PREPARATION AND CHARACTERISATION OF HYDROPHOBIC ULTRAVIOLET-CURABLE FLUORINATED POLYURETHANE ACRYLATE USING ULTRAVIOLET-LIGHT EMITTING DIODE PHOTOPOLYMERISATION

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To my beloved parents and siblings who unceasingly took the risk in believing and giving me all they have

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ABSTRACT

Nowadays, the green aspects of the ultraviolet (UV) curing technology have been extensively explored in order to make the technology more energy-efficient and more environmental-friendly. The elimination of mercury, low energy consumption and low operation cost make the ultraviolet light emitting diode (UV-LED) system seem to be a promising alternative. Nevertheless, the UV-LED system also has several challenges such as limited photoinitiators and surface cure issues. Therefore, it would be necessary to reformulate the coating composition to match the irradiation profile of UV-LED. In this study, UV-curable coating was formulated based on aliphatic urethane acrylate oligomer (BOMAR™ 7432-GB), 2-ethylhexyl acrylate, methyl methacrylate, trimethylolpropane triacrylate and commercial photoinitiators (Chivacure® 300 and Irgacure® 184). The feasibility of the UV-LED system to replace conventional UV-mercury method was first conducted by comparing its curing behaviours with respect to irradiation time. From the Fourier transform infra-red (FTIR) spectra obtained, the C=C absorption peak observed at 1635 cm^{-1} and 810 cm^{-1} were found to be decreasing upon UV irradiation indicating the proceeding of photopolymerisation. A non-tacky coating was achieved after 25 minutes of curing and the degree of conversion and gel fraction measurement were 98% and 95%, respectively indicating that the photopolymerisation via UV-LED is superior to UV-mercury. Since UV-LED system showed promising results in parallel with its inherently environmental friendly (mercury-free) nature, the hydrophobic UV-curable coating was prepared with the sufficient curing time of 25 minutes. One of the strategies to create hydrophobic surface is to reduce its surface free energy (SFE) by incorporating heptadecafluorodecyl methacrylate monomer (HDFDMA). The presence of fluorine group in the hydrophobic coating was examined by FTIR and nuclear magnetic resonance analysis. It is well accepted that fluorine-based material can change the surface wettability due to its exceptionally low SFE. The water contact angle of the coating evolved from 88.4° to 121.2° as the HDFDMA content increased which in turn, reducing the calculated SFE from 32.85 mJ/m^2 to 9.68 mJ/m^2. Scanning electron microscopy and atomic force microscopy confirmed the migration of the fluorine component towards the coating surface as it is the key factor that contributes to the hydrophobicity. However, the transparency of the cured coating dropped markedly with increasing HDFDMA content. Analogously, these results may attain various potential applications such as liquid-repellent coating and anti-fouling coating. In conclusion, the utilisation of UV-LED in this research was a great initiative to develop green aspect for photopolymerisation.

ABSTRAK

Pada masa kini, pembangunan aspek hijau dalam teknologi pengawetan ultraungu (UV) telah banyak dilakukan untuk menjadikannya lebih cekap tenaga dan lebih mesra alam. Penyingkiran merkuri, penggunaan tenaga dan kos operasi yang rendah menjadikan sistem ultraungu diod pemancar cahaya (UV-LED) muncul sebagai alternatif yang menjanjikan. Walau bagaimanapun, terdapat beberapa cabaran seperti fotopemula yang terhad dan isu-isu pengawetan permukaan. Oleh itu, komposisi salutan perlu diformulasikan semula mengikut kesesuaian profil penyinaran UV-LED. Dalam kajian ini, salutan awetan-ultraungu telah diformulasikan berdasarkan oligomer uretana akrilat alifatik (BOMAR™ 7432-GB), 2-etilheksil akrilat, metil metakrilat, trimetilolpropana triakrilat dan fotopemula komersil (Chivacure® 300 dan Irgacure® 184). Kebolehlaksanaan sistem UV-LED untuk menggantikan sistem konvensional UV-merkuri telah dilaksanakan terlebih dahulu dengan membandingkan kelakuan pengawetan. Berdasarkan spektra infra merah transformasi Fourier (FTIR), puncak penyerapan C=C pada 1635 cm^{-1} dan 810 cm^{-1} telah berkurangan apabila ia terdedah kepada penyinaran UV dan ini menunjukkan berlakunya fotopempolimeran. Salutan tidak lekat telah dicapai selepas 25 minit pengawetan dan darjah penukaran serta pengiraan pecahan gel masing-masing adalah 98% dan 95%, menunjukkan bahawa fotopempolimeran UV-LED adalah lebih baik daripada UV-merkuri. Berdasarkan keputusan yang ditunjukkan oleh sistem UV-LED dan juga sifatnya yang mesra alam (bebas merkuri), salutan awetan-UV yang hidrofobik telah dihasilkan dengan masa awetan selama 25 minit. Salah satu strategi untuk menghasilkan permukaan hidrofobik ialah dengan merendahkan tenaga bebas permukaan (SFE) iaitu dengan memasukkan monomer heptadekaflorodesil metakrilat (HDFDMA). Kehadiran kumpulan fluorin di dalam salutan hidrofobik ini diperiksa dengan FTIR dan analisis resonans magnetik nuklear. Kebolehan bahan berasaskan fluorin untuk mengubah kebolehbasahan permukaan dapat diterima disebabkan oleh SFE fluorin yang sangat rendah. Sudut sentuhan air salutan telah berubah daripada 88.4° kepada 121.2° apabila kandungan HDFDMA bertambah, dan ia juga menurunkan SFE salutan daripada 32.85 mJ/m^2 kepada 9.68 mJ/m^2. Mikroskop pengimbas elektron dan mikroskop daya atom mengesahkan migrasi komponen fluorin ke permukaan salutan dan ini merupakan faktor yang menyumbang kepada sifat hidrofobik. Walau bagaimanapun, kelutsinaran salutan menurun secara mendadak apabila kandungan HDFDMA bertambah. Secara analog, hasil kajian ini mempunyai pelbagai potensi penggunaan seperti salutan penghindar cecair dan salutan anti-kotoran. Kesimpulannya, penggunaan UV-LED dalam kajian ini merupakan inisiatif yang terbaik dalam membangunkan aspek hijau bagi fotopempolimeran.

