SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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FABRICATION AND CHARACTERIZATION OF UV-CROSSLINKED PDMS HYDROGEL

By

THAI GAR LOCK

Supervisor: Dr. Zuratul Ain Abdul Hamid

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled: "**Fabrication and Characterization of UV-crosslinked PDMS hydrogel**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

Name of student : Thai Gar Lock Signature:

Date : 3 July 2017

Witnessed by

Supervisor : Dr. Zuratul Ain Bt. Abdul Hamid Signature:

Date : 3 July 2017

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ABBREVIATIONS

CROP	Cationic Ring Opening Polymerization
D_4	Octamethylenecyclotetrasiloxane
DSC	Differential Scanning Calorimetry
ES	Equilibrium swelling
FTIR	Fourier Transform Infrared
NMR	Nuclear Magnetic Resonance
PDMS	Polydimethylsiloxanes
PEGDA	Polyethylene glycol
PEGDA	Poly(ethylene glycol) diacrylate
T_g	Glass Transition Temperature
T_m	Melting Temperature
TPA	Texture Profile Analysis
UV	Ultraviolet

LIST OF SYMBOLS

°C	Degree Celcius
ρ	Density
H^+	Hydrogen ion
K	Kelvin
kJ/mol	Kilo joule per mol
mg	Milligram
ppm	Part per million
%	Percent
wt%	Weight percent

FABRIKASI DAN PENCIRIAN UV-SAMBUNG SILANG PDMS HIDROGEL

ABSTRAK

Hidrogel adalah salah satu bio bahan yang sesuai untuk kejuruteraan tisu. Hidrogel ditakrifkan sebagai struktur polimer yang membengkak apabila terdedah kepada air. Polidimetilsiloksana biasanya digunakan bio bahan untuk kejuruteraan tisu kerana sifat lengai dan tidak toksik. Walau bagaimanapun, terdapat kelemahan utama bagi polidimetilsiloksana iaitu sifat semula jadinya yang hidrofobik. Untuk mengatasi kelemahan ini, polidimetilsiloksana telah disambung silang dengan polietilena glikol untuk meningkatkan sifat hidrofiliknya. Allil metakrilat dan polidimetilsiloksana 1k telah digunakan sebagai pelarut reaktif untuk membentuk hidrogel silang ultraviolet. Polidimetilsiloksana-SiH dan Polidimetilsiloksana-MA yang telah disintesis disahkan dengan jelmaan fourier spektroskopi inframerah (FTIR) dan resonans magnet Nuklear (NMR). Ultraviolet sambung silang hidrogel telah dicirikan dengan ujian pembengkakan, imbas siasat mikroskopi (SPM), kalorimetri pengimbasan pembezaan (DSC), sudut sentuhan dan Tekstur Profil Analisis (TPA). Daripada analisis, didapati bahawa peningkatan dalam kandungan pelarut reaktif tidak mempunyai kesan yang ketara ke atas pembengkakan, hablur yang lebih stabil, peningkatan nilai kekerasan dan penurunan pada pelekatan dan daya tahan dan kesan tidak tetap pada sudut sentuhan. Ia juga didapati bahawa dengan meningkatkan kandungan polietilena glikol, pemisahan fasa berlaku pada peringkat yang lebih teruk, peratusan pembengkakan telah meningkat, puncak penghabluran semula terhasil, peningkatan nilai kekerasan, penurunan nilai pelekatan dan daya tahan dan kesan tidak tetap pada sudut sentuhan.

FABRICATION AND CHARACTERIZATION OF UV-CROSSLINKED PDMS HYDROGEL

ABSTRACT

Hydrogel is one of the biomaterial that is suitable for tissue engineering. Hydrogel is defined as polymeric structure that swollen when expose to water. Polydimethylsiloxane is commonly used biomaterials for tissue engineering due to inert and nontoxic properties. However, there is the main drawback of polydimethylsiloxane which it is hydrophobic in nature. To overcome this limitation, polydimethylsiloxane was crosslinked with polyethylene glycol in order to enhance it hydrophilic property. Allyl methacrylate and polydimethylsiloxane 1k was utilized as reactive diluent to form ultraviolet crosslinked hydrogel. Polydimethylsiloxane-SiH and Polydimethylsiloxane-MA that was synthesized had been confirmed with Fourier transform infrared (FTIR) spectroscopy and Nuclear magnetic resonance (NMR). Ultraviolet crosslinked hydrogel had been characterized by swelling test, Scanning Probe Microscopy (SPM), Differential Scanning Calorimetry (DSC), contact angle and Texture Profile Analysis (TPA). From the analysis, it was found that increasing in reactive diluent content had no significant effect on swelling, more stable crystal structure, increased in hardness value and decreased in adhesiveness and resilience and fluctuating effect on contact angle. It also found that with increasing polyethylene glyco content, phase separation happens at a more severe level, swelling percentage had increased, recrystallization peak form, fluctuating effect on hardness value, decreased in adhesiveness and resilience and contact angle decreased.

