

NOVEL UV LED PHOTOPOLYMERIZATION AND CHARACTERIZATION
FOR POLYACRYLAMIDE AND POLY(*N*-ISOPROPYLACRYLAMIDE)
HYDROGELS

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A thesis submitted in fulfillment of the
requirement for the award of the degree of
Master of Engineering (Polymer)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

JULY 2016

To my families, supervisor and friends, thank you for all your support along the way

ACKNOWLEDGEMENTS

In the name of Allah SWT, The Most Beneficent and The Most Merciful. Alhamdulillah, all praise to Almighty Allah SWT, my thesis was now completed. I would like to acknowledge and extend my heartfelt gratitude to the following persons who have made the completion of this thesis.

First and foremost, I would like to thank my supervisor of the project, Dr Nadia binti Adrus for the valuable guidance and advice. With her constant encouragement and inspiration, the process in getting this thesis was made much smoother and easier. My appreciation also goes to my co-supervisor, PM. Dr. Shahrir Hashim and Dr Hafiz Dzarfan bin Othman for their willingness to contribute tremendously to this project in terms of ideas and facilities.

An honorable mention goes to my parents, Ayub bin Abdullah and Saripah bte Mohd Salleh and also my sisters, for without their continuous support and understandings the tasks of completing the project and handling the obstacles that I went through would not be so easy.

I would also like to thank all the staffs and my friends especially for those who provided valuable information and their guidance on this project. The list of those who contributed towards the completion of the project goes on. However, it would not be possible for me to list all of them. Nonetheless, my appreciation also goes to them.

ABSTRACT

In this study, polyacrylamide (PAAm) and poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels were synthesized via ultraviolet light-emitting diode (UV LED) ($\lambda \sim 365$ nm) photopolymerization system. UV LED technology has offered better alternative than UV mercury (Hg) system for curing technology especially for temperature-sensitive polymeric hydrogels as it can be operated without heat generation and with fast curing response. The control experiment using commercial photoinitiators has shown that UV LED system was suitable to polymerize hydrogels provided that; photoinitiator has the overlap emission with UV LED spectra. However, most commercial photoinitiators have limited solubility in water. Thus, suitable water soluble photoinitiator (WSPI) for UV LED system (i.e. $\lambda \rightarrow 330$ -365 nm) was prepared in order to synthesize UV LED curable hydrogel in purely water formulation. The water soluble photoinitiator was obtained from complexation of 2,2-dimethoxy-2-phenylacetophenone (DMPA) and methylated- β -cyclodextrin (M β CD). According to the results presented in this work, high monomer conversion (> 90 %) was achieved with WSPI-initiated hydrogels. The non-responsive and responsive behavior of PAAm and PNIPAAm hydrogels towards temperature were demonstrated by swelling and rheological measurements. In addition, swelling and rheological methods gave good correlation for determination of mesh sizes. From rheological measurements, the elastic modulus (G') was higher than the loss modulus (G'') and both parameters were independent to the measured frequency window. It has shown that UV LED cured hydrogels possessed ideal rubber characteristic. Tensile properties of the hydrogels showed similar trend curve as commercial contact lenses reported in the previous study. Clearly, this study has revealed that UV LED system is a good tool to synthesize hydrogels by using the excellent choice of photoinitiator.

ABSTRAK

Dalam kajian ini, hidrogel poliakrilamida (PAAm) dan poli(*N*-isopropilakrilamida) (PNIPAAm) telah disintesis melalui sistem fotopolimeran sinaran ultraungu diod pemancar cahaya (UV LED) ($\lambda \sim 365$ nm). UV LED teknologi telah memberikan alternatif yang lebih baik berbanding sistem sinaran ultraungu merkuri (UV Hg) kerana teknologi pempolimerannya lebih cepat dan sistemnya tidak menjana haba. Ciri-ciri ini amat sesuai untuk hidrogel polimer yang sensitif terhadap haba. Eksperimen kawalan menggunakan foto pemula komersial telah menunjukkan bahawa sistem UV LED sesuai untuk pempolimeran hidrogel dengan syarat foto pemula tersebut mempunyai pertindihan spektra dengan sistem UV LED. Walau bagaimanapun, kebanyakan foto pemula komersial tidak larut dalam air. Oleh itu, foto pemula larut air (WSPI) yang sesuai untuk sistem UV LED (iaitu $\lambda \rightarrow 330-365$ nm) telah disediakan bagi membolehkan sintesis formulasi hidrogel yang berasaskan air menggunakan teknik pempolimeran UV LED. Foto pemula larut air telah diperolehi melalui pengkompleksan 2,2-dimetoksi-2-fenilasetofenon (DMPA) dan metil- β -siklodekstrin (M β CD). Berdasarkan hasil kajian, penukaran monomer yang tinggi (> 90%) telah diperolehi bagi formulasi hidrogel yang menggunakan WSPI. Sifat tidak responsif dan responsif hidrogel PAAm dan PNIPAAm terhadap suhu telah dipamerkan melalui darjah pembengkakan dan pengukuran reologi. Di samping itu, darjah pembengkakan dan pengukuran reologi ini juga memberi korelasi yang baik untuk menentukan saiz jaringan. Melalui pencirian pengukuran reologi hidrogel, modulus elastik (G') adalah lebih tinggi daripada modulus kehilangan (G'') dengan kedua-dua parameter ini tidak bergantung pada ukuran frekuensi. Ini menunjukkan hidrogel yang diperolehi mempunyai ciri getah yang ideal. Sifat tegangan bagi hidrogel pula menunjukkan keputusan lengkung yang sama seperti kajian yang dilaporkan sebelum ini. Secara umumnya, kajian ini telah membuktikan bahawa sistem UV LED berpotensi tinggi dalam mensintesis hidrogel dengan menggunakan foto pemula yang sesuai.