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LIST OF SYMBOLS AND ABBREVIATIONS

γ_{sl}	-	Interfacial tension between solid and liquid
γ_{lv}	-	Interfacial tension between liquid and vapour
γ_{l}	-	Liquid surface tension
γ_{s}	-	Solid surface free energy
λ	-	Wavelength or lambda
phr	-	Part per hundred
2-EHA	-	2-ehtylhexyl acrylate
AATCC	-	American Association of Textile Chemist and Colorist
AFM	-	Atomic Force Microscopy
An	-	Anthracene
ATR	-	Attenuated Total Reflectance
BAPO	-	Bisacylphosphine oxide
BP	-	Benzophenone
CP	-	Cationic polymerisation
DIM	-	Di-iodomethane
DMPA	-	Dimethoxy-2-phenyacetophenone
EPOX	-	Epoxycyclohexylcarboxylate
FRP	-	Free radical polymerisation
FTIR	-	Fourier Transform Infra Red
GO	-	Graphene oxide
HDDA		1, 6-hexadiol diacrylate
HDFDMA	-	Heptadecafluorodecyl methacrylate
HDI	-	1,6- hexamethylene diisocyanate
FHPA	-	Fluorinated hyperbranched polyacrylate

ITX	-	Isopropyl thioxanthone
LED	-	Light Emitting Diode
MDI	-	4, 4’- diphenylmethane diisocyanate
MMA	-	Methyl methacrylate
NMR	-	Nuclear Magnetic Resonance
PDMS	-	Polydimethyl siloxane
PFA	-	Fluorinated polyacrylate
PFEUMA	-	Perfluoroether urethane methacrylate
PFUA	-	Fluorinated polyurethane acrylate
PI	-	Photoinitiator
PIS	-	Photoinitiating system
PPS	-	Phenylene sulphide
PUA	-	Polyurethane acrylate
Py	-	Pyrene
R_a	-	Average roughness
RMS R_q	-	Root mean square roughness
SEM	-	Scanning Electron Microscopy
SFE	-	Surface free energy
TMPTA	-	Trimethylolpropane triacrylate
Tz	-	Triazine
UV	-	Ultra Violet
VOC	-	Volatile Organic Compound
WCA	-	Water contact angle
XPS	-	X-ray Photoelectron Spectroscopy

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Surface properties of materials such as hydrophobic have been enthusiastically explored recent years (Yoshimitsu *et al.*,2002; Ha *et al.*, 2005; Shen *et al.*, 2005; Boinovich and Emelyanenko, 2008; Latthe *et al.*, 2009; Lalevée e*t al.*, 2009; Faustini *et al.*, 2010; Nadargi *et al.*, 2010; Subasri *et al.*, 2012; Yang *et al.*, 2015; Jiang *et al.*, 2016). Practically, hydrophobic surface is characterised by the water contact angle exceeding 90°. Instead of resistant towards water, the hydrophobic surface also offers other fascinating benefits including anti-fouling, corrosion resistance, anti-icing and self-cleaning effects (Zhang *et al.*, 2005; Zhu *et al.*, 2010; Faustini *et al.*, 2010; Park *et al.*, 2011). Consequently, this unique feature has been a desirable criterion in many applications such as optical devices, metal coating, fabrics and textile industry as well as in the automotives sectors.

