IMPRINTING OF NANOTEXTURED POROUS POLYMER USING POROUS SILICON SCAFFOLD

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

Porous polymers are invading ubiquitously the engineering markets as well as other fields.

They are constantly earning attention and scientist's curiosity owing this to their inimitable chemical, physiochemical, optical, mechanical and surface area properties and morphology. Polymers whether natural, polymerized, modified or synthesized; they are manufactured based on the background of their particular chemical arrangement. In this research, an all-purpose manufacturing progression desired to work out with all liquid or powder polymers cross linked to a flexible phase to imprint their surface with any desired porosity.

The work is founded into two micro-casting phases. The project can be described as stamping. The basic stamp is a microchip made of porous silicon (PS) template prepared based on xenon difluoride (XeF_2) dry etching technique. The former "stage 1" forms a layer of polymer complement to the silicone sample where this latter layer is complemented to get a final version cloning the pores of the silicon porous sample. The last version is just "dressmaking fashioned polymer" that is identical to the texture of the silicon pores. A laidback, bendable scheme that permits to manufacture porous polymer textured with the intended pores using a sought after pore size and configuration porous silicon prototypes.

This work offers a future hope and ambitions that are extended to the solicitation of stamped Poly-ethyl hydrosiloxane (PMHS), Poly-Dimethylsiloxane (PDMS) using porous silicon and Poly-methyl methacrylate (PMMA) scaffolds or any silicon-polymer combination to reach the final porous polymer suitable to the desired biomedical application.

Keywords: Polymer, porous silicon, PMMA, PDMS, PMHS, micro-molding

ÖZET

Gözenekli polimer mühendislik piyasasini ve diğer alanları tumuyle yanı sıra işgal vardır istila ediyor.

Onlar sürekli dikkat ve bilim adamının merak bu onların eşsiz kimyasal, physiochemical, optik, mekanik ve yüzey alanı özelliklerini ve Morfoloji nedeniyle kazanç vardır. Polimerler olsun doğal, polimerli, değiştirilmiş veya sentez; Onlar kendi belirli kimyasal düzenleme arka plan üzerinde göre üretilmektedir. Bu araştırmada, tüm sıvı ile çalışacak bir çok amaçlı üretim ilerlemesi istenen veya onların yüzey ile istediğiniz herhangi bir gözeneklilik Künye için esnek bir aşaması için toz polimerler çapraz bağlanmış.

Çalışma iki mikro-döküm aşamalar halinde kuruldu. Proje damgalama olarak tanımlanabilir. Hazırlanan gözenekli Silisyum (PS) şablon / yapılan bir mikroçip xenon difluoride üzerinde (XeF_2) tekniği aşındırma kuru dayalı temel damgasıdır. Eski "1. aşama" formları polimer bir katman nerede bu ikinci katman silikon gözenekli örnek gözeneklerin klonlama a sonda gelen yorum almak için tamamlanmaktadır silikon örnek tamamlıyor. Sadece "terzilik moda polimer" en son sürüm olan silikon gözenekleri doku için aynı. Bir aranan sonra gözenek büyüklüğü ve yapılandırmasını gözenekli Silisyum prototip kullanarak hedeflenen gözenekli bir laidback, gözenekli polimer üretim izni bükülebilir düzeni dokulu.

Bu eser gelecek umut ve damgalı Poly-etil hydrosiloxane (PMHS), Poli-Dimethylsiloxane (PDMS) son gözenekli polimer istediğiniz Biyomedikal uygulamaya uygun ulaşmak için gözenekli Silisyum ve Poly-metil metakrilat (PMMA) İskele veya silikon polimer bunlarınbir kullanımı talep için genişletilmiş emelleri sunmaktadır.

Anahtar Kelimeler: Polimer, Gözenekli polimer, PMMA, PDMS,

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PMMA: Poly (methymethacrylate)

PDMS: Poly (dimethylsiloxane), bis (3-aminopropyl) terminate

PMHS: Poly (methylhydrosiloxane)

PDS: Photo-detection coordination

SE: Spectroscopic ellipsometrical

SEM: Scanning electron microscope

XeF_2: Xenon difluoride

Si : Silicon

SiF_4: Tetrafluorosilane

Xe: Xenon

NO_2: Nitrogen dioxide

H_2O: Water

O_2: Oxygen

HNO_3: Nitric acid

HNO_2: Nitrous acid.

NO: Nitric oxide.

SiO_2: Silicon dioxide.

HF: Hydrogen fluoride.

SOI: silicon-on-insulator.

PS: Porous silicon.

H_2O_2: Hydrogen peroxide (H2O2).

He-Ne: Helium-Neon.

WE: Working electrode.

(MWE): Metal working electrode.

(SCE): Standard calomel electrode.

(PtE): Point counter electrode.

(Tc): Critical temperature.

CHAPTER 1
INTRODUCTION

1.1 Introduction

Over the last few decades numberless progresses has been achieved in structural and functional substances all along to many developments in materials used in biomedical technology (Bar-Cohen, 2004). These materials known as biomaterials are intended to interface with biological systems to evaluate, treat, augment, or replace any tissue, organ, or function of the body (Dumitriu, 2001).

In order to interact with biological systems, biomaterials necessitate a crucial and fundamental requirement that is “biocompatibility”. Many materials has been tested and proved as biocompatible. These can be divided into four major classes: polymers, metals, ceramics (including carbons, glass ceramics, and glasses) as well as natural materials from both plants and animals (Wu, Hu, Wang and Mou, 2010). Occasionally, two materials belonging to different classes may be combined to develop a composite material. One of these composite materials is polymers. Polymers form a versatile class of biomaterials that have been extensively investigated for medical and related applications and this is can be clearly depicted from the Figure 1.1.

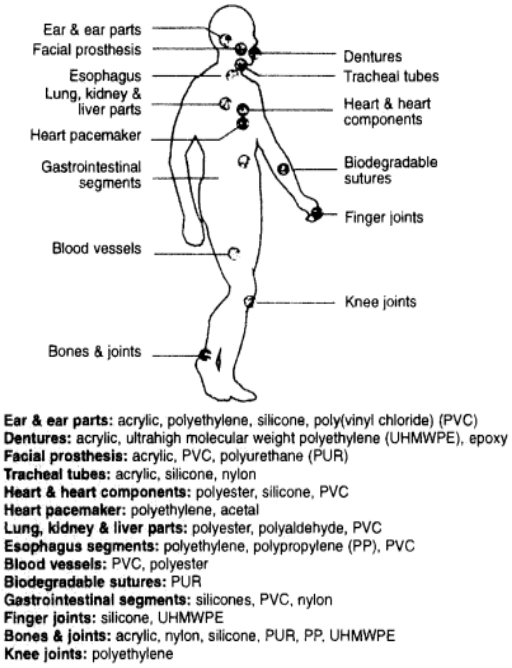


Figure 1.1: Picture depicting the clinical applications and types of polymers used in medicine (Shtilman, 2003)

The main difference between polymers and metals or ceramics is that these former materials are made up of repeated units called "mers" that are characteristically grouped together under the structure of chains or macromolecules rather than lattice structures (Ravichandran, 2010).

Materials made of polymers set up their final structure based on covalent bonds and secondary interactions (Bar-Cohen, 2004). Their fundamental structure is composed of a backbone along to side or pendant groups (Mathew and Alocilja, 2005). The backbone is made up of atoms connected by covalent bond extending from one side to another closing stage part. The backbone is often not only carbon but rather may contain other atoms such as N, O, or Si. The ramified parts are the hydrogen atoms in organic and inorganic groups connected to the backbone. Covalent bonds are utilized along the backbone of the chain but only weak secondary forces such as hydrogen bonds or van der Waals forces are used for cohesion between chains (Mavromatidis, Mankibi, Michel, and Santamouris, 2012).

These polymeric biomaterials account as a crucial for several biomedical applications that assist to improve the human life or compensate the malfunction in human organ or function. Some of these applications are orthopedic such as bone Cements, joint

Prostheses; cardiovascular applications such as heart valve, vascular graft, stents, pacemakers and blood oxygenators; Ophthalmic Applications like contact Lenses, suture Materials and tissue Engineering.

Porous polymers are polymers having an amorphous surface with various pore size and shape. These porous materials are invading the world and grabbing wide interest due to their large quiet field of applications. They are capturing augmented interest in quite few field and applications due to their large surface area and unique physiochemical properties (Murugan and Ramakrishna, 2007). They are characterized by special physiochemical properties and can account for wide range of application flourishing from the human body to controlled drug delivery along with electrically activated tissues such as brain, heart and muscles given that it can be coupled with animals or computer/machine's interface opening the door of developmental innovation in nanotechnology (Murugan and Ramakrishna, 2007).

Their exceptional properties expand to cover the following characteristics: lightweight, fracture tolerant, bendable, compromises the possibility of being contemplated to almost any feasible form to fit the intended application. All along some features may be settled, controlled and customized as the desired features to accomplish and perform any task beyond the human expectations (Bar-Cohen, 2004). Nowadays, they are invading a great range of applications as biomaterials and catching the spot of huge adaptability and multi-purpose usage for a mass of biomedical solicitations (Bhatti, Chaudhary, Pandya, and Kashyap, 2008).

These materials are being embraced in almost each discipline in medicine scanning extracorporeal device to implants integrated into the human body where each application demands special criteria different manufacturing processes to provide special chemical and physiochemical are in need (Dumitriu, 2001). Some of which may stay as long as it can retain while others must be degradable as fast by means of potential to make available space for tissue to replace it. By mean of both intentions the results from the usage of these polymers concluded in more preferable results than the applications of biological objects (Shtilman, 2003). From here the innate needs initiated to shift from the realm of transplantation and application to the empire of fabrication to decrease the complications for any application.

Porous polymers are conventionally manufactured using specific processes related to the chemical structure of each polymer. Each liquid polymer needs a specific fabrication process that includes the variation in pressure, temperature, and the cross-linking reagent used to solidify the polymer. Accordingly, there is a range of methods that can be utilized to prepare porous polymers. These methods include gas foaming, phase separation, small liquid drops templating, colloid crystal templating, templating via self-assembly, molecular imprinting, and bio-templating using natural biological templates. The dimension and characteristics of the porous phase required differs according to the application of the porous structural polymer that is to be produced and the manufacturing technique employed.

The methods applied for pores formation necessitate a time all along to a very complicated processes. The new approach related to the formation of porous polymers is to use a generic recipe that forms a porous surface in regards to the type of polymer used. A template of porous silicon will be used to form a scaffold of the polymer upon the usage of different cross-linking reagents to solidify the liquid polymer.

1.2 Literature Review of Polymers

Introduction of degradable polymers in biomedical application was established in the 1960 when the idea of employing them as a resorbable matrices (Folkman and Long, 1966). The start was with a drug delivery system diffusing small molecules from one side to another side of a silicon rubber tubing wall.

Then polymers were started to be used in temporary surgical implant and repair for damaged tissue (Kulkarni, Pani, Neuman, and Leonard, 1966; Schmitt and Polistina, 1969). After the success that has encountered with these polymers once interfered with human body; biodegradable polymers and aliphatic polyesters were proved to be useful various applications in medical field such as prosthetics, vascular graft, artificial skin implant, screws and stents as well as plates for implant and short-term inner fixation of the bone, pins, resorbable sutures for surgeries and so on.

With all the critical improvement that accompanied any application using polymer; these polymers turn out from being barely a point of interest to researcher to become a crucial material employed in biomedical applications.

Exploration on polymers and their wide applications has been dramatically increased over last few decades due to the successful results resulting from any application using polymers. Researchers were able to prove that some of these polymers are biocompatible, may be sterilized, and stable for storage. Some of these polymers are Poly (methy methacrylate) (PMMA), PDMS or Poly (dimethylsiloxane), bis (3-aminopropyl) terminate and PMHS or simply Poly (methylhydrosiloxane).

1.3 Contributions of the Proposed Work

This thesis is a contribution to the nano-technology and MEMS market. This thesis is a part of the continuing research of nanotechnology innovations that are day by day invading our daily life to exist in numerous materials and applications all along to invade human body to help for recovery or compensation of any malfunction. Nevertheless, this research offers a new approach that may be applied to develop porous polymer in a chemistry lab without necessitation of any high level technology or equipments. The procedure is a simple straight forward procedure comprised of two micro-molding steps and a template scaffold that is a porous silicon chip.