Chapter 1

INTRODUCTION

1.1 Research Background

Biocompatible polymers are polymers whether synthetic or natural that used to function in intimate contact with living tissue or replace part of a living system. Biocompatible polymers are created to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body. Example of biocompatible polymers are hydrogel that used to replace damage ear membrane. Biocompatibility is a term used to describe the suitability and sustainability of a polymer when exposure to the body. A polymer will be considered biocompatible if it allows the body to function without any complications such as allergic reactions or other adverse side effects (Vert et al, 2012).

Biocompatibility may be defined as "ability of a biomaterial to perform its desired function, generating the most appropriate beneficial cellular or tissue response to that specific situation, and optimizing the clinically relevant performance without eliciting any undesirable effects in the recipient.". In general, a biomaterial is defined as any substance, except food and medications, that can be used for a length of time as part of a system that aims to treat or to replace any tissue, organ, or body function.

Since researcher published a proposal on the usage of the hydrogel in 1960, hydrogels have generated interest in the biomedical materials research supporting its use as biomaterials. It has the potential to be made for applications in tissue engineering as

polymer scaffold, in wound healing, in cell delivery and in diagnostic devices as electroconductive biomaterials. Hydrogels have the capability to imitate the functional role of extracellular matrix in tissue. Synthetic polymers used for the synthesis of hydrogels can be further classified into two categories, which are synthetic neutral and synthetic charged. (Ahmed.2015).

Over the years, researchers have defined hydrogels in many ways. The most common definition of the hydrogel is a water-swollen, and cross-linked polymeric network produced by the reaction of monomers. Other definition of hydrogel is they exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water (Ahmed, 2015). In the past of 50 years, hydrogels have received considerable attention due to their exceptional function in biomaterial field. They possess also a degree of flexibility very similar to natural tissue due to their water absorption ability. The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains.

PDMS is an inorganic polymer which is biocompatible, low glass transition temperature, hydrophobic, exhibits excellent gas permeability, and exceptional elasticity when lightly crosslinked. The stability, lack of toxicity, and excellent biocompatibility of PDMS make these materials well suited for use in personal care, pharmaceutical, and medical device applications. (Ratner et al, 2004). Other than that, it is chemically inert, thermally stable, simple to handle and manipulate, exhibits isotropic and homogeneous properties as well as lower cost than silicon (McDonald and Whitesides, 2002).

PDMS also shows some drawbacks. One the main drawbacks for cell biology is that PDMS can absorb small hydrophobic molecules like biomolecules and drugs from the solution. Also, many researchers noticed adsorption of proteins on the PDMS surface which has been identified as a major problem for molecular biology. PDMS's hydrophobicity also has been a noted stumbling block. Although the surface can be made hydrophilic, this is not a natural act for the polymer, and it will revert back to its hydrophobic self in air. The relapse can be a major problem because unwanted phenomena such as adsorption of proteins to the surface start to happen (Ahmed, 2015). To overcome this problem, numbers of PDMS treatments have been developed depending on the application. Hence, in this project, PDMS will be blend with other hydrophilic polymer which is PEGDA to overcome its drawback.

Poly(ethylene glycol) diacrylate (PEGDA) based hydrogels have been extensively utilized as scaffolds for the regeneration of tissues including bone, cartilage, nerve, and vascular tissue. PEGDA hydrogels are particularly useful for biomaterial study because of their intrinsic resistance to protein absorption and cell adhesion. PEGDA chains of any length can be easily synthesized by the controlled polymerization of ethylene oxide or ethylene glycol in aqueous solution. PEGDA is highly biocompatible and well-suited for use in hydrogels for biological studies. Its repeating alkane-ether motif makes PEGDA not only very hydrophilic, which is important for nutrient and waste transport, but also biochemically inert. PEGDA is also non-immunogenic and resistant to protein adsorption, making it suitable for in vivo as well as in vitro studies. However, unlike natural polymers that are used in hydrogels, PEGDA is not biodegradable (Agrawal and Robert, 2001).