One of the prevailing strategies to alter surface properties is by incorporating low surface free energy materials. For that purpose, fluorinated monomer or polymer has been material of interest due to its exceptionally low surface free energy. It also has been well-known that fluorinated polymer has outstanding and peculiar properties mainly caused by the unique features of fluorine atom. Their unique properties including high thermal, chemical and weather resistance, low refractive index, low dielectric constant and have high inertness towards moisture adsorption as well as interesting water and oil repellence (Brassard *et al.*, 2012; Ganesh *et al.*, 2012; Lee *et al.*, 2013; Shin *et al.*, 2013; Çanak and Serhatli, 2013; Yao *et al.*, 2014; Li *et al.*, 2014; Milionis *et al.*, 2016). Thus, this niche fluorinated material has been widely used in many applications such as chemical resistance coating, non-corrosive materials, anti-fouling coating and as interlayer dielectric.

In order to develop hydrophobic coating by following more environmentally friendly routes and preparation methods that do not involve harmful or flammable solvent, ultraviolet (UV) radiation coating technique was adopted. Since, basic formulation of radiation coating only consisted of three major components which are oligomer or prepolymer, monomers and photoinitiator respectively, this technique produced high solid formulation and eliminated the uses of solvent in its formulation. Indeed, the method provides environmentally friendly condition and energy saving attribute to its fast cure speed (Decker, 2002).

Among prepolymer used for UV-curable coating, urethane acrylate oligomer is mainly used due to the combination of remarkable properties of polyurethane and acrylate when cured. Urethane acrylate oligomer is one of the important materials in UV system that exhibits outstanding properties such as high toughness, flexibility and high abrasion resistance. With the benefits of polyacrylate that endows prominent performances in weatherability, water resistance and chemical resistance, polyurethane acrylate can exhibit several improved properties. This is resulted from its segmented structure and modification with acrylate (Qiu *et al.*, 2012; Çanak and Serhatli, 2013).

Meanwhile in UV technology, ultraviolet-light emitting diode (UV-LED) has been rapidly emerging in various fields such as ink and printing, dental application, adhesive, stereo-lithography and wood coating (Hubert and Dimas, 2003; Xie and Li, 2011; Dietlin *et al.*, 2015; Landry, *et al.* 2015; Yang *et al.*, 2016). UV-LED photopolymerisation or curing refers to the method of curing by utilising the energy output from the LED in UV spectrum. Elimination of harmful mercury and extraction of ozone makes the UV-LED system inherently environmentally friendly. Besides that, LEDs longer lifetime, suitability for heat sensitive materials and the capability of instant on/off operation makes the UV-LED system superior to existing UV mercury. In addition, UV-LED consumes 50% less energy than the equivalent mercury arc lamp due to its instant on/off capability as well as no unnecessary wavelength emitted (narrow wavelength distribution) (Kiyoi, 2013; Landry *et al.*, 2015).

In this study, the feasibility of UV-LED as the UV light source instead of mercury for urethane acrylate coating was carried out. The curing behaviour for both photopolymerisation was compared in terms of C=C conversion and gel fraction measurement as well as cure grade determination. As the UV-LED photopolymerisation was envisioned to give promising outcomes, the virtues of polyurethane and fluorinated polymer were combined to create solvent-free hydrophobic coating via UV-LED system. In brief, UV-LED technology greatly stimulates the key interest of the research.

1.2 Problem Statements

Historically, solvent-borne coating was the most employed method involving 50% to 70% the usage of organic solvent (Schwalm, 2007). Solvent-borne coating demonstrates excellent properties of the coating and lowers operation cost. It is also easy to handle in terms of processing. Since health and environmental apprehension become an important and crucial concern in coating sectors, the development of coating products with minimal environmental impacts such as low emission of volatile organic compounds (VOCs), energy consumption reduction and toxicity continue to be in high demand. Therefore, UV radiation coating was a smart approach since it offers remarkable properties such as low energy consumption, solvent-free formulation and time efficient without compromising desired coating performance.