1.4 Aim of Thesis

Porous polymers are of huge interest in human life since they account for billions of revenue for the international market and they help to improve or recover the human quality of life. Therefore, this project aims to develop a generic recipe that may be applied to develop porous polymers in regards to the type of the polymer used. The intentions are to use a porous template that is the scaffold a porous silicon chip previously manufactured using XeF_2 etching method. The polymers that are intended to be employed will be linked using a corresponding cross-linker at the consequent temperature.

All along the polymers must be biocompatible since this is the major necessary factor that must be present when working within the human body. Any debris or residual resulting from the materials used throughout the fabrication process may affect the biocompatibility properties of the polymer surface membrane. The generic recipe intends to use only liquid polymers in the formation of the porous polymers, eliminating the probability of forming any residuals which could affect the compatibility of the polymer surface membrane within the human body.

Another aim is to develop porous polymer having good optical and mechanical characteristics that's why these two factors were tested and accounted. Also, the other target was to neglect the pressure factor while developing the porous polymer where no need for complicated calculations in order to achieve a pressure to volume ratio within the surface of the structure.

The overall aim was to develop a porous polymer having important optical, biocompatible and mechanical properties using a generic recipe. This recipe is applicable to any liquid polymer regardless of the pressure and just by acquainting the corresponding cross-linker and temperature of the cross-linking procedure while using a template that is a porous silicon chip.

1.5 Thesis Overview

The developed thesis is divided into 6 chapters that are structured as following:

Chapter 1: It introduces and defines polymers and shows its field of applications. It discusses the aims settled all along to the contributions, and motivations. Additionally, it highlights and shows the structure of the thesis.

Chapter 2: It provides an introduction about the polymers and porous polymers applications and manufacturing processes. All along, it discusses an introduction about porous silicon and porous silicon manufacturing technique. This chapter describes and explains briefly the proposed generic recipe.

Chapter 3: It shows a thorough clarification about the proposed generic recipe beside the materials and chemicals used. This chapter presents a clear explanation about the polymers

employed that are PMMA and PDMS all along to their corresponding cross-linker. Additionally this chapter explains briefly the experimental procedures applied in the aim of achieving the most optically and mechanically efficient curing formula to undergone surface modification. Also, it explains the tests used to assess the efficiency of the recipe applied.

Chapter 4: It discusses the different obtained sample polymer resulting from the different experiments for both PMMA and PDMS. It shows the elected experiment parameters based on the optical and mechanical tests efficiencies; those that will be employed when pouring them on top of the corresponding scaffold. It also shows the optical and mechanical efficiency of the samples experiments through tables and charts.

Chapter 5: It shows morphology, microstructure and Reflection properties analysis of the porous polymer samples developed using SEM. All along it presents the pictures of the obtained porous polymers. Moreover this chapter highlights the comparison phases that show the novelty of the proposed generic recipe

Chapter 6: It shows the final conclusion and recommendations for further work in this research.

CHAPTER 2
POROUS POLYMERS AND POROUS SILICON CHIP: TYPICAL APPLIED METHODS AND APPLICATIONS

This chapter provides a review background about the critical applications of polymers in general and porous polymers in particular. The techniques used to make porous polymers from bulk polymers will be explained. Discussion about silicon material and porous silicon manufacturing techniques will be explained in general and the employed scaffold manufacturing technique in detailed. All along a brief explanation of the proposed generic recipe will be presented.

2.1 Polymers Vital Applications

Polymers play a vital role in human life since they may be employed in several applications in biomedical field as well as any other field. These materials help to improve the quality of human life since they made up a significant number of machine and medical instruments. All along; they may replace or compensate a failure or malfunction of any function in the human body.

The chief characteristic that sets polymers apart from metals and ceramics is that polymers are made up of repeated units called “mers”. These subunits are typically grouped together in the form of chains or macromolecules rather than lattice structure which is the case of ceramics. Polymeric materials employ covalent bonds all along to secondary interactions to establish their basic structures.

They have been proven to be an appropriate environment for molecules proliferation and contact. All along they provide an improvement of the steadiness, sensitivity and speed of diverse biomedical devices and equipment (Jian et al., 2012). They have unique properties of their surface area, special physiochemical properties (Wu, Hu, Wang, and Mou, 2010) inexpensive and ease of manufacturing and multipurpose usage. Some of these polymers are conducting materials with electronic and ionic conductivity. They can open wide range of promising applications that help improving the human quality of life. These applications

range from appliances implanted in the human body to controlled drug delivery. Polymers may interfere and work in parallel with electrically activated tissues in the human body such as brain, heart and muscles. They also can be coupled with animals or computer/machine interface opening the door of developmental innovation in nanotechnology and back propagation neural network applications (Ravichandran, 2010). Their exceptional and very important properties are countless. They have lightweight, fracture tolerant, bendable, compromises the possibility of being mulled over to almost any feasible form to fit the intended application along with customized features to acquaint results that are beyond of desires (Bar-Cohen, 2004). Nowadays, polymers are invading a great range of applications as biomaterials and are catching the spot of enormous flexibility and multi-purpose usage for numerous targets in biomedical field (Bhatti et al., 2008).

These biomaterials are being employed in almost each discipline in medicine. They are parts of extracorporeal device; implants integrated into the human body as well as other many other applications. Each of these applications demands special criteria and different manufacturing processes to provide polymers with special chemical and physiochemical properties corresponding to the function they are intended to perform (Dumitriu, 2001). Some of them may stay as long as it can retain in the human body. Others must be degradable after a certain period in order to allow the cells to regenerate to its original shape.

Biopolymers have resulted with more satisfying results in any intended application and function rather than any biological objects (Gad-el-Hak, 2005). Also these materials have lessened the complications encountered with any contact in human body that use to be depicted with old biological systems. From here the innate needs initiated to shift from the realm of transplantation and application to the empire of fabrication to decrease the complications for any application.

There are two types of polymers human made polymers or synthetic polymers and natural or biopolymers that exist naturally in the environment. Each of these consists comprise a broad range properties that plays an important and ubiquitous role in everyday life. Synthetic and natural polymers were employed independently or combined to fit the need of several biomedical applications.

Based on the advantages and improvement in the quality of functions and successful results of any application with polymers over other materials; many researchers invested them in biomedical field. These polymeric biomaterials have extensively revolutionized orthopedics field. They have proved to be serviceable in two main applications in this area. In the first application, polymers are employed for the purpose of fixation such as PMMA; they act as a structural interface between the implant component and the bone tissue. In the other application, polymers are used for one of the articulating surface components in a joint prosthesis where Polyethylenes are widely used (Gad-el-Hak, 2005). They have also played a crucial role in cardiovascular applications including mechanical heart valves, vascular grafts, stents, pacemakers, and blood oxygenators. Earlier in old mechanical valves design silicone rubber ball contained within a cage made up of Lucite also known as poly-methyl methacrylate Where new ones employ only polymers. Moreover, these polymers have improved the function of ophthalmic applications including in contact and intraocular lenses, as well as intra-corneal implants (Kumari, Bugaut, Huppert, and Balasubramanian, 2007).

Polymers both synthetic and natural have been an innovation in biomedical field that helped to assist the human quality of life all along to compensate any failure of malfunction. Polymers are offered the resemblance of many parts in the human body or application that is intended to deal with the human body. There is countless of research taking place on both tried and the new showing potential both natural and synthetic polymers mutually with their relevance as implantable materials, controlled-release carriers, scaffolds for tissue engineering or any other biomedical applications based on polymer-composite materials.

2.2 Modification of Polymers Surfaces Properties for Improving their Functionality

Polymer surface is the outside layer of the polymeric material. The bulk polymer defines its characteristics; material stability, its good performance and proper function over a long time. The surface of the material will define the face of interaction with the surrounding, its acceptance or rejection in cell society from the early stage of contact. Since it is very hard to achieve these both characters at the same time good performance versus reliable interaction phase; a new approach was admitted by researcher. The new procedure was

manufacturing of polymeric materials with tolerable bulk characteristics followed by surface modification to improve its properties (Kumari et al., 2007).

Porous polymers are bulk polymers that have undergone surface treatments. Their surface is sculptured with different architectural morphology based on the fabrication and polymerization process. Their success in performing successful outcome in numerous applications invested in many fields turned into making them the center of interest for scientist and a gambling machine that won the lottery and accounts for billions of dollars in revenue every year (Aad et al., 2014).

These porous structures have exceptional physiochemical properties (Lin & Hollister, 2009), great surface extent, interrelated pores (Kumari et al., 2007), small pores size (Nischang, 2013), insulating properties (Solomos, Kallos, Mavromatidis, and Kushta, 2012), ionic exchanging competencies (Nischang, 2013). Based on these features porous polymers have been engaged s in several applications ranging from insulating systems and membranes (Solomos et al., 2012), ion exchange polymers (Nischang, 2013), filters and refinement structures (Mavromatidis et al., 2012), bone crafting implant (Jiang et al., 2002), catalytic substances (Schmalz et al., 2011), restriction of proliferation and active species for several intended applications (Jiang et al., 2002), in medicine field and applications (Schmalz and Galler, 2011), sensors (Müller, Anders, Titus, and Enke, 2013) and the myth never ends to include many other applications.

Porous materials are usually characterized by their size distribution, shape, pore size, extent of interconnectivity and total amount of porosity. Depending on the application of the porous material that is to be produced, the dimensions and characteristics of the pores are alternated (Müller et al., 2013). Pores have been classified, according to the International Union of Pure and Applied Chemistry (IUPAC) they are defined as micro-pores, meso-pores (widths ranges from 2 to 50 nm) and macropores (pores width dimensions are larger than 50 nm) (Sammak, Azimi, Mohajerzadeh, Khadem-Hosseini, and Fallah-Azad, 2007). "Nano" is a concept representing a size from 1 to 100 nm; therefore all of the above discussed three kinds of porous materials can be designated as nano-porous materials.

The revelatory innovation of nanotechnology and its crucial success in many applications led to the endorsement of nano-porous polymers in numerous biomedical applications (Karasiński, Tyszkiewicz, Rogoziński, Jaglarz, and Mazur, 2011). Nano-porous polymers are being used in numerous applications coming up with satisfactory results and performance. Still the unique characteristic and pores morphology and size of each porous polymer necessitates specific fabrication procedure. The fabrication methods develop pores on the surface of the bulk polymers based on the need of the application (Khaira et al., 2009).

As the demand for porous polymers with more complex structures and functions has elevated, so has the capability to manufacture such polymers with tunable properties and a diversity of pore characteristics. Accordingly, there is a range of methods that can be utilized to prepare porous polymers. Each technique necessitates special equipments, environments, time and costs. All along each technique results with a different pores morphology.

2.3 Fabrication of Porous Polymer

Each liquid or powder polymer requires a specialized fabrication technique that affects its last morphology. These factors are pressure, temperature, and the cross-linking reagent utilized to solidify the polymer. In equivalence, a broad range of methods may be applied for texturing polymer with intended pores (Aubert et al., 2002). These approaches consist of gas foaming, phase separation, small liquid drops prototyping, colloid crystal prototyping, fashioning template via self-assembly, molecular imprinting, and bio-template by means of natural biological templates (Silverstein, Webster, Kiemle, and Bryce, 2014). Porous polymers are created by means of a product of "porogen" into the polymer and then removing it. Where porogen is a substance that may serve as a template that will be removed later to spawn pores (Fujiwara, Okada, Takeda, and Matsumoto, 2014). An important issue that the porogen might have innumerable morphology presents in the liquid or gaseous state (Jacobs, Lamson, George, and Walsh, 2013).

All along there are few factors that affect the polymers fabrication that are the temperature, pressure and the cross-linking reagent used. Temperature a crucial factor to be engaged

into consideration; based on the fact that cross-linking reagents must workout at a low temperature approximately at room temperature to dodge any mutilation to the pores located in the surface of the structure (Barillaro, Nannini, and Piotto, 2002). Pressure is the other factor to be looked after keen on deliberation throughout the fabrication realm of the porous polymer where different values are indulged.

2.3.1 Applied Methods for Porous Polymer Development

As mentioned earlier several may be applied in the aim of pores formation on the surface of bulk polymers, these methods will be explained briefly to show how complicated, costing, and time demanding they are.

Gas Foaming is a technique can be described as multi-phase materials characterized by a solid continuous matrix surrounding a gaseous phase (Salerno, Zeppetelli, Di Maio, Iannace, and Netti, 2011). As a restatement, polymer foams stands for porous polymers chock full by means of a very great volume portion of gas-filled pores. During the course of time flow, foams were consuming much interest to gain the battle to be integrated in many numerous applications such as thermal insulation, tissue engineering (TE) scaffolds along with acoustic isolation (Salerno et al., 2011).

