionic acid
DTG	-	Derivative weight analysis
FT-IR	-	Fourier Transform Infra-red
HCl	-	Hydrochloric acid
HDI	-	Hexamethylene diisocyanate
IPDI	-	Isophorone diisocyanate
MDI	-	Diphenylmethane diisocyanate
Mw	-	Molecular weight
NaCl	-	Sodium chloride
NCO	-	Isocyanate
NCO/OH	-	Isocyanate to hydroxyl molar ratio
NCO/OH_{PEG}	-	Isocyanate to hydroxyl (PEG) molar ratio
NH_2	-	Amine
NMDEA	-	N-methyl-diethanolamine
NMP	-	N-methyl-2-pyrrolidone
OH	-	Hydroxyl
PdI	-	Polydispersity
PDMS	-	Polydimethylsiloxane
PEG	-	Polyethylene glycol
PU	-	Polyurethane
PUD	-	Aqueous/ waterborne polyurethane dispersion
Ra	-	Surface roughness
$T_{d,1/2}$	-	Temperature at 50 % weight loss during degradation
$T_{d,max}$	-	Temperature at each maximum degradation stage

T$_{d,onset}$	-	Onset of degradation
TDI	-	2,4-Toulene diisocyanate
TGA	-	Thermogravimetric Analysis
TMP	-	Trimethylolpropane