In order for PEGDA hydrogel to act as biomaterial polymer, precisely tuneable chemical and physical properties are crucial. For PEGDA hydrogels, crosslink density and mechanical properties may be tailored by simply varying the molecular weight or the concentration of PEGDA. However, since PEGDA hydrogels are single-component systems, the ability to uncouple various material properties, such as modulus and swelling, is limited. Thus, hydrogels that maintain the benefits of PEGDA while extending the ability to tune and uncouple material properties would further enhance the ability to establish relationships between cell behavior and scaffold properties (Ifkovits and Burdick, 2007).

In this project, the base polymer which is PDMS-MA 12k was synthesized. Then, it will be blend with PEGDA which get directly from manufacturer at different ratio to produce hydrogel by UV-crosslinking. The hydrogels reported herein are two component systems and so the ratio of both macromonomers was used to tailor hydrogel properties. The chemical properties of the hydrogels were switched from purely inorganic PDMS to inorganic-organic PDMS-PEGDA by introducing increased levels of PEGDA. In addition, the effect of hydrogel composition on physical properties, including, equilibrium swelling, contact angle, thermal properties, texture analysis was examined.

1.2 Problem Statement

PDMS is a very suitable material for tissue engineering due to inert behavior and nontoxic but there is the main drawback on PDMS which is its hydrophobic behavior. Adsorption of protein on the PDMS surface noticed by many researchers which have been identified as a major problem for molecular biology. (Coady and Marois, 2001). Hence, PDMS need to be modified for it to use in tissue engineering field. One of the suitable material to blend with will be PEGDA. PEGDA is a hydrophilic material which is also non-toxic, inert, high water content and physical properties similar to soft tissues, including high permeability for oxygen, nutrients, and other water-soluble metabolite which make PEGDA a good candidate to blend with PDMS (Mazzoccoli et al, 2010).

PDMS can be produced into desired molecular weight by acid-catalysed cationic ring opening polymerization (CROP). High molecular weight polymer will have a better physical properties which are more suitable to be fabricated into hydrogel. To produce hydrogel that combine high molecular weight PDMS blend with PEGDA, reactive diluents shall be used to ease the polymerization and UV crosslinking (Hamid, 2016). The effect of this reactive diluent towards the properties of the hydrogel is unknown.

Addition of PEGDA in PDMS will result in phase separation. Phase separation is not desired in hydrogel as the different area will have different properties such as hydrophobicity which cause protein adsorption. The effect of different PEGDA ratio on the hydrogel properties and the severity of phase separation which follow by the increasing amount of PEGDA from literature review are insufficient to determine the hydrogel properties. Hence, further study need to be carried out.

The outcomes of this project are important to determine the potential of using UV-crosslinked PDMS-PEGDA hydrogel as synthetic ear membrane in order to cure Tympanic membrane perforations (TMP). Currently, there are two therapeutic procedures which function to restore the TM integrity and close TM perforations. Although both techniques have a high success rate, they require surgery and incision to obtain the graft material. Furthermore, surgery complications can result in multiple interventions required to achieve a complete closure of the perforation. Hence, there is a need for non-surgical, safer and cost-effective alternatives. Thus, tissue engineering is put in action to restore the anatomy (McDonald and Whitesides, 2002).

1.3 Research Objectives

i. To study the effect of different types of reactive diluents on the hydrophobicity, thermal properties and physical properties of PDMS-MA/PEGDA hydrogel

ii. To study the effect of PDMS-MA/PEGDA ratio on the hydrophobicity, thermal properties and physical properties of PDMS-MA/PEGDA hydrogel

iii. To study the phase separation between PDMS-MA and PEGDA via topography study.

1.4 Scope of Study

This project focuses on synthesis and characterization of PDMS-MA/PEGDA hydrogel. The base polymer PDMS-MA was synthesized and mix with PEGDA. The synthesis was conducted in three stages. The first stage is the synthesis of PDMS-SiH and followed by stage two, synthesis of PDMS-MA by changing the functional group. Then PDMS-MA were mix with PEGDA at different ratio and produced hydrogel. Various tests were carried out to identify the structure and measure the thermal properties, and physical properties of PDMS-MA/PEGDA hydrogel.