Main stream of polymer foams are created via gaseous media. Foaming of polymers with gases or supercritical fluids allowed the successful production of microcellular polymers. However, supercritical fluids may be described as the fact that fluid's temperature must exceed the critical temperature (Tc), regardless of the pressure or any material that have the temperature and pressure higher than their critical values along to a density close to or higher than its critical density. The employed substance or gas; once they turned into gas phase, acts as a porogen to generate pores within a polymer (Dong et al., 2012). Porogen is a substance that can be used as a template and then removed to generate pores and may be presented in various forms either liquid or gas.

The second method is Phase Separation where this technique involves an initial phase separation followed by a solidification to fix the morphology and finally the removal of the

minor separated phase (Ismail et al., 2000). Phase separation can be triggered during polymerization and cross-linking in several ways including includes adding a non-solvent to a polymer-solvent mixture, addition of chemical or thermal induction.

Small Liquid Drops Templating (Soft Templating) is another method that is used as a versatile method for the preparation of highly porous organic polymers, inorganic materials, and inorganic-organic composites (Tsivintzelis, Musko, Baiker, Grunwaldt, and Kontogeorgis, 2013). In this strategy, preformed domains of a liquid component are stabilized by a surfactant or a stabilizer in order to prevent macroscopic phase separation.

In addition, soft colloidal templates (emulsion, micro-emulsion, breath figures), hard particles may be also employed for the production of porous polymers (Xing et al., 2013). Colloidal crystal templating is a hard templating approach in which porosity is directly modeled by the colloid crystal, which is the periodic array of uniform colloidal particles.

Molecular imprinting is another approach through which highly selective recognition sites can be generated in a synthetic polymer. Molecular imprinting mainly revolves around the assembly of a cross-linked polymer matrix around templating structure. As a consequence of removing the templates, cavities or recognition sites are established which are complementary both in terms of shape and functionality to the original template present in the sites. In other words, this synthesis technique is usually executed by copolymerization of functional and cross-linking monomers in the presence of a molecular template (imprint molecule). The functional monomer and template molecules will then have to interact either by covalent or non-covalent bonding (Sacchetin, Morales, Moraes, and e Rosa, 2013). This is followed by the removal of the molecule template after polymerization. The removal is done via extraction or chemical cleavage leaving behind molecular imprinted cavities which are compatible with the imprint molecules.

Biological structures having complex morphology and of diverse shapes and types have been immeasurably employed as templates to prepare porous materials with customized structures (Fetter and Walecka, 2003). The superstructure used may be used as a bio-template to produce ordered macro-porous fibers. As a result, the cell wall and inter-

filament spaces will be mineralized and the final porous structure will be resulting after the removal of the bio-templates by subsequent heat treatment.

2.4 Porous Silicon: Definition and Background

Porous silicon Porous silicon is simply a silicon wafer mined with wholes where their size and morphology highly rely on the manufacturing techniques and the application. High accessibility and efficiency of pores size and morphology may be achieved at the surface of the bulk silicon. It's a nanostructure mass similar to a sponge with contracting pores of wavering morphology and shape reliant on request (Moreno et al., 2009). This porous material grants several intriguing characteristics converging from large surface area, chemistry surface, luminescence properties (Shtil′man, 2003), in vivo biocompatibility (Aad et al., 2012), easy surface chemical modification, stress-free regulation over porous arrangement (Santiago-Moreno et al., 2009), operation mode similar to chemical sensor, electrical and/or optical signal, quantum confinement, Surface to volume ratio (S/V) along to particular surface termination (Aad et al., 2012), controllable pores size, efficient emission of visible light overcoming the problems of chemical stabilities accompanied with the maturing of the material chemistry (Santiago-Moreno et al., 2009), allowance of current flow when being under voltage indulged in few application as sensors, efficient room temperature photoluminescence optics and electronics applications. All the mentioned stormy innovations vacant by porous silicon material a flood fountain of researches poured down on wandering their concern from silicon-based optoelectronics to silicon micro fabrication technologies with application outside the range of optoelectronics and invading the world of biomedical (Pavesi, Dal Negro, Mazzoleni, Franzo, and Priolo, 2000), The enhancement was manifesting as biomedical sensors, manipulating detection of the confined glucose oxidase (GOX) at low concentration-glucose recognition, DNA (Sailor and Park, 2012) along to protein (Palestino, Legros, Agarwal, Pérez, and Gergely, 2008). Moreover this porous innovation is capable of bio-categorization, bio-sensing, immune-isolating and liberating biological molecules (drug delivery); Used in smart drug delivery system, artificial organs (Mathew and Alocilja, 2005). The surface pore morphology enable it with high absorption assets that make them a magnet enticing molecules while assisting binding sites to provide the foundation of detecting mechanism.

Interest in this accidental discovery at Bell Laboratories of porous silicon arose in the prompt 1950s. Couple working on electrochemical research on silicon wafer for microelectronic circuits tumbles with fine wholes instead of uniform dissolution. Followed by altered fluctuations of dedicated interest, this discovery starts gaining lights in the early 1970s and later, gains the battle to overcome and become the pioneers for medical market and applications (Chinwalla et al., 2002).

2.4.1 Causes for the Limitation of Porous Silicon Biological Applications

Silicon enlarged realms have found limitations due to its failure to pass every bio-qualification tests (Chinwalla et al., 2002), as well as summiting longstanding- span physical and chemical stability requests for confrontation with host tissue without rejection (Mathew and Alocilja, 2005). The focus is getting converge toward micro reactors due to their ability to decrease costs along to ecological properties, absorbing organic species such as toxic chemicals and turning them into harmless substances (Adiga, Jin, Curtiss, Monteiro-Riviere, and Narayan, 2009) while this fail for silicon application in biological field.

2.5 Porous Silicon Manufacturing Techniques

Different conventional methods may be used to prepare porous silicon templates. These methods may be either wet etch also known as liquid-phase technique or dry etching technique also known as plasma-phase. Each of these phases exists in several varieties. In wet etching process, the material is dissolved at the time of immersion in a chemical solution while dry etching technique consists of sputtering or dissolving the silicon chip through usage of reactive ions or a vapor phase etchant.

2.5.1 Porous Silicon Manufacturing Using Wet Etching

Wet etching techniques are commonly achieved by applying nano-crystalline silicon wafer to electrochemical oxidations in ethanol diluted hydrofluoric acidic solution. Pores morphology highly relies on the current or potential applied as well as on the time of preparation or the solution composition. These techniques are arranged under the branch of galvanostatic methods. There are several methods that will be highlighted briefly in the following paragraphs.

Gas-etching method is one of the wet-etching techniques used to make porous silicon. Throughout this process a mixture of oxygen (O_2) and nitrogen dioxide (NO_2) gases will be combined with hydrogen fluoride (HF) and water vapors to produce photo-luminescent porous silicon layers. The process of pore formation is achieved through several steps. Combination of the following chemical reactions will lead the porous silicon. The start is the formation of nitric acid followed by oxidation of silicon then etching of silicon dioxide. The gas etching technique consists of exposing silicon samples to a mixture of O_2 and NO_2 gases in addition to HF and water vapors. The pores size and density resulting from this method were found to be strongly dependent on the O_2: NO_2 flow rate ratio (Boughaba and Wang, 2006).

Strain etching is another technique of liquid-phase technique. This method is conducted on p-type and n-type silicon wafers having different doping concentrations. Different porosity gradients may be conducted to overcome the pore wall. Doping materials used may be boron or phosphorus. The solutions for strain etching may contain concentrated hydrofluoric acid and nitric acid with ratios between: (50:1) and (500:1). The formation process of strain-etched Porous silicon layer is defined by the gravimetrical and the spectroscopic ellipsometrical measurements. These parameters will reveal constant dissolution of the top surface of the layer and synchronized shaping of pores on the surface of the crystalline silicon. This technique has self-limiting thickness when either n-type substrates or low doped p-type substrates are employed (Lehmann and Föll, 1990).

Photo-chemical Etching Method is another method of galvanostatic wet etching process (Ozaki-Kuroda et al., 2001). Usually these methods necessitate anodization process that is difficult to apply for porous silicon development on a silicon-on-insulator (SOI) structure or on multilayered integrated circuit. Scientists have developed a technique that employs

an n-type silicon wafer that will be located at the base of a vessel filled with an etchant. The etchant may be mixture of hydrogen fluoride acid solution (HF) and hydrogen peroxide (H_2O_2). The concentration of the etchant is a variable factor relying on HF: H_2O_2 volume ratio. For the formation of photochemically etched silicon; the silicon chip will be irritated by He-Ne laser under the form of a visible laser for 5 to 45 minutes. Through the process a silicon atom will be etched from the wafer where the H_2O_2 oxidant will remove the electrons left in the substrate all along molecular H_2O_2 and H^+ ions will turn into water molecules.

Other technique that may be applied to form porous silicon using wet etching is chemical fabrication. Usually porous silicon is fabricated under anodic polarization in an electrochemical cell. This technique is introduced to form porous silicon without the use of any external source. Etching will occur by the formation of a galvanic cell, with the silicon acting as local anode and the metal as local cathode. An n-type or p-type silicon with a resistivity ranging from 2 to 5 Ω may be employed, this one will be etched with a diluted solution of HF. Ethanol may be added in the aim of prevention of hydrogen bubbles formation and Oxygen will be employed as an oxidizing agent for the galvanic cell. There are two types of this technique that are type 1 chemical fabrication and type 2 chemical fabrications. The main advantage of the galvanic porous formation technique is that a special sample holder to contact the Si is not required. This makes the technique suitable for batch fabrication of porous silicon devices. The contact between the silicon sample and a layer of noble metal is mandatory. The etching rate may be controlled by the metal/Si area ratio and the concentration of oxidizing agent in the solution.

Pulsed Current Etching is another liquid- phase technique. This technique for porous silicon formation is based on pulsed current anodic etching. The technique offers the possibility of fabricating luminescence material with selective wavelength emission depending on cycle time (T) and pause time (T_{off}) of pulsed current during the etching process (Ashruf, French, Bressers and Kelly, 1999). Pulse current anodization of porous silicon is applied by a sequence of current pulses. During the pause period of anodic current, H_2 bubbles will desorbs. Desorption of the H_2 bubbles allows fresh HF species inside the pores to react with a silicon wall that sustains the etching process at an appreciable rate. This process will increase the thickness of the porous silicon layer thus enhancing the porous layer intensity. The PS formation sequence according to the current

burst model will firstly be a direct dissolution of silicon pursued by oxidization of silicon that will be dissolved after a slow surface passivation by H_2 that will start to occur at the clean surface. This process allows the manufacturer to free access of choice available in peak spontaneous emission wavelength.

2.5.1.1 Advantages and Draw Back of Porous Silicon Manufacturing Using Wet Etching

The advantages of liquid phase etching processes may be summarized in the following factors: the simplicity of the equipment employed in the etching process and the easiness to implant, the high etching rate throughout the etching course, and high selectivity for the majority materials.

The disadvantages are however much more than the advantages. This procedure is commonly isotropic that produce substrate matter beneath the masking material after the removal of the etchant chemical. It is insufficient to identify features sizes that are less than 1µm. All along, there is a big probability of chemical handling hazards or the contamination possibility of wafer contamination concerns. Due to the use conventional integrated circuit technology, the wet etching methods are not compatible with the widespread use of gas cluster tools. All along this process necessitate big amount of chemical etchant that results in large quantities of dangerous waste in the manufacturing environment (Syverson and Novak, 1990).

The drawbacks of this phase are much more than the advantages this is why a substitution technique was needed to replace it.

2.5.2 Porous Silicon Manufacturing Using Dry Etching

Dry etching techniques or plasma-phase is a process applied to develop porous silicon. The procedure methodology is based on ion Bombardment or chemical reactive applied in the presence of a vacuum chamber. It is based on accelerated ions from plasma (Syverson and Novak, 1990).

2.5.2.1 Dry Etch Fabrication of Porous Silicon Using Xenon difluoride (XeF_2)

There are several methods of dry etching that are sputter etch ion milling, HDPE RIE milling, plasma etch, Barrel etcher and XeF_2 dry etching. The most important and preferred over any method is the XeF_2 dry etching method.

Silicon micromachining for the development of complex three dimensional microstructures typically use xenon difluoride (XeF_2). XeF_2 plasma-less etching technique roots an augmentation in the silicon surface roughness in the course of the etching development (figure 2.1). XeF_2 is based on the reaction of fluorine ions, which is the main etchant, with the bulk silicon to produce volatile gas SiF_4 at room temperature.