Traditionally, UV mercury lamp was extensively used as the light sources for the radiation curing due to its broad wavelength distribution which easily matched the absorption of photoinitiator. However, it is often offset by the production of harmful ozone and mercury. Due to its toxic nature, there is an urge to eradicate its usage worldwide. According to the European Union's "Reduction of Hazardous Substance" directive or known as RoHS 2, the usage of UV mercury lamp needs to be eliminated in all instances. In contrast for the curing purposes, they have been exempted up until 22 July, 2016 and if the exemption is not extended, their usages will be banned especially in Europe (Mawby, 2014). Hence, in order to develop green aspect in UV coating, UV-LED has been utilised as a new alternative to the conventional UV curing (Mawby 2014; Salih *et al.*, 2015; Landry *et al.*, 2015).

Based on the study conducted by Jamaluddin (2012), a series of UV-LED curable urethane acrylate mixtures were prepared. This is because, the previous study was done by employing mercury-based lamps and it is already known that the lamp is hampered by the toxic nature of mercury. In the meantime, the UV-LEDs have several challenges to cope such as limited matching photoinitiator (PI), surface cure issue as well as complement UV chemistry formulation (Kiyoi, 2013). Subsequently, this research presents a suitable coating formulation through UV-LED photopolymerisation with the aid of Chivacure® 300 as the photoinitiator. Since different UV light or UV irradiation profiles can produce different properties of UV cured coating, this equivalent work presents the effect of UV-LED and UV-mercury as the light source toward curing behaviour of urethane acrylate coating.

Copolymerisation of fluorinated monomers with common polymers such as polyacrylate and polyurethane is interesting to improve surface properties of parent polymer. However, the utilization of fluorinated monomers is limited owing to their incompatibility with certain polymer. Since then, numerous of studies conducted to synthesis fluorinated monomer which could overcome the stated imperfection in order to further utilize the benefits conferred by fluorinated group. For this reason, fluorinated methacrylate monomer is one of the candidates because it has good reactivity with other monomers or polymer. On one hand, low crystallinity and good solubility of the fluorinated methacrylate with other monomer can improve its processibility (Yao *et al.*, 2014).

Some studies have been conducted on the UV-curable polyurethane acrylate but mostly employed the UV-mercury curing system (Tasic *et al.*, 2004; Lee *et al.*, 2006; Lin *et al.*, 2008; Park *et al.*, 2008; Kunwong *et al.*, 2011; Džunuzović *et al.*, 2012; Qiu *et al.*, 2012; Jančovičová *et al.*, 2013; Çanak and Serhatli, 2013; Shin *et al.*, 2013; Park *et al.*, 2014; Llorente *et al.*, 2016). Moreover, there has been limited work to date on UV-curable copolymer urethane acrylate oligomer and acrylate monomer possessing fluorinated group especially by using UV-LED technology. The combination of polyurethane acrylate and fluorinated methacrylate monomer is expected to be effective in an attempt to fabricate hydrophobic coating assisted by UV-LED photopolymerisation.

1.3 Objectives

In this research, a solvent-free UV-LED curable coating was prepared based on urethane acrylate oligomer and fluorinated methacrylate monomer. This study was further classified into following goals:

a) To investigate the feasibility of UV-LED technique in photopolymerisation to replace current UV-mercury lamp according to their curing behaviour by varying the irradiation time

b) To characterise the effect of fluorinated acrylate monomer content towards coating surface properties of UV-LED curable coating

1.4 Scopes of Study

In this research, UV-LED technology was employed to cure the hydrophobic coating replacing the current UV radiation technique which is mercury-based lamp. The first part of this study reported the curing behaviour of the curable coating via UV-LED and UV-mercury techniques respectively. The UV irradiation time was varied in order to determine suitable curing time. In addition, the UV-LED intensity was kept constant and commercial photoinitiator, Chivacure® 300 (λ~300-400nm) was used in the photopolymerisation as it matches the UV-LED spectral output. Similar with the UV-LED system, UV-mercury lamp intensity also was kept constant and Irgacure® 184 was used as the photoinitiator. The curing behaviour was evaluated based on conversion and gel fraction measurements as well as their tackiness.

Meanwhile, the second part of this research involved the study regarding the influences of the fluorinated methacrylate monomer towards coating properties. For that purpose, heptadecafluorodecyl methacrylate content or HDFDMA (97%) was varied from 0 phr to 10 phr in order to find the appropriate content with high contact angle and other favourable properties. The versatility of the hydrophobic mixture was also assessed by coating onto different substrates such as paper, PET textile and PMMA plate.

The surface properties of the coating were characterised by measuring its surface free energy from contact angle data using CAM 101, KSV Instrument optical contact angle system. In addition, surface topography of the coating was also examined using Scanning Electron Microscopy (JEOL, JSM-6390LV) and Atomic Force Microscopy (JPK Instrument) determined its surface roughness. Meanwhile, its optical transparency was characterised using UV-Visible spectrophotometer (UV-1800, Shimadzu).

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