1.5 Organization of thesis component

Chapter 1 Introduction

In this chapter, research background of hydrogel, problem that currently facing in order to produce UV crosslinked PDMS-PEGDA hydrogel, project objectives and scope of study had been discussed.

Chapter 2 Literature review

In this chapter, detail explanation about hydrogel, PDMS, PEGDA and hydrogel properties had been discussed.

Chapter 3 Methodology

In this chapter, full detail of materials, procedures to prepare hydrogel and characterization had been fully discussed and proposed.

Chapter 4 Results and Discussions

In this chapter, hydrogel had been characterized by FTIR, NMR, DSC, SPM, TPA, swelling and contact angle. Results from the testing had been plotted in graph and discussed.

Chapter 5 Conclusion

In this chapter, main findings from the project; statement about the main contributions of the research and recommendations for future work had been summarized.

Chapter 2

LITERATURE REVIEW

2.1 Tissue Engineering

Tissue engineering is the use of a combination of cells, engineering and materials methods, and suitable biochemical and physicochemical factors to improve or replace biological tissues. For a medical purpose, tissue engineering involves the use of scaffold for the formation of new viable tissue (Whitney et al, 2014).

Scaffolds are materials that have been engineered to cause desirable cellular interactions to contribute to the formation of new functional tissues. Cells are 'seeded' into these structures capable of supporting three-dimensional tissue formation. Scaffolds mimic the extracellular matrix of the native tissue, recapitulating the in vivo milieu and allowing cells to influence their own microenvironments. They usually function to deliver and retain cells and biochemical factors, allow cell attachment and migration, enable diffusion of vital cell nutrients and expressed products and biological influences to modify the behaviour of the cell phase (Whitney et al, 2014)

Many different materials such as PDMS and PEGDA have been investigated for the use of scaffolds. Most of these materials especially hydrogels have been known in the medical field before the advent of tissue engineering as a research topic. Examples of these materials are PDMS and PEGDA (Whitney et al, 2014)

2.2 Hydrogel

Hydrogels are polymer networks that swell significantly in water due to the diffusion and entrapment of water molecules in 3D crosslinked polymeric structure. For the last two decades, synthetic hydrogels were replaced natural hydrogel with its excellent properties which are high gel strength, high capacity of water absorption and long service life. Example of natural hydrogel are collagen, gelatine, fibrin, silk, agarose, hyaluronic acid, chitosan, dextran and alginate while example of synthetic hydrogels are poly(ethylene glycol)(PEG), Poly(lactic acid) (PLA), poly(2-hydroxypropyl methacrylamide) (pHPMAm), poly(vinyl alcohol) (PVA) and poly(hydroxyethyl methacrylate) (pHEMA). Synthetic hydrogel's degradability and functionality can be tailored by its structures that can be modified. Hence, it what make synthesis hydrogel a better candidate to natural hydrogel. Hydrogels can be synthesized from purely synthetic components. Also, the hydrogel can remain stable despite the conditions of sharp and strong fluctuations of temperatures (Ahmed, 2015).

Recently, hydrogels have been defined as two or multicomponent systems that consist of 3D network of the polymer chain that water are able to fill the space between macromolecules. Typically, in the swollen state, the total mass content of water in hydrogel are usually higher than then total mass content of the polymer. In practice, to achieve high degrees of swelling, it is common to use synthetic polymers such as poly(vinyl alcohol) and cellulose chemical derivatives (carboxy methyl cellulose CMC) that are water-soluble when in non-crosslinked form (Niloofar et al, 2016).

Hydrogels can synthesize in different ways. These include one-step procedures like polymerization and parallel cross-linking of multifunctional monomers, as well as

multiple step procedures involving synthesis of polymer molecules having reactive groups and their subsequent cross-linking, possibly also by reacting polymers with suitable cross-linking agents. The polymer engineer can synthesize and design polymer networks with control over polymer structure such as cross-linking density and with tailored properties, such as chemical and biological response to stimuli, biodegradation and mechanical strength (Peppas and Harland, 1991).

2.2.1 Classification of hydrogel products

The hydrogel can be classified on different bases as below:

i. Classification based on source

Classification according to polymeric composition. These can be explained further by the following:

(a) Homopolymeric hydrogels are referred to polymer network synthesis from a single kind of monomer. Homopolymers have cross-linked skeletal structure depend on the polymerization technique and nature of the monomer.