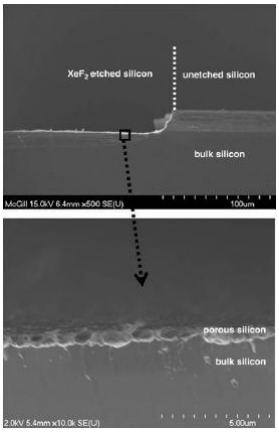


Figure 2.1: Cross sectional SEM image of porous silicon material undergoing XeF_2 etching (Kronfeld et al., 2013)

The XeF_2 etching pattern demands a source bottle of XeF_2. Xenon difluoride is a dense white crystalline solid with a vapor pressure of roughly 4 Torre at room temperature grasped by a vacuum pump, an expansion and etching chambers.

The stages of fabrication would initiates through provision of the etching chamber by dint of XeF_2 throughout a series of small periods of time separated by evacuations. A cubed or full silicon wafer burdened within the etching chamber. The wafer placed horizontally with side textured by XeF_2 fronting up. The etching chamber located beneath vacuum. Etching process launched at a pressure of 0.03 mbar. Flow of XeF_2 from the source bottle into

expansion chamber to etching chamber specifies the cycles of the etching development. Completion occurs at expulsion of etching chamber with no need for drying.

Silicon etching mechanism via XeF_2 tracks throughout an arrangement of steps. The exposed area of bulk silicon will absorb dissociated gaseous XeF_2. This absorbed gas will dissociate into xenon and fluorine. Fluorine ions will act in response with silicon in order to yield SiF_4. This latter will dissociate in turn into a gas at room temperature. The out coming result from these steps is the harvesting of a porous silicon surface achieved via chemical reaction of etching of silicon by XeF_2 abridged through the subsequent equation:

$$Si + 2XeF_2 \rightarrow SiF_4 + 2Xe \quad (2.1)$$

2.5.2.2 Advantages and Disadvantages of Dry Etching Method

Dry etching techniques present lots of advantages; the main important one is its ability to automate and reduces the consumption of materials. It may be employed when removal in vertical direction and high anisotropy is vital. All along it offers accessibility for physical removal or a combination of physical removal and chemical and selective reactions as the application demands. This technique is apt to define small pore sizes that are less than 100 nm.

However; this technique is not perfect it is also encountered with lots of drawbacks. They lack high anisotropy, it accounts for higher costs since it needs more specific equipments that are hard to implant and products than wet etching (Syverson and Novak, 1990).

2.6 Proposed Generic Recipe

The generic recipe proposed in the thesis for the fabrication of nano-textured porous polymers using porous silicon scaffolds is represented via a diagram that will show the different steps applied. The generic recipe projected will use a silicon chip manufactured using XeF_2 dry etching technique as a scaffold. This scaffold will be used as a template for the intended porous polymer to be fabricated.

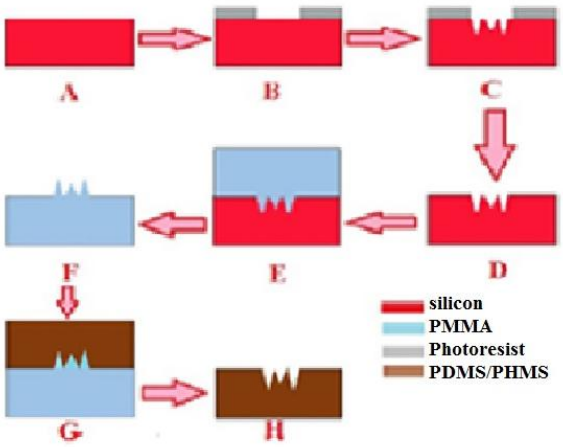


Figure 2.2: Schematic representation of the proposed generic fabrication process of porous polymer (El Ahdab, 2015)

Figure 2.2 represents the proposed generic fabrication process that can be applied to all types of liquid polymers in order to give their surfaces a texture that has a desired porosity for a specific application. The process consists of two micro molding-based steps. The first step which determines the final porosity of the polymer, starts with a piece of silicon substrate that will be spin coated with a layer of photoresist and photolithographical pattern to expose a specific and well determined pattern in the silicon wafer bulk achieved via Xef_2 etching technique. The second step is pouring Poly-methyl methacrylate (PMMA) on the silicon surface. Once the PMMA is cured, it is gently peeled off. The PMMA thusly represents the second mold for the final polymer. Then PDMS will be poured on the top of this mold; once cured it will textured with the same porosity of silicon scaffold.

CHAPTER 3
GENERIC FABRICATION PROCESS: POROUS POLYMER IMPRINTING STAGES

This chapter discusses briefly the first phase of the proposed recipe that is the technique of manufacturing the porous silicon scaffold. Then a clear and detailed explanation about the second phase of the thesis that is the manufacturing of the porous polymer that have exact pores morphology as the silicon template will be presented. All along a general information and description about the different polymers employed will be represented.

3.1 Curing Polymers Process

Polymer curing also called polymer hardening is a chemical reaction denoting the toughening or hardening of a polymer substance via a specific cross-linking reagent. The process decoded is the hardening of polymer chain of the polymer chain achieved through addition of an organic compound: chemical or electron beam alteration as well as heat factor modification (Carroll, Turro and Koberstein, 2010). Moreover, another additive may be applied by means of ultraviolet where the process is referred to as UV cure (Osswald and Menges, 2003). It is artistic exclusive work that may be portrayed as an added agent that will react with polymer's constituents, by adding bounds to them throughout founding inter-molecular and intra-molecular cross-links all over foaming progression experiencing hardening. The chemical structure of the polymer will undergo reduced density, cumulated thermal and acoustic insulation, along with comparative stiffness (Redenbach et al., 1996).

3.2 Proposed Generic Recipe Methodology

In the thesis a generic recipe will be applied for the fabrication of nano-textured porous polymers using porous silicon scaffolds. The proposed design was shown in the previous chapter in Figure 2.2.

However Figure 2.2 illustrates the suggested standard production course that can be applied to all types of solidified liquid polymers in the aim of texturing their surfaces with a desired porosity for a particular application. The course consists of two micromolding-based steps. The first step determines and specifies the final desired porosity because silicon chip is the porous template. Then PMMA will be cured on the surface of this porous chip so that the pores formed will be a complement of the pores existing on the silicon chip. After having a porous PMMA, this one will serve as a template for PDMS. PDMS will be cured on the surface of porous PMMA so that it will complement the pores existing on the template. After is being cured; PDMS will become porous polymer similar to the porous silicon chip.

The procedure starts with a piece of silicon chip substrate spin coated with a layer of photoresist. This chip will be patterned photo lithographically intending to expose a definite and well determined hole-in-the-wall of the silicon wafer slice.

The imprinting steps may be illustrated as first the cleaning of the silicon chip with acetone; Poly-methyl methacrylate (PMMA) powder is then poured on the silicon surface. As soon as the PMMA is cured by the mean of the considerable reagent, this layer is peeled off gently. This developed PMMA layer symbolizes the second mold for the final polymer.

In the last step, Poly-methyl hydrosiloxane (PDMS) will then be poured on the PMMA surface. As the before step this polymer after undergoing curing will be removed from the PMMA surface. Complementing the pores, this final PMHS polymer will be identical to the porous silicon template.

One crucial point to be held in consideration, Poly-dimethyl siloxane (PDMS) might be replaced in the second molding step by Poly-methyl hydrosiloxane (PMHS). However, PDMS was employed based on the fact that this latter provides a wider range of usable applications than PMHS (Luo, Meng and Francis, 2006).

3.3 Porous Silicon Scaffold

The first step determines and specifies the final desired porosity. The procedure flinches with a piece of silicon chip substrate spin coated with a layer of photoresist. This chip will be patterned photo lithographically intending to expose definite and well determined pores on the silicon wafer slice.

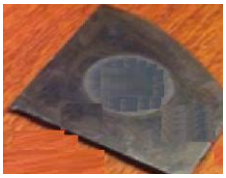


Figure 3.1: Figure displaying the basic of the project the silicon chip

In the Figure below the illustration displays the first step in the procedure; the silicon chip is modeled by the stage A. The silicon chip or template is the phase A described and illustrated in reality as to be the silicon wafer used manufactured and prepared at McGill owing a pores morphology that will be prototyped by the cured polymer after fusion of the photoresist around the pores.

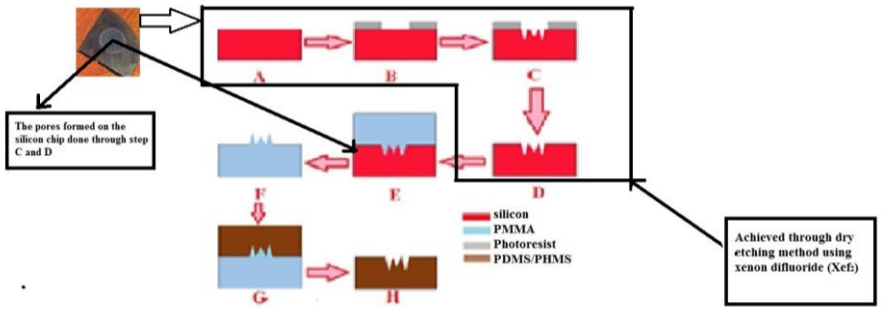


Figure 3.2: Illustration displaying the pores on the silicon chip and its according step in the generic recipe applied

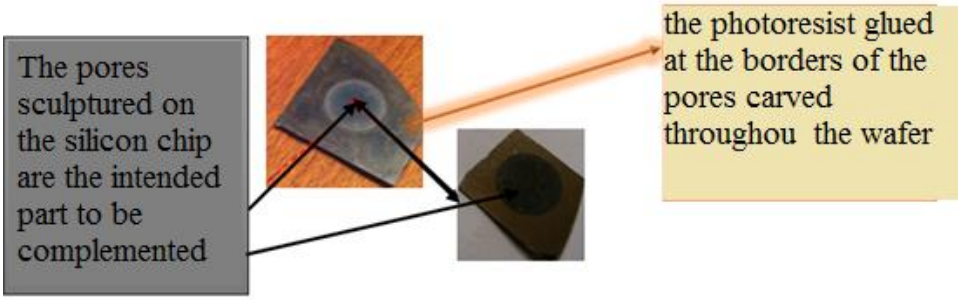


Figure 3.3: An illustration showing the porous part on two silicon samples

3.3.1 Porous Silicon Scaffold Manufacturing Technique

As mentioned previously the applied method for porous silicon manufacturing was dry etch Fabrication using xenon difluoride (XeF_2). This method was applied because the pores size intended were in nano-scale and cutting off the chemical hazardous was the second aim.

Xenon difluride (XeF_2) is an applied gas employed in silicon micromachining in the aim of developing a multifaceted three dimensional microstructures. This technique may be described as plasma-less etching scheme rooting an increment in the surface roughness of the silicon all over the etching course (Figure 3.4). XeF_2; is mainly based on the main etchant, the fluorine ions acting in response along with the bulk silicon in the intention of producing at room temperature, volatile gas SiF_4 (Bassiri-Gharb, 2008).

XeF_2–based etching final product is a hard-baked layer of photoresist serving as a masking deposit. This method is employed in the manifestation of CMOS-integrated circuits based on the fact that the latter is rather inert to photoresist, silicon dioxide, silicon nitride and aluminum.

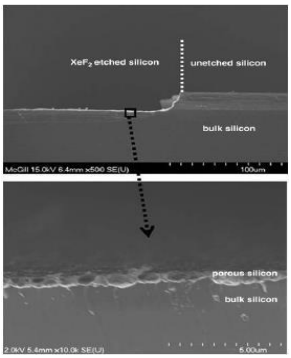


Figure 3.4: Picture depicting the dry etching of bulk silicon and creation of pores (Kronfeld et al., 2013)

XeF_2 etching arrangement comprises a source bottle of XeF_2; a dense white crystalline solid devouring a vapor pressure of approximate 4 tor extended by a vacuum pump at room temperature along with an expansion chamber and an etching chamber.

The employed silicon chips used as a template in this work were fabricated through the following procedure. The start was a provision of the etching chamber by XeF_2 all through an array of short epochs of time alienated by evacuations. The next step included a stacking of a diced or full silicon wafer in the etching chamber followed by a horizontal deposition of the wafer with a facing up of the side to be textured by XeF_2. The etching chamber is under vacuum. The launching of etching process is initiated at a pressure of 0.03 mbar.

Cycles of the etching process are signposted by the Flow of XeF_2 from the source bottle into the expansion chamber and then to the etching chamber. By the time the etching process is complete, the etching chamber is found to be vented and that there is no need for drying.