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LIST OF ABBREVIATIONS

3D	-	Three dimensional
AAm	-	Acrylamide
APS	-	Ammonium persulfate
BDMM	-	2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)-1-butanone
Chivacure 300	-	Oligo[2-hydroxy-2-methyl-1-[4-(1-ethylvinyl)phenyl]propanone]
Darocur 1173	-	2-hydroxy-2-methyl-1-phenyl propan-1-one
DMPA	-	2,2-Dimethoxy-2-phenylacetophenone
FTIR	-	Fourier Transform Infrared Spectroscopy
Irgacure 2959	-	1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one
LCST	-	Lower Critical Solution Temperature
MBAAm	-	<i>N,N'</i> -methylenebisacrylamide
MBS	-	Sodium 4-[2-(4-morpholino)benzoyl-2-dimethylamino]butylbenzenesulfonate
NIPAAm	-	<i>N</i> -isopropylacrylamide
NMR	-	Nuclear Magnetic Resonance
WSPI	-	Water soluble photoinitiator
PAAm	-	Polyacrylamide
PET	-	Poly(ethylene terephthalate)
PHEMA	-	Poly-2-hydroxyethylmethacrylate
PMMA	-	Poly(methylmethacrylate)

PNIPAAm	-	Poly(<i>N</i> -isopropylacrylamide)
SP	-	Smart Polymer
SRH	-	Stimuli Responsive Hydrogels
TEMED	-	<i>N,N,N',N'</i> -tetramethylethylenediamine
TOC	-	Total Organic Carbon
UV	-	Ultraviolet
UV LED	-	Ultraviolet light-emitting diode
UV Hg	-	Ultraviolet mercury based lamp
UV-Vis	-	Ultraviolet visible spectroscopy
VOC	-	Volatile Organic Compounds

LIST OF SYMBOLS

C_N	-	Characteristic ratio
G'	-	Elastic modulus
G''	-	Loss modulus
l	-	Length
L_B	-	Length at break
L_O	-	Original length
M	-	Molar mass
M_c	-	Crosslinking points
N	-	Newton
N_A	-	Avogadro's number
Q	-	Degree of swelling
T	-	Temperature
W_d	-	Mass of dried samples
W_s	-	Mass of swollen samples
wt	-	Weight
γ	-	Strain amplitude
λ	-	Wavelength
ξ	-	Mesh sizes
ω	-	Angular frequency

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CHAPTER 1

INTRODUCTION

1.1 Research Background

In recent years, the development of polymer based hydrogels has increased worldwide. Hydrogels are hydrophilic polymers which built up of three dimensional polymeric networks [1]. Nowadays, the development of polymer based hydrogels has attracted great attention especially in biomedical applications, such as drug carriers, tissue engineering and actuators [2]. This is attributed to the characteristics of hydrogels that similar to biological tissue and at the same time compatible with the human body [1, 3].

Hydrogels have soft consistency and high water content [3] which tend to swell and retained water in its structure due to the crosslinking structure with the presence of hydrophilic groups [4]. According to their swelling behavior, hydrogels can be divided into two categories; i.e., conventional and stimuli responsive hydrogels (SRH) [5]. In this study, conventional polyacrylamide (PAAm) hydrogels and SRH poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels were chosen as both hydrogels were derivatives and usually synthesized for UV curing photopolymerization.

Free radical photopolymerization is one of the conventional methods used to polymerize hydrogels. Photopolymerization converts monomer into polymeric hydrogels with the help of photoinitiators [6]. Some of the researchers preferably

chose photopolymerization due to its several advantages; i.e., it can be created in situ, fast curing rates as well as temporal and spatial control over the polymerization process [6, 7].

Ultraviolet light-emitting diode (UV LED) system is a green technology and environmental friendly system. It can offer fast curing rate, reduction in down time associated in maintenance and cost effectiveness. UV LED system produced less energy than UV mercury (UV Hg) system which cause no temperature builds up and very little heat is generated [8]. Up to date, UV LED system has been used for few materials, such as adhesives and coating technology [8, 9]. Hence, this light source is envisioned to be effective for curing hydrogels as well since UV LED was successfully used for coating technology.

UV LED system emits monochromatic radiation. Typical UV LED emission wavelengths are 365, 385 and 405 nm. Oligo(2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone) under the trade name Chivacure 300 and 2,2-dimethoxy-2-phenylacetophenone (DMPA) are examples of commercially available photoinitiators. These photoinitiators have only moderate solubility in water.