Example: use of poly (2-hydroxyethyl methacrylate) (polyHEMA) as a monomer, polyethylene glycol dimethacrylate as cross-linking agent and benzoin isobutyl ether as the UV-sensitive initiator

(b) Copolymeric hydrogels refer to two or more different monomer species that arranged in alternating, block or random configuration along the polymer chain network with at least one hydrophilic component.

Example: biodegradable triblock poly(ethylene glycol)-poly(ε-caprolactone)-poly(ethylene glycol) (PECE) co-polymeric hydrogel

.

(c) Multipolymer Interpenetrating polymeric hydrogel (IPN) refer to two independents cross-linked natural or synthetic polymer component that contained in a network form. In semi- IPN hydrogel, one component is crosslinked polymer and another component is non-cross-linked polymer.

Example: polyethyleneglycol diacrylate (PEGDA) hydrogels modified with β-chitosan

ii. Classification based on configuration

The classification of hydrogels depends on their chemical composition, crystallinity and physical properties which include:

(a) Amorphous (non-crystalline).

(b) Semicrystalline

(c) Crystalline.

iii. Classification based on type of cross-linking

Hydrogels can be divided into two categories. It is based on the physical or chemical nature of the cross-linking. Chemically cross-linked networks have permanent junctions and physical networks have transient junctions that arise from physical interactions or polymer chain entanglements. This includes hydrophobic interactions ionic interactions and hydrogen bonds. Example of physical crosslinking are PEO–PPO–PEO which based on hydrophobic interaction and chemical crosslinking which is acryloyl group polymerization of hydrogel.

iv. Classification based on physical appearance

The technique of polymerization involved in the preparation process of hydrogel will hydrogels appearance as film, microsphere or matrix.

v. Classification according to electrical charge

Based on presence or absence of electrical charge located on the crosslinked chains, hydrogels can be categorized into four groups:

(a) Nonionic (neutral).

(b) Ionic (including anionic or cationic).

(c) Amphoteric electrolyte (ampholytic) which include both acidic and basic groups.

(d) Zwitterionic which include anionic and cationic groups in each structural repeating unit (McDonald and Whitesides, 2002).

2.3 Polydimethylsiloxane (PDMS)

Polydimethylsiloxane (PDMS) belongs polymeric organosilicon compounds group that referred to as silicones. PDMS is the most widely used silicon-based organic polymer. PDMS is inert, non-toxic, optically clear and non-flammable. It is also called dimethicone and it is one of the several types of polymerized siloxane. Its applications range from elastomers, contact lenses to medical devices; it is also present in, caulking, lubricants shampoos, food and heat-resistant tiles. After polymerization and cross-linking of PDMS, it will present an hydrophobic surface. This surface will appear shiny and metallic although the substrate is clear. This hydrophobic surface makes it difficult for polar solvents to wet its surface. It also leads to adsorption of hydrophobic contaminants (JACC report No 26, 1994). Figure 2.1 shows the chemical structure of octamethylcyclotetrasiloxane which is the monomer of PDMS.

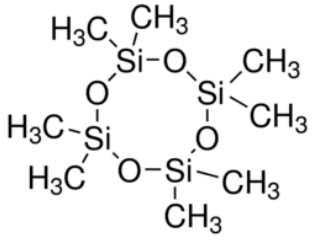


Figure 2.1: Chemical structure of octamethylcyclotetrasiloxane

2.4 Poly(ethylene glycol) diacrylate (PEGDA)

Polyethylene glycol diacrylate (PEGDA) has been used in many biomedical applications due to its non-toxicity, biocompatibility and ease of use. Some of the applications include tissue engineering, wound healing, hydrogel development for drug delivery and electrospinning processes for bioapplications. Hydrogels are constructed from water-soluble polymers such as PEGDA. PEGDA that are crosslinked into water insoluble 3D polymer networks, content mostly water and resemble human tissue. Nutrients and water can penetrate the hydrogel to provide the necessary to support cellular growth and then tissue development. (Mazzoccoli et al, 2010).

US Food and Drug Administration (FDA) have approved PEGDA for clinical usage due to it being biocompatible, non-toxic and non-immunogenic. Besides, PEGDA stiffness is similar to human tissues in the swollen state. It is due to PEGDA's capacity for high water content. (Peppas, 1986).