Silicon etching mechanism surveys a sequence of steps. The beginning is a dissociated gaseous XeF_2 absorbed by the exposed area of bulk silicon. The dissociation of into absorbed gas xenon and fluorine were the next achieved act. The latter act may be described as the reaction of fluorine ions with silicon in the aim of producing SiF_4 that will dissociate into gas at room temperature (Lehmann and Föll, 1990). The left behind is a porous silicon surface used in this research. The chemical reaction of silicon etching may be described by the chemical equation: $Si + 2XeF_2 \rightarrow SiF_4 + 2Xe$

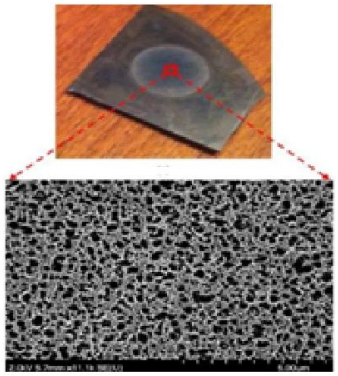


Figure 3.5: Porous silicon template on the top and in the bottom Scanning electron micrograph of a porous silicon template textured with XeF_2

3.4 Porous Polymer Development

In order to prepare a porous polymer having porosity similar to the silicon scaffold a porous polymer having a complement pores of those presented on the silicon chip must be prepared first followed by a preparation of porous polymer that will have a porous morphology complement to the developed "complement polymer of the silicon". The complement of the complement is just a copy from the original.

In order to fashion the surface of any polymer with a desired porosity, this polymer must be liquid polymer. The polymers available in the market are raw polymers. In order to have liquid form, raw polymers must be cured.

As mentioned earlier, curing may take place via several techniques. The method applied in this research is the addition of corresponding cross-linking reagent. Mixing the polymer with its corresponding cross-linker is not the whole process. The aim is to find the consequent ratio showing the quantity of raw polymer vs. amount of added cross-linker that result with the most efficient cured polymer. Once this ratio is settled the curing process have to take place on the surface of the scaffold intended to complement.

3.4.1 Porous PMMA Polymer Development Phase

3.4.1.1 PMMA Chemical Characteristics

Poly (methyl methacrylate); generallyrepresented by PMMA. This polymer is a synthetic resin deducted from the polymerization of methyl methacrylate as shown in the Figure below.

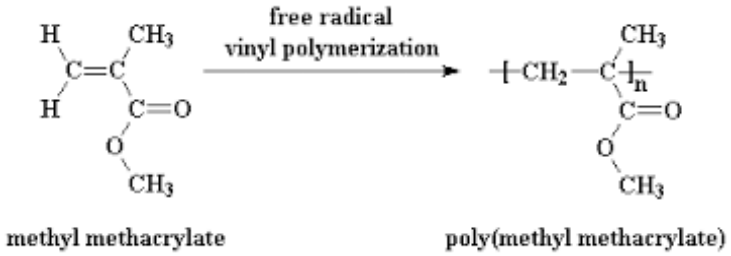


Figure 3.6: Picture denoting thepolymerization of methyl methacrylate toPoly (methyl methacrylate) (Lee and Jang, 1996)

Polymethyl methacrylate or (PMMA) involved under the form of powder, having an auto ignition temperature set at 580°F, molecular weight average M_n ~39,500 by GPC average and M_w ~101,000 by GPC, composition of < 5 wt. % of ethyl acrylate along with a transition temperature T_g (DSC) 104°C (onset) ("Sigma Aldrich Product Catalog." Sigma Aldrich. N.p., 2009, Web.16 Mar. 2015).

This polymer is a transparent, offers a great light transmission that permit its usage in many optical applications, rigid plastic (Anseth, Bowman and Brannon-Peppas, 1996), PMMA is elected among any other polymer since it's an economical substitute for polycarbonate (PC), where the former even it does not offer great strength but lack the existence of harmful bisphenol-A. It is also easy for handling and processing, and low cost can attain high scratch and impact resistance (Konaganti and Madras, 2010). Other advantages stands for tremendously long service life, high resistance to Ultra Violet light, enduring, unlimited coloring, perfectly crystal clear options along with the greatest surface hardness of all thermoplastics well as 100% recyclable and most important feature biocompatibility.

When using PMMA some safety procedure must be considered. It is of acute toxicity (oral, dermal, inhalation), may cause Skin and eyes irritation and sensitization.

3.4.1.2 PMMA Cross-Linking Reagent: Dichloromethane

In this research dichloromethane was used as a cross-linking reagent for curing PMMA. This: chemical organic compound known as methylene chloride or abbreviated as DCM. It has the molecular formula CH_2Cl_2 shown below. DCM was used under colorless liquid, as a volatile liquid with a soberly sweet aroma in a 1, 4, and 4×4 L in aluminum bottles. This liquid has a density of 1.325 g/ml at room temperature and it is used as a solvent. It has a molar mass equal to 84.93 g/mol. DCM contains amylin as a stabilizer with a boiling point 39.8-40.0ºC and melting point of -97ºC. It is Non-immiscible with water and used as a blowing agent in biomedical application.

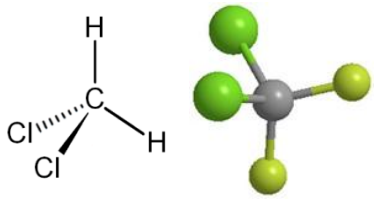


Figure 3.7: Figure displaying the chemical structural formula of dichloromethane (Portalski, 1963)

3.4.1.3 PMMA Curing Recipe Parameters

Setting the parameters; the ratio defining the quantity of polymer mixed with the corresponding quantity of cross-linker and the temperature, is the basic step to get a clear and flexible polymer that will undergo surface treatment. Since Sigma Aldrich doesn't provide consistent curing parameters; developing a clear and flexible polymer through cross-linking needed a corresponding recipe to discover. Few experiments were held to develop the clearest possible polymer before complementing the pores of the silicon chip and later the developed polymer stamping silicon pores.

Based on previous developed experiments; it has been declared that PMMA curing traits were taking place for the following parameters: when 25 mg of PMMA powder is mixed with 90 ml of dichloromethane at room temperature. That is a ratio (m_{PMMA}:V_{DCM}) of (1:4). After a contact with the supplier: Sigma company, they provide us with the curing temperature that was either at room temperature of at a temperature ranging from 120-130ºC.

Based on the provided data several experimental trials were held where the ratio and temperature were close to previous experiments performed and the temperature parameters provided by Sigma. Different alterations of the ratio (m_{PMMA}:V_{DCM}) : (1:4) has been made all along to temperature parameters that were held between 120-130ºC or at room temperature.

For all experiments the electronic scale was rounded to zero after putting the petri dish on the scale. The defined mass of powder PMMA that were mainly either a 25 or 50 grams samples mixed with the corresponding volume of dichloromethane. The experiments with the most important results will be shown throughout the report.

3.4.1.4 Cured PMMA Experiments Efficiency Testing

The efficiency of the resulting cured PMMA after addition of the cross-linker reagent dichloromethane is evaluated by means of its clearance and flexibility.

The transparency efficiency was evaluated based upon standard alignment of the UV source and collection of the transmitted light. The efficiency of light transmission is assessed through transmittance coefficient (T).

In details; assessment of light emission degree were made upon quantitative analysis mainly based on the Fresnel formulas for the transmission and reflection of a plane light wave crossing two different media while interface media sustains an considerably thin medium the micro pores on the polymer. The two main formulas are:

- $E_T = E_i - E_r$ Where r, i and t denotes reflected, incident and transmitted light wave.

- $A = 1 - T - R$ where A is negligible; T refers to transmission coefficient and R for reflection coefficient

The measurements were made using a scalar network analyzer (Agilent HP 80350A 8756A-10 MHz to 40 GHz) shown in the figure below. The arrangement comprises a sweep generator, an indicator unit and a waveguide reflectometer. The European standards specifying the measurement methods for the reflectivity of electromagnetic wave (EMA) absorbers for the normal incident wave were smeared. The ratios of transmitted light /input source light and reflected beam /input beam from source light were ensued at 35 GHz. The consequential results are shown in the graphs below.

Figure 3.8: Network analyzer (Agilent HP 80350A 8756A-10 MHz to 40 GHz*).*

The mechanical performance is evaluated established upon 40 cycles of concaving and conveying the curvature of the polymer and assessing the elongation through measuring Δl by a ruler. Based on the greatness of Δl's value the flexibility of the sample is assessed. The applied formula is:

$Y = \left[L_i - \frac{\sum_{n=1}^{n=40} \Delta l}{m}\right]$ Where y refers to average deformation occurred, n: the number of curvatures performed and m: the total rounds that is to be 40.

3.4.1.5 Porous PMMA Development

In this part, the best recipe resulting with the best cured polymer will be applied all over again but this time on top of the silicon chip template. Once curing process is

accomplished, the polymer will be peeled out of the silicon and the results is going to be a porous polymer. The porous PMMA will have pores structure complements

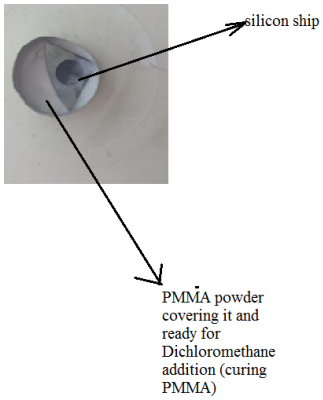


Figure 3.9: an illustration depicting the addition of PMMA on the top of silicon template before curing process

By performing this procedure this may be illustrated as stage G on the developed diagram of the proposed generic recipe.

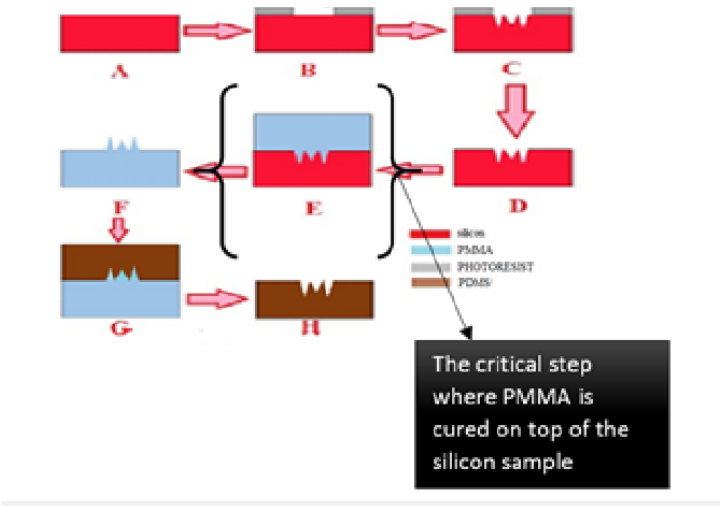


Figure 3.10: An illustration representing the critical step in the proposed generic recipe; PMMA complementing the pores of silicon template throughout curing process

3.4.1.6 Characterization of Porous Cured Polymer

The pores morphology of cured porous PMMA polymers will be assessed in details via the use of Low-End Compact Mini SEM: Scanning electron microscopy (SEM).SEM images were recorded using AIS1800C SEI archetypal. The images registered were aimed to disclose the external surface as well as to show the highly porous morphology of the developed polymers. PMMA samples were metalized with copper before being introduced into the microscope; where copper was evaporated from an overhead electrode and smeared to PMMA sample's then bathed in an acidic solution.

The picture's setup parameters were made under different scales, magnification, acceleration and working distance (WD) (the distance between the sample and electron source).

3.4.2 Porous PDMS Polymer Development Phase

3.4.2.1 PDMS Chemical Characteristics

Poly(dimethylsiloxane)bis(3-aminopropyl) or simply PDMS. This polymer chemical formulation: [H_2N (CH_2)3Si (CH_3)2O [Si (CH_3)2O]nSi(CH_3)2(CH_2)3NH_2].