From recent studies, new water soluble photoinitiators can be synthesized by several methods; i.e., introduction of hydrophilic groups or attachment of ionic groups [10-12]. Self-assembly between monomer and photoinitiator is one of the method that have been widely used due to their effectiveness and rapidness in producing modified water soluble photoinitiator [11].

In this study, PAAm and PNIPAAm hydrogels was prepared using water soluble photoinitiator via UV LED photopolymerization. Studies on physical properties of hydrogels are also very limited since hydrogels were known to have low mechanical strength. Therefore, the efficiency of modified water soluble photoinitiator towards the physical and tensile properties of hydrogels was analyzed.

1.2 Problem Statement

Recently, a considerable amount of research reported on PAAm and PNIPAAm hydrogels and most of it proposed the use of UV Hg curing system. However, several limitations of using UV Hg system were encountered; for example high energy consumption, heat generation and takes longer time to warm up.

No study has been reported yet on photopolymerization of hydrogels using UV light from LED source. Elimination of the harmful mercury and ozone extraction and reduction in down time associated in maintenance are some of the benefits that UV LED can offer [8]. Thus, development of UV LED system for hydrogels curing is a promising technology to replace UV Hg system.

The success of photopolymerization technology depends on the availability and action of appropriate photoinitiators. Successful of photopolymerization process does not only depending on the UV systems chosen, but also the efficiency of photoinitiator [13]. For such applications, 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure 2959, $\lambda \sim 280$ nm) is the most commonly used photoinitiator, by virtue of its moderate water solubility. On the contrary, this initiator has an absorption wavelength that far below the wavelength of UV LED light ($\lambda \sim 365$ nm); make it inefficient for UV LED system.

For certain applications, water soluble photoinitiator was required to create free organic solvents condition. There is no significant published research with regard to hydrogels formulation using water soluble photoinitiator via UV LED system [12]. Thus, novel water soluble photoinitiator, WSPI with the absorption wavelength near 365 nm was produced in order to suit the UV LED system.

Water soluble photoinitiator was synthesized by several methods such as self-assembly, sulfonation process and addition of quaternary group. Self-assembly was simple and effective method among these studies [14]. This is because self-assembly

method allowed for straightforward complexation to obtain new photoinitiator from the commercial photoinitiator with similar performance.

In brief, UV LED system is envisioned to be the most effective UV source for synthesis and curing of PAAm and PNIPAAm hydrogels. Suitable and efficient water soluble photoinitiator was prepared. It is expected that desired final properties of resulting hydrogels with high monomer conversion was obtained. Hydrogels with high monomer conversion shows a good integration hydrogels and very useful in many biomedical applications.

1.3 Objectives of the study

This study revolves on the development of PAAm and PNIPAAm hydrogels using the UV LED system with. Specifically, the aims are:

- a) To synthesize and characterize PAAm hydrogels using UV LED system based on optimized photopolymerization conditions obtained for UV Hg system using commercial photoinitiators.
- b) To synthesize and characterize WSPI for UV LED curable PAAm and PNIPAAm hydrogels system.
- c) To synthesize and characterize the monomer conversion, swelling, mesh sizes, rheological and tensile properties of PAAm and PNIPAAm hydrogels using WSPI via UV LED system.

1.4 Scope of the study

In this study, the first task was to synthesize PAAm and PNIPAAm hydrogels from acrylamide (AAm) and *N*-isopropylacrylamide (NIPAAm) monomers, respectively with *N,N'*-methylenebisacrylamide (MBAAm) as a crosslinker monomer. Polymerization of PAAm and PNIPAAm hydrogels were conducted via UV LED systems. The conditions for polymerization were adopted from the optimized photopolymerization conditions of UV Hg system in the previous study. The polymerizations were initiated using three different commercial photoinitiators; Irgacure 2959, Chivacure 300 and DMPA.

In the second task, WSPI was prepared through complexation of DMPA and methylated- β -cyclodextrin (M β CD). WSPI obtained was further tested with fourier transform infrared spectroscopy (FTIR), UV-Visible spectroscopy (UV-VIS), nuclear magnetic resonance (NMR) and solubility test.

PAAm and PNIPAAm hydrogels were prepared using synthesized WSPI via UV LED systems. Proper tuning on photopolymerization conditions has to be achieved for completion of monomer conversion. This includes UV time and photoinitiator concentrations. Various amount of photoinitiators concentration were added to the hydrogel formulation, varying from 1-5 wt.% relative to AAm/NIPAAm and UV times (2.5 – 20 minutes).

The scope of the work also included characterization of physical and structural properties of resulting bulk hydrogels. After polymerization, monomer conversion was determined. For further hydrogels characterization, swelling measurements in pure water as function of temperature were performed. Mechanical properties of cured hydrogels were studied by using oscillatory rheometer and texture analyzer. Using rheology, photopolymerized bulk PAAm and PNIPAAm hydrogels were characterized to determine their viscoelasticity, temperature responsiveness of the hydrogels and microstructure. Mesh sizes of the hydrogels were calculated from degree of swelling and rheology measurement.

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