Due to good biocompatibility, little to no immunogenicity and high hydrophilicity, hydrogels based on PEGDA have been widely used for tissue engineering applications. PEGDA is non-toxic at molecular weights above 400 Da and can be readily cleared by the kidneys. PEGDA are approved by the US-FDA for internal consumption. The PEGDA molecule inherently has resistance for protein adsorption and neutral when crosslinked. Any other molecules are prohibited from closing the polymer surface due to the surrounding water molecules which accumulated at the hydrogel surface. It is a consequence of the ability of PEGDA molecule to be heavily hydrated in aqueous media (Zhu and Marchant, 2011).

PEGDA can dissolve in many solvents such as methylene chloride, toluene, water, methanol, dichloromethane, diethyl ether, ethanol, acetone, chloroform, and hexane. At low molecular weights, PEGDA is viscous and colorless liquids. However, at higher molecular weights, they white-coloured solids and waxy. The usual range of molecular weight of linear PEGDA used in biomedical applications is between few hundreds to 20 kDa (Coady et al, 2014). Figure 2.2 shows the chemical structure of PEGDA.

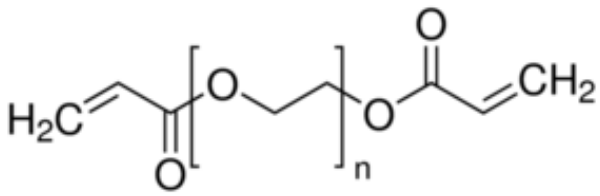


Figure 2.2: Chemical structure of Poly(ethylene glycol) diacrylate

2.5 Photopolymerization

Hydrogel is allowed to be generated in vitro or in vivo by photopolymerization from the oligomer, low viscosity solution of monomer or low molecular mass polymer by the free radical pathway. A light-sensitive compound which is the photoinitiator interact with visible or UV light to create free radicals that initiate polymerization to form crosslinked hydrogels. Photopolymerization has also been used in optical materials, membranes, polymeric materials, electronic materials, printing materials and coatings and surface modifications (Sherbiny and Yacoub, 2013).

Photoinitiator plays a very important role in any successful UV-crosslinking polymer. Since reactive diluents or oligomers do not produce initiating species, photoinitiator is required for initiating the polymerization. Photoinitiator absorbs the UV-radiation and gets excited to an excited state. It is followed by photolysis into free radicals. Then, the free radicals attack the unsaturated functional groups present in the monomer or polymer chain to start the chain propagation step. (Eal et al, 2008).

Photopolymerization has several advantages over conventional polymerization techniques. These include temporal control and spatial over polymerization, fast curing rates which typically within seconds to few minutes at room or physiological temperatures with minimal heat production. One major advantage of photopolymerization is that hydrogels can be created in situ from aqueous precursors using photopolymerization in a minimally invasive manner (Eal et al, 2008).

Fabrication of polymers in situ is attractive for a variety of biomedical applications. This allows polymers to form complex shapes that conform and adhere to

tissue structures. However, polymerization conditions for in vivo applications are difficult since biological systems require a narrow range of pH, the absence of toxic materials such as most monomers and organic solvents and acceptable temperatures. Some photopolymerization systems such as photo-induced grafting and photo-induced polymerization can overcome these limitations because the polymerization conditions are sufficiently mild to be carried out in the presence of cells and tissues (Nguyen and West, 2002).

UV light curing is possible to obtain space and time controlled polymerization. The ability to carry out controlled polymerization has provided the chance to apply photopolymerization in different fields. For example, electronic materials, optical materials, membranes, dentistry and surface modification. Some photoinitiator used in UV-crosslinking systems generate free radicals and others generate cations. The free radical can be used for curing acrylates and the cations can be used for curing cycloaliphatic epoxide-based systems. Sources for UV radiation include Electrodeless Vapor Lamps, Pulsed Xenon Lamps, Lasers and Medium Pressure Mercury Vapor Lamps, (Ifkovits and Burdick, 2007). Figure 2.3 shows the chemical structure of photoinitiator 2,2-dimethyl-2-phenylacetophenone which used in this project.