Polydimethylsiloxane is industrial manufactured through mixing dimethyldichlorosilane with water H_2O based on this reaction: n $Si(CH_3)_2Cl_2$ + $n+1$ H_2O → HO[-Si $(CH_3)_2O$-] $_n$ H + 2nHCl (Jo, Van Lerberghe, Motsegood and Beebe, 2000).However for medical solicitations; in order to reduce toxicity of the polymerization reaction, chlorine atoms in the silane precursor may be substituted with acetate groups. In this way, hydrogen chloride is avoided and replaced by acetic acid that is less toxic. The resulting polymer from polymerization process is the one employed in this research. It is known as H_2N (CH_2)3Si (CH_3)2O [Si (CH_3)2O]nSi(CH_3)2(CH_2) and have the structural formula below:

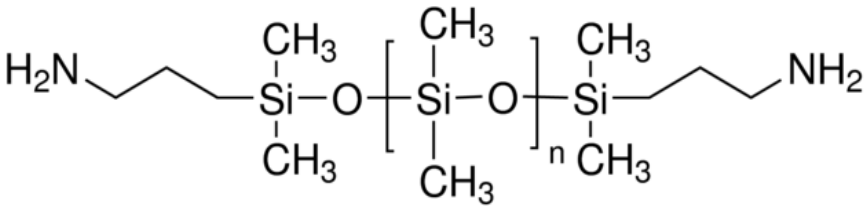


Figure 3.11: Figure displaying the chemical structural formula of Poly (dimethylsiloxane), bis (3-aminopropyl) terminate ("Sigma Aldrich Product Catalog." Sigma Aldrich. N.p., 2009, Web. 16 Mar. 2015)

PDMS belongs to polymeric organo-silicon's group. It is recognized for its uncommon rheological (or flow) assets. This latter is optically clear polymer, inert, non-toxic as well as non-flammable; that make it an appropriate polymer for biological and medical applications ranging from contact lenses and medical devices to elastomers.

This polymer is employed under the form of viscous liquid (viscoelastic), acts as rubber at low temperature; having density of 0.98 g/ml at room temperature. After polymerization it presents a hydrophobic surface (Armani, Liu and Aluru, 1999). It has an average molecular weight M_n ~2,500, a viscosity of 50 cSt (lit.), stocked in 50 ml poly bottle. PDMS has a Flash Point (F) > 234.5°Fand must be employed with personal protecting equipment.

3.4.2.2 PDMS Cross-Linking Reagent: Glutaraldehyde

Glutaraldehyde, a chemical organic compound expressing the molecular formula $CH_2(CH_2CHO)_2$ or simply: $C_5H_8O_2$and structural molecular formula displayed on figure 3.12. This organic is also denoted as glutaral,1,5-pentanedione, potentiated acid glutaraldehyde, sonacide and glutardialdehyde. This item is stored at a temperature 0°C, a molecular weight of 100.1g/mol., a density 1.016 g/ml and supplied as 0.5% (w/w) solution in water of grade 1, 25% in H_2O. This compound is used in sterilization, fixation, cross-linking processes, as a component of hydraulic fracturing "fracking" fluid as well as other applications. It is toxic and a sturdy nuisance.

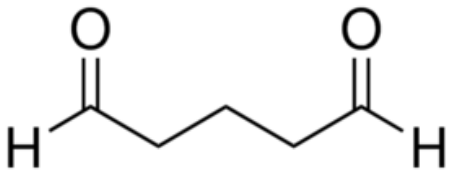


Figure 3.12: Figure displaying the chemical structural formula of Glutaraldehyde ("Sigma Aldrich Product Catalog." Sigma Aldrich, N.p., 2009, Web. 16 Mar. 2015)

In this research Glutaraldehyde was used as a cross-linking reagent for curing PDMS.

3.4.2.3 PDMS Curing Recipe Parameters

As in the case of PMMA the same procedure must be applied in PDMS curing procedure. Lots of papers mentioned different curing methods using catalysis. However, the main intention was to find a corresponding cross-linker. The first one proposed was poly (ε-caprolactone) (PCL), but this one failed to cure PDMS. In the realm of experimental flow; another basic was applied, the beaker containing liquid PDMS was placed into the oven for 1 hour at 70 °C. But this method failed to cure PDMS.

Gluteraldehyde was a corresponding cross-linker that was able to cure PDMS . Experiments were held to come out with the best recipe of PDMS curing generating the clearest and most flexible polymer. In Both cases, heat through usage of a digital oven and at room temperature; along with alternative values of added cross-linker (glutaraldehyde) sets of experiments were held.

Several experiments were held to obtain the targeted results. First of all, a small amount of sample of PDMS liquid polymer was tested with different amounts of glutaraldehyde to ensure the formation of the polymer surface and test the degree of solidification of each volume of cross-linking reagent added.

In the first step in the realm of experimental procedure, the primarily ratio that lunched the trials for the corresponding recipe initiated from (1:1). Then, the quantity of PDMS was increased by adding 1 to the ratio applied.

3.4.2.4 Cured PDMS Experiments Efficiency Testing

The efficiency of the resulting cured PDMS after addition of the cross-linker reagent was evaluated by the same procedure applied to those of PMMA. The transparency efficiency using scalar network analyzer and mechanical performance based on Δl evaluation.

3.4.2.5 Porous PDMS Development

In this part, the best recipe resulting with the best cured polymer will be applied all over again but this time on top of the developed porous PMMA. Poly-dimethyl siloxane (PDMS) will then be poured on the PMMA surface. And throughput the curing course this polymer will complement the pores existing on the surface of porous PMMA. This final resulting porous polymer will be the complement of the complement which is identical to the porous silicon template.

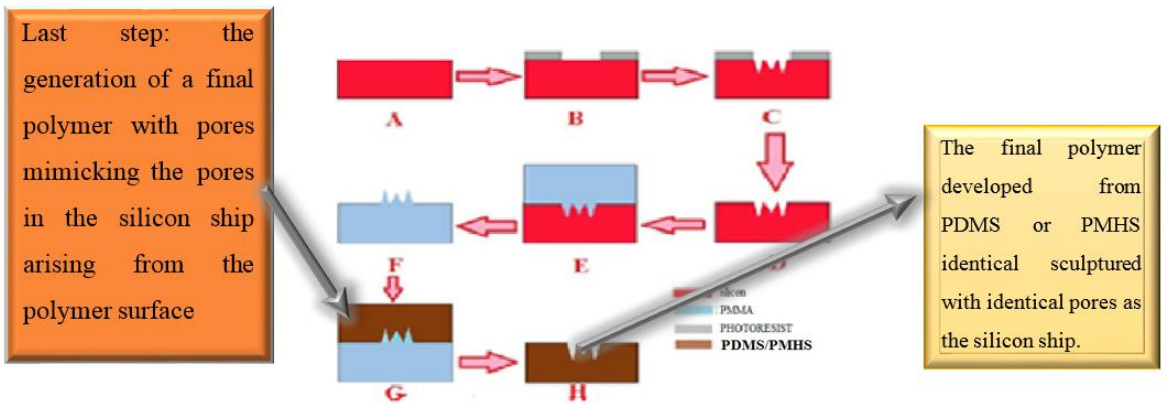


Figure 3.13: An illustration showing the last step resulting with the development of final porous PDMS identical to silicon scaffold

3.4.2.6 Characterization of Porous Cured Polymer

The same methodology applied for PMMA pores morphology study mentioned earlier will be applied for the developed porous PDMS.

CHAPTER 4
POROUS POLYMER MIMICKING SILICON SCAFFOLD DEVELOPMENTAL STAGES

This chapter will discuss the different curing experiments held for both PDMS and PMMA. All along it will show the results from transparency and mechanical efficiency tests made for each sample developed. The reason we relied on for selecting the experiment parameters for curing PMMA and PDMS once poured on the top of the defined scaffold will be highlighted and shown via pictures and graphs. The samples obtained will be shown. Analysis of the resulting samples from different experiment parameters will be also revealed. All the experiments held and their results will be shown in graphs and charts.

4.1 PMMA Polymer Curing Process

4.1.1 PMMA Curing Experiments and Resulting Polymers

The table below displays the ratio of mass vs. volume (m_{PMMA} : $V_{Dichloromethane}$)applied in the experiments performed. Many sets of ratio have been applied in the aim of getting the clearest cured polymer.

Table 4.1: Table showing the conditions (temperature and r (m_{PMMA}:$V_{Dichloromethane}$)) used for each experiment

Experiment	Sample	Temperature	(m_{PMMA}: $V_{Dichloromethane}$)
Experiment 1	Sample 1	Room temperature	(1:6)
Experiment 2	Sample 2	Room temperature	(1:8)
Experiment 3	Sample 3	Room temperature	(1:4)
Experiment 4	Sample 4	126°C for 2 min	(1:6)
Experiment 5	Sample 5	Room temperature	(1:6)

In the flow Realm the following experiments the following alternatives were made for experiment 1:0.25g of PMMA cured with 1.5 ml of Dichloromethane where ratio (m_{PMMA}:$V_{Dichloromethane}$) is (1:6) at room temperature; the obtained resulting polymer after two trials is shown in Figure 4.1.

Figure 4.1: Two similar samples of PMMA cured with experiment 1 parameters

The second experiment with the ratio (m_{PMMA}:$V_{Dichloromethane}$) (1:8). 0.25g of PMMA was cured with 2 ml of cross-linking Dichloromethane at room temperature; the resulting sample 2 shown in the Figure 4.2.

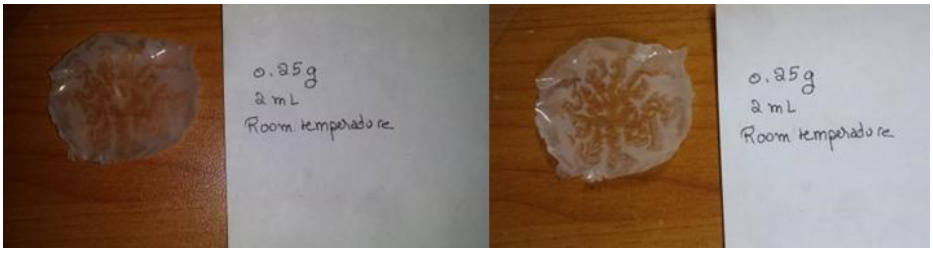


Figure 4.2: Two PMMA samples cured at room temperature with experiment 2 parameters

The third set of values for experiment 3 claimed and experienced in the aim of a clear cured polymer were 0.25 g of polymer and 1 ml of Dichloromethane. The ratio (m_{PMMA}:$V_{Dichloromethane}$) is (1:4).The resulting sample 3 polymer is displayed in the Figure 4.3.

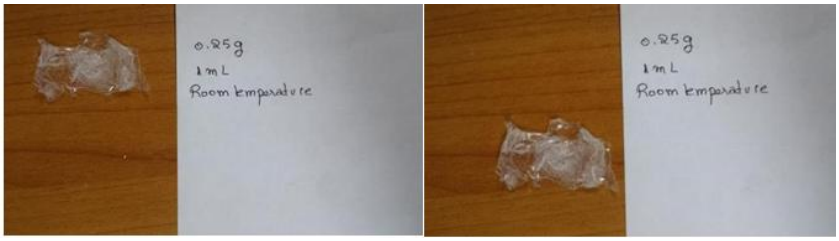


Figure 4.3: Pictures of two samples obtained after being cured with experiment 3

The intentions of the outcome were aiming for curing polymers at room temperature based on the fact of avoiding the use of oven and accessibility along to the complications and drawbacks when dealing with the oven.

The use of the oven was a must to come up with the most efficient curing reaction where experiment4 was driven using 25 mg and 1.5 ml as a ratio (m_{PMMA}:$V_{Dichloromethane}$) of (1:6) at 126°C for 2 minutes. The resulting liquid polymers are revealed in the following pictures.

Figure 4.4: Pictures of cross-linked PMMA in the oven at 126°C for 2 minutes

For experiment 5; 25 mg cured based on ratio (m_{PMMA}:$V_{Dichloromethane}$) = (1:3) with 0.7 ml of cross-linking DCM at 126°C for 2 minutes. The results of sample 5 are displayed in the Figure 4.5.

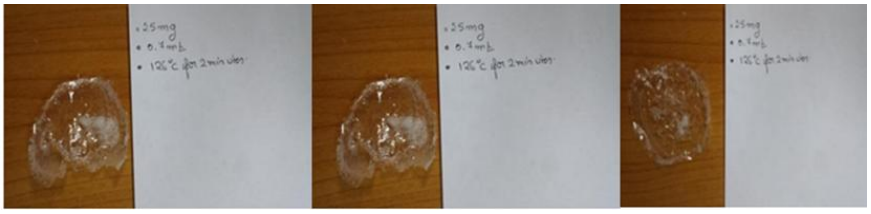


Figure 4.5: Three different samples resulting from experiment 5 prepared at 126°C for 2 minutes

The experiment 5 was repeated for 3 times. The obtained resulting samples shown in the figure 4.5 gave almost same polymer. The obtained similar results show that this experiment didn't happen by coincident but rather it is a credible experiment where the parameters applied are consistent.

After trials, the best sample developed and admitted was sample 5 resulting from experiment 5. The ratio (m_{PMMA}:$V_{Dichloromethane}$) was (1:3) and 25 mg of PMMA mixed with 0.7 ml of Dichloromethane at 126 °C for 2 minutes in the oven. The choice was based on the fact that this recipe generated a clear flexible polymer. Bubbles within the polymer were a result of the air. Getting rid of these bubbles is achieved throughout the use of vacuum machine throughout the curing process.

4.1.2 PMMA Curing Experiment Efficiency Evaluation

4.1.2.1 PMMA Transparency Test Analysis and Evaluation

Assessment of light emission degree made upon quantitative analysis based on the formulas: $E_i + E_r = E_t$ and $T = 1 - R$ where A to be the absorption coefficient has come up with the following results.

For sample 1: The ratio (m_{PMMA}:$V_{Dichloromethane}$) applied was (1:6). The obtained resulting graph of the transmission % of light in terms of incident light is shown in the graph below

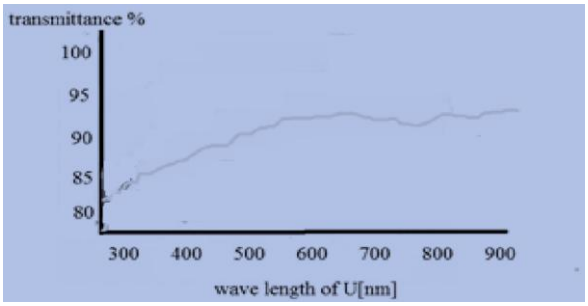


Figure 4.6: The transmission percentage of the cured polymer by experiment 1 by UV visible spectrophotometer

For sample 2: with the ratio (m_{PMMA}:$V_{Dichloromethane}$): (1:8). The gotten consequential diagram of the % light transmission in terms of incident light is revealed in the diagram 4.7

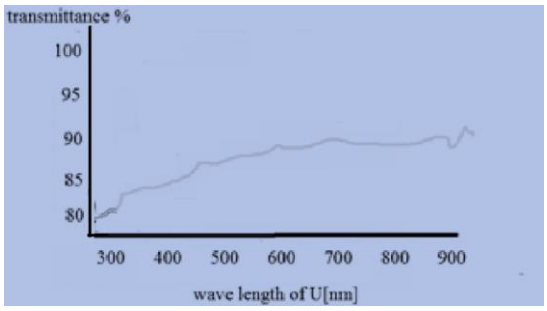


Figure 4.7: The transmission percentage of the cured polymer by experiment 2 upon an emitted UV wave length

For sample 3: resulting from experiment 3 applying ratio (m_{PMMA}:$V_{Dichloromethane}$) = (1:4). Diagram 4.8 screens the collected the reflected beam results rendered in the drawing of the % light transmission in terms of incident light.

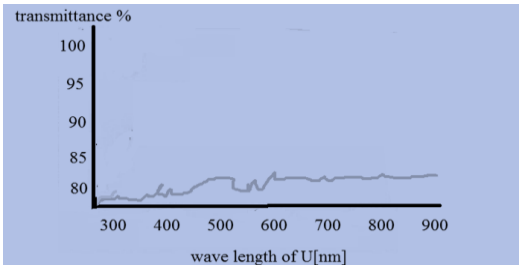


Figure 4.8: The transmission percentage of the cured polymer by experiment 3 upon an emitted UV wave length

For sample 4: The ratio (m_{PMMA}:$V_{Dichloromethane}$) applied is (1:6). Diagram below reveals the coming out far-reached results rendered in the drawing of the % light transmission in terms of incident light.

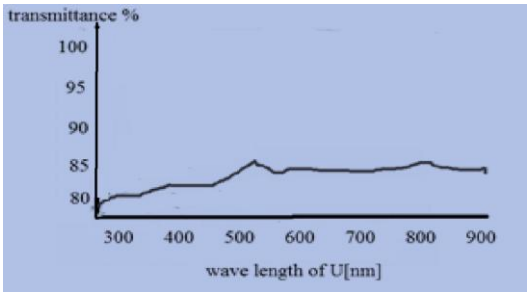


Figure 4.9: The transmission percentage of the cured polymer by experiment 4 upon an emitted UV wave length

For sample 5: The ratio (m_{PMMA}:$V_{Dichloromethane}$) applied is (1:3). The chart of figure 4.10 tells the coming the outcome results gotten in the sketch of the % light transmission in terms of incident light.

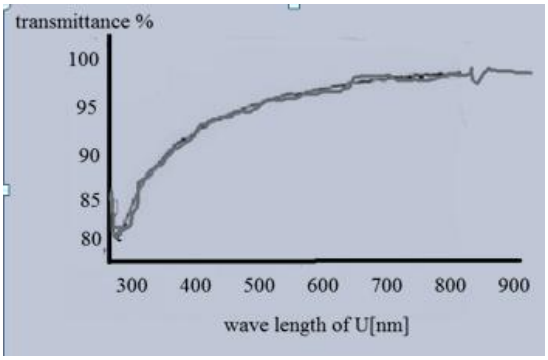


Figure 4.10: The transmission percentage of the cured polymer by experiments 5 upon an emitted UV wave length

In the chart below the % efficiency of the five applied recipe are all depicted in one chart in the aim of comparison for the best efficient recipe. These results were inserted in the table below.

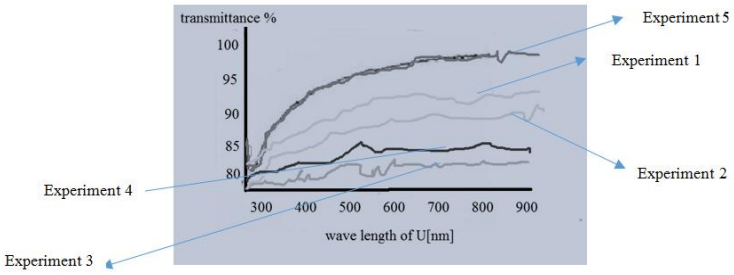


Figure 4.11: The transmission percentage of the cured polymer via the 5 different experiments performed upon an emitted UV wave length.

The obtained cured polymer from different experiment ratio (amount of PMMA: Volume of Dichloromethane) and their average percentage of the efficiency success of obtaining a clear and transparent polymer are drawn in the table 2 and graph of Figure 4.12.

Table 4.2: Table depicting the calculated average % efficiency of each recipe applied for a developed polymer based on the light reflection basis

Experiment	Sample	Temperature	(m_{PMMA}: $V_{Dichloromethane}$)	Average % of Efficiency of the experiment
Experiment 1	Sample 1	Room temperature	(1:6)	92%
Experiment 2	Sample 2	Room temperature	(1:8)	86%
Experiment 3	Sample 3	Room temperature	(1:4)	68%
Experiment 4	Sample 4	126°C for 2 min	(1:6)	81%
Experiment 5	Sample 5	Room temperature	(1:6)	96%

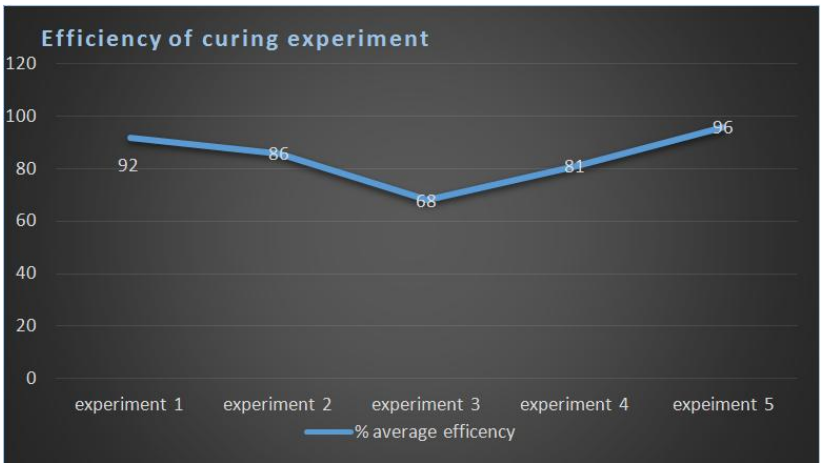


Figure 4.12: Chart depicting the amelioration of efficiency throughout experiment's ratio experimental realm

4.1.2.2 PMMA Mechanical Performance PMMA Cured Polymers

As described in chapter 2, for testing the mechanical performance is assessed based on the elongation caused within the polymer without the occurrence of a breakage in the samples. The applied formula:

$Y = \left[L_i - \frac{\sum_{n=1}^{n=40} \Delta l}{m}\right]$. Where L_i denotes the diameter measured by a ruler between the extremities of the samples developed. And Δl=L_f – L_i where Δl is the elongation that resulted after 40 sets of concaving and conveying deformation. The diameter of each cured PMMA sample will be measured before and after the 40 deformation cycle. The

subsequent results after being replaced in the formula and averaged are listed in the table below.

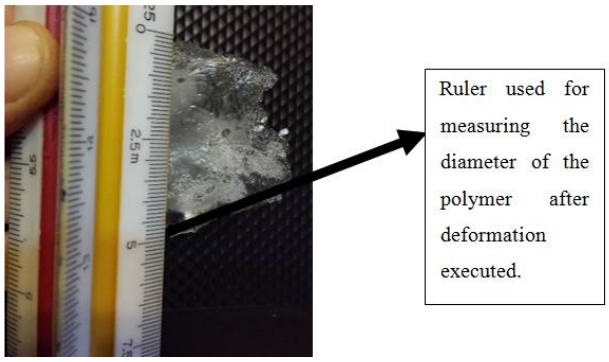


Figure 4.13: Picture showing the measurements of the diameter of the polymer after deformation realized

Table 4.3: Table showing the % Average deformation ensued for several trials for each developed polymer

Polymers cured	% Average deformation occurred
Sample 1	78 % with no cracking
Sample 2	33% numerousbristles of crakes
Sample 3	3 % sample cracks at 10th trial
Sample 4	55% some bristles of crakes
Sample 5	88% with no cracking

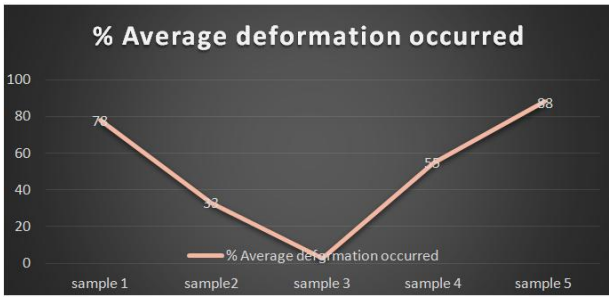


Figure 4.14: A graph depicting the % average deformation taking place in the polymer after deformation

4.1.2.3 PMMA Curing Polymer Experiment Selected

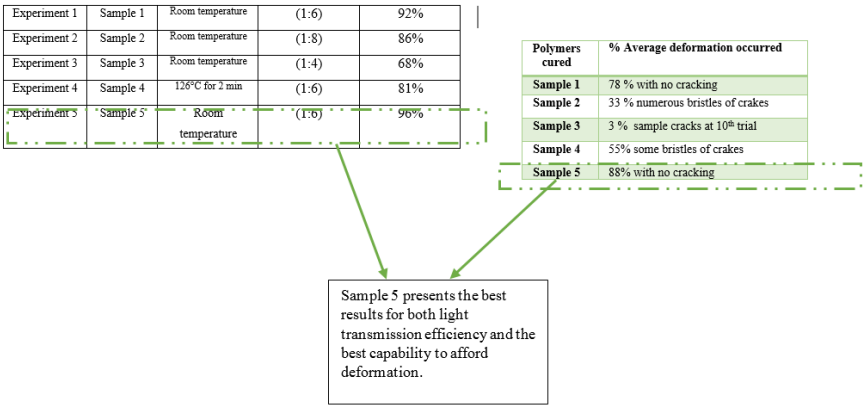


Figure 4.15: Assessment for the most efficient curing experiment to be applied to complement pores on the silicon chip

From the obtained results from the test applied and through comparison; the carefully selected recipe to be applied when curing the polymer on top of the silicon chip is experiment 5 where the ratio (m_{PMMA}: $V_{dichloromethane}$) is (1:3) at the experiment must be held at 126°Celsius for 2 minutes.

4.1.3 Development of Porous PMMA by Application of Selected Experiment

Once it was agreed on the corresponding, most accurate and efficient curing recipe for powder PMMA; experiment 5 with ratio (1:3), it was time for applying the experiment on top of the silicon chip template.

In this part, the approved experiment 5 is applied. The silicon template chip was covered with 25 mg of PMMA and then dropped into a beaker containing 75 ml of Dichloromethane. This mixture was whisked vigorously with a spatula for almost 4 minutes till the dichloromethane was uniformly distributed throughout PMMA powder. The uniformed mixture was inserted in the oven prepared and settled at 126° C. The mixture is left for 2 minutes in the oven before being removed and left for cooling.