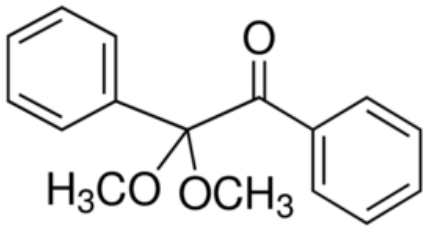


Figure 2.3: Chemical structure of photoinitiator 2,2-dimethyl-2-phenylacetophenone

2.6 Hydrogel characterization

2.6.1 Swelling percentage

Water content can be used to estimate the crosslinking extent of hydrogels. It is expressed as the weight ratio of water in the hydrogel to the whole wet hydrogel. Hydrogels with water contents over 90% are called superabsorbent hydrogels. The swelling ratio is defined by the weight of the swollen gel divided by the weight of the same sample in the dry state. Volumetric Swelling Ratio is another parameter which also applied for describing the swelling behavior of hydrogel. It is defined by the volume of the hydrogel in the swollen state divided by the volume of the hydrogel in dry state (Ahmed, 2015)

Equilibrium swelling ratio and equilibrium water content increase as PEGDA ratio increased. It is due to the incorporation of the hydrophilic effectively increase the water capacity of the hydrogels. In this system, the initial volume fraction of the PEGDA and PDMS controlled the swelling capacity in the hydrophilic phase. Assuming PDMS did not swell in water, the swelling ratio in the PEGDA phase linearly increased with the decrease of PDMS content. Thus, the swelling capacity of this PDMS/PEGDA hydrogel system can be tuned by the ratio of total content of PEGDA to PDMS (Niloofar et al, 2016)

Mechanical properties of a hydrogel are also dependent on its water content. For example, yield and modulus strength decrease as the water content increases but elongation has the opposite behavior. The swelling ratio is considered as an important parameter especially in pharmaceutical and biomedical applications. It is due to the influence of swelling behavior of hydrogels on important factors such as the surface

wettability and mobility, solute diffusion coefficient, optical properties, and mechanical properties (Ahmed, 2015).

In general, higher swelling ratio would prefer for soft tissue. PEGDA will play its role in crosslinked hydrogel to control swelling ratio because of it hydrophilic nature while PDMS-MA is hydrophobic in nature. The low swelling ratio of the UV-crosslinked hydrogels was mainly attributed to the overwhelming of the hydrophobic effect to its role of flexibility in PDMS-MA solution. Although the UV-crosslinked hydrogels were more flexible, its water permeability becomes lower due to a lower number of hydrophilic site for water adsorption (Hamid, 2015).

2.6.2 Fourier transform infrared spectroscopy (FTIR)

FTIR is one of the most preferred methods of infrared spectroscopy. When infrared radiation is passed through a sample, some radiation is absorbed by the sample and some passes through the sample. The resulting signal at the detector is a spectrum representing a molecular fingerprint of the sample. The usefulness of infrared spectroscopy arises because different chemical structures produce different spectrum (Paula et al, 2009).

2.6.3 Contact Angle measurements

Contact angle is a quantitative measure of spreading of a solid by a liquid. It is defined as the angle formed by a liquid at the three-phase boundary where a liquid, gas and solid intersect. Young equation shown below describes the balance at the three-phase contact of solid, liquid and gas (Marmur, 1994)

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta_{Y} \quad (1)$$

Contact angle measurement gives information on the wetting properties of the UV-crosslinked hydrogels. The higher the hydrophilicity of the UV-crosslinked hydrogels, the lower the contact angle. The static contact angle is the contact angle with the contact area between liquid and solid is not changed from the outside during the measurement. (Marmur, 1994). Figure 2.4 shows the contact angle at various degree.

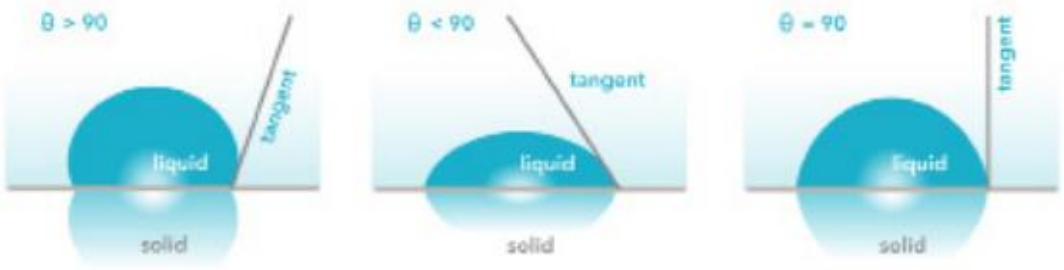


Figure 2.4: Contact angle at various degree

From Figure 2.4, the low contact angle values show that the liquid spreads on the surface while high contact angle values show poor wetting. If the contact angle is less than 90 ° it is said that the liquid wets the surface with zero contact angle representing complete wetting. If the contact angle is greater than 90 °, the surface is non-wetting by the liquid. Static contact angles are measured when the droplet is stationary on the surface and the three-phase boundary is not moving. Static contact angles are utilized in research, product development and in quality control (Marmur, 1994).