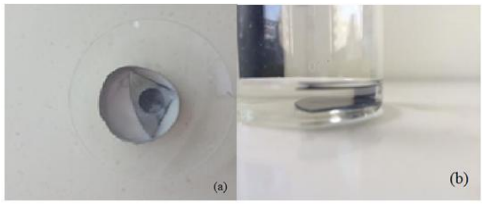


Figure 4.16: Figures depicting silicon chip covered with 25 mg of PMMA after being weighted on an electronic scale on the left side while on the right side 75 ml immersed PMMA and Dichloromethane just before curing process

4.2 PDMS Polymer Curing Process

4.2.1 PDMS Curing Experiments and Resulting Polymers

Experiments held on PDMS curing failed for many applied experiments. experiments to be mentioned as a failure experiment were the following ones: experiment 1 with ratio (V_{PDMS}:$V_{Gluteraldehyde}$):(1:1) ;1 ml of PDMS is mixed with 1ml of Glutaraldehyde at room temperature left for 10 days without any curing results. The curing process felt for ratios ($V_{PDMS:}$ $V_{Gluteraldehyde}$) (1:2), (1:3), (1:4), (1:5) and (1:5). Some curing signs started to show just with experiment of ratio (1:7).

Experiment 2 of ratio ($V_{PDMS:}$ $V_{Gluteraldehyde}$) :(1:9) cured PDMS but the resulting polymer was not clear and not flexible it bent from the 1st concaving movement. The resulted sample is shown in Figure 4.18.

Experiment 3 of ratio ($V_{PDMS:}$ $_{VGluteraldehyde}$) (1:10) gave a more consistent resulting polymer more flexible and clearer but it wasn't the level of efficiency needed for the application. The cured polymer is revealed in the Figure 4.19.

The experiment 4 with ratio ($V_{PDMS:}$ $V_{Gluteraldehyde}$): (1:11) where 1 ml of Glutaraldehyde is mixed with 11 ml of PDMS at room temperature for 36 hours was a successful experiment. The obtained cured polymer was clear and flexible. All along the curing time was reasonable. The cured polymer is also depicted in Figure 4.20.

Figure 4.17: Pictures depicting experiment 1 that failed to give the desired results for curing PDMS

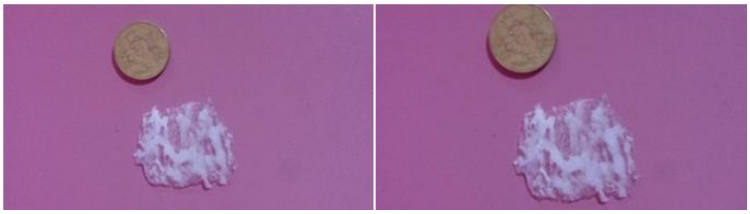


Figure 4.18: Pictures depicting the cured polymer with the experiment of ratio ($V_{PDMS:}$ $V_{Gluteraldehyde}$): (1:9)

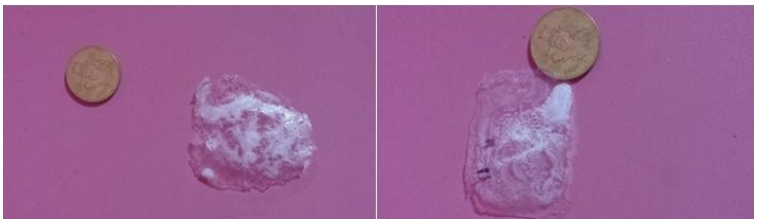


Figure 4.19: Pictures depicting the cured polymer with the experiment of (V_{PDMS}: $V_{Gluteraldehyde}$) ratio equal (1:10)

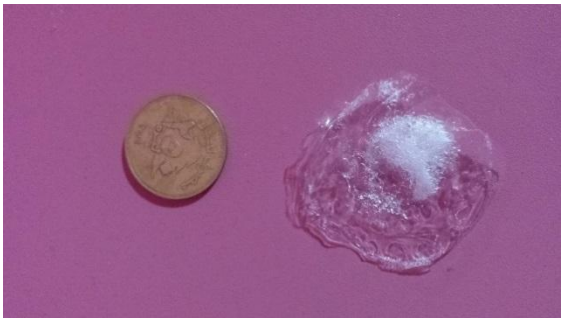


Figure 4.20: PDMS cured at room temperature for (V_{PDMS}: $V_{Gluteraldehyde}$) : (1:11) ratio application

The best experiment obtained and elected for application to complement the PMMA pores was the one with ratio (1:11) where 1 ml of PDMS is cured with 11 ml of Dichloromethane at room temperature for 36 hours. The optimal was grounded on the detail that this experiment produced a reasonable clear flexible polymer corresponding for an application. Bubbles within the polymer were eliminated through whisking for 20 min the polymer and curing agent once mixed.

4.2.2 PDMS Curing Experiment Efficiency Evaluation

4.2.2.1 PDMS Transparency Test Analysis and Evaluation

For experiment agreed at where ratio (V_{PDMS}: $V_{Gluteraldehyde}$) applied is (1:11), the results gotten after transparency test were depicted in the graph below. The results of the transmission % of light in terms of incident light are shown in the following graph.

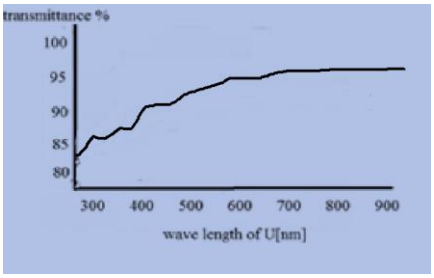


Figure 4.21: The transmission percentage of the cured PDMS upon an emitted UV wave length 680 nm

The graph strained upward clearly highlights the resulting efficiency for light transmission to be about 93% efficiently transparent cured polymer. The results of the transmission % of light in terms of incident light are satisfactory.

4.2.2.2 Mechanical Performance of PDMS Cured Polymers

The 40 sets of 20 concaving bending followed by other 20 conveying movements of PDMS cured monitored by elongation measurements gave the following results. The obtained results made throughout numerical analysis were 79 % with no cracking which is somehow a satisfying result.

Based on the efficiency test results; the judgment to apply the selected experiment with ratio (V_{PDMS}: $V_{Gluteraldehyde}$): (1:11) for curing PDMS is going to be applied on the top of the PMMA cured porous polymer.

4.2.3 Development of Porous PSMS by Application of Selected Experiment

In this fragment of the research PDMS and Gluteraldehyde were mixed based on the ratio (V_{PDMS}: $V_{Gluteraldehyde}$):(1:11) where 2 ml of PDMS were cured with 22 ml of the curing reagent and whisked for 25 minutes. Just after the start of air bubbles evaporation the porous PMMA was dropped on the mixture experiment and left for 36 hours at room temperature. Once cured the two polymers were peeled out from each other. The taken off PDMS has the same texture as the silicon sample.

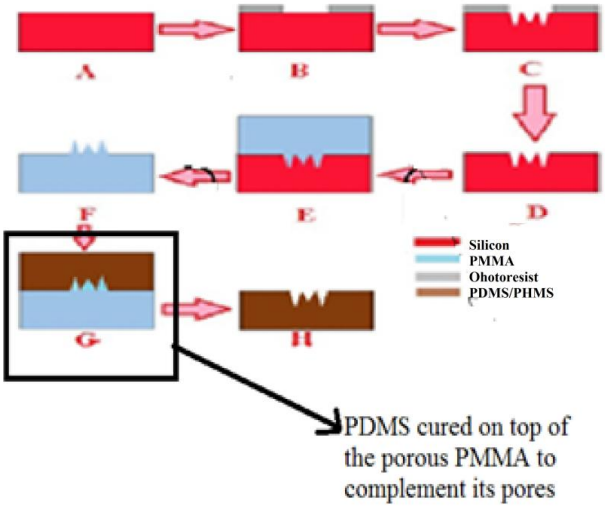


Figure 4.22: An illustration clarifying the step of generating porous PDMS step on the generic experiment diagram

CHAPTER 5
RESULTS AND DISCUSSION

This chapter will present the development of porous PMMA complementing silicon template and porous PDMS complementing PMMA while being cured with the experimental parameters settled in chapter four. The resulting polymers sample will be shown through pictures and compared to top of pen or a coin to show their true scale. The microstructure assessment of porous PMMA and PDMS will be presented. At the end a comparison between typical porous polymer fabrication method and the proposed technique applied in the thesis will be highlighted.

5.1 Development of Porous PMMA

As mentioned in chapter four the selected experiment parameters are the one applied in experiment five. The silicon template chip was covered with 25 mg of PMMA and then dropped into a beaker containing 75 ml of Dichloromethane. This mixture was whisked vigorously with a spatula for almost 4 minutes till the dichloromethane was uniformly distributed throughout PMMA powder. The uniformed mixture was inserted in the oven prepared and settled at 126° C. This step may be illustrated as stage E from the diagram of the proposed generic recipe. The mixture was left for 2 minutes in the oven before being removed and left for cooling.

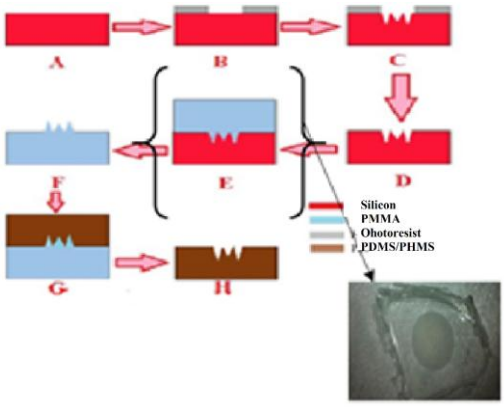


Figure 5.1: Illustration clarifying the resulting porous PMMA on the generic experiment diagram

After cooling the PMMA sample is peeled off the silicon scaffold. This step is stage F of the diagram of the proposed recipe. The developed porous PMMA is shown in figure 5.2. This sample will be compared to the top of a pen in order to show and approximate its true scale.

Figure 5.2: An illustration depicting the porous polymer PMMA

Figure 5.3: Picture showing the true scale of porous PMMA compared to a pen

Compared to a pen the true scale of the resulting polymer can be averaged to be $A = \pi r^2$. Where r is 1.8 cm and A= $\pi(1.8)^2 \cong 10.2$ cm^2.

5.1.1 PMMA Morphology and Microstructure Properties Analysis

After peeling the PMMA from the top of the silicon, cooling and undergoing treatment with copper; the sample were examined via SEM where the pores were assessed. The pictures were registered under different dimensions. Where figure 5.4 depicts the pores of the PMMA sample at the scale of 5µm, magnification of 6KV, an acceleration of 20KV and a working distance (WD) sets at 25,2mm. Figure 5.6 shows other images taken at different angels to show the aspects of the pores was achieved throughout increasing the scale up to 10µm and dropping the magnification to 3KV. The last registered image 5.7 was obtained by enlarging the scale up to 50µm for extra details and decrementing the magnification up to 1KV. Other sets of pictures were also taken from different angle to show different parts of the porous site of PMMA sample.

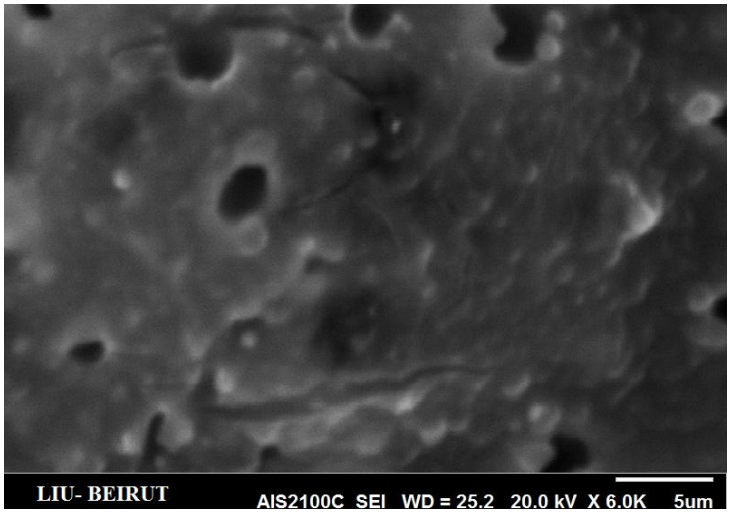


Figure 5.4: Picture taken by the SEM for porous PMMA