Pure PEGDA UV-crosslinked hydrogels have lower contact angle which due to its well-known hydrophilic nature. Therefore, the lower the contact angles of UV-crosslinked hydrogels, the better the wetting properties of UV-crosslinked hydrogels. Hence, adjustment of PEGDA to PDMS-MA ratio is important to counterbalance its mechanical properties and hydrophilic properties in designing a customized UV-crosslinked hydrogel (Yuan and Lee, 2013).

2.6.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference amount of heat required to increase the temperature of a sample and reference is measured. Both the sample and reference are maintained at the same temperature throughout the experiment and heat supplied is measured. Generally, the temperature program for DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample which normally refers to aluminum should have a well-defined heat capacity over the range of temperatures to be scanned (Wunderlich, 1990).

Low glass transition temperature (T_g) of PEGDA: PDMS-MA UV-crosslinked hydrogels was attributed to the higher loading of PDMS-MA. Both PDMS-MA and PEGDA macromolecules attributed to the flexibility of PEGDA-based hydrogels. However, PDMS-MA owned its lower and exceptional flexibility due to two main structural features which are the Si-C substituent linkages and the alternation of the Si-O-Si, the relatively long Si-O main chain bonds and O-Si-O bond angles along the backbone chains. (Hamid, 2016).

2.6.5 Texture Profile Analysis (TPA)

Texture Profile Analysis is a popular double compression test for determining the texture properties of foods. Other industries such as gels, pharmaceuticals and personal care also used TPA to carry out testing. During a TPA testing, samples are compressed twice using a texture analyzer to provide insight into how samples behave when chewed. The TPA test was often called the "two bite test" because of the texture analyzer similar to the mouth's biting action (Brandt et al, 1963).

The strength of TPA as an analytical method is that it can quantify multiple textural parameters in just one experiment which include hardness, adhesiveness, and resilience which are crucial to the properties of the hydrogel. The data can be collected from the force vs time graph plotted by the machine. Hardness is a measure of how resistant solid matter is to various kinds of permanent shape change when a compressive force is applied. Macroscopic hardness is generally characterized by strong intermolecular bonds, but the behavior of solid materials under force is complex. Hardness is dependent on strain, strength, toughness, ductility, elastic stiffness, plasticity, viscoelasticity, and viscosity (Brandt et al, 1963).

Adhesion is the intermolecular and interatomic interaction at the interface of two surfaces. It is a multi-disciplinary topic which includes surface chemistry, stress analysis, polymer physics and fracture analysis. In material science, resilience is the ability of a material to absorb energy when it is deformed elastically, and release that energy upon unloading. Resilience defined by a measure of how well a product fights to regain its original position which is a parameter that similar to elasticity. But it is expressed as a ratio of energies instead of a ratio of the distance (Brandt et al, 1963).

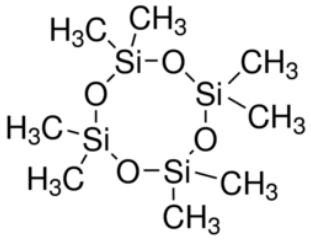
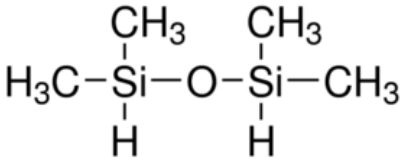
Chapter 3

METHODOLOGY

3.1 Materials

Table 3.1 shows the materials that used to synthesis PDMS-SiH, PDMS-MA and PDMS-MA/PEGDA hydrogel.

Table 3.1: Materials and their properties

Material	Chemical structure
Octamethylcyclotetrasiloxane (98%) CAS-No.: 556-67-2 (Sigma-Aldrich) Molecular weight: 296.62 g/mol Form: liquid	
1,1,3,3-Tetramethyldisiloxane (97%) CAS-No.: 3277-26-7 (Sigma Aldrich) Molecular weight: 134.32 g/mol Form: liquid	
Trifluoromethanesulfonic acid CAS-No.: 1493-13-6 (Sigma-Aldrich) Molecular weight: 150.08 g/mol Form: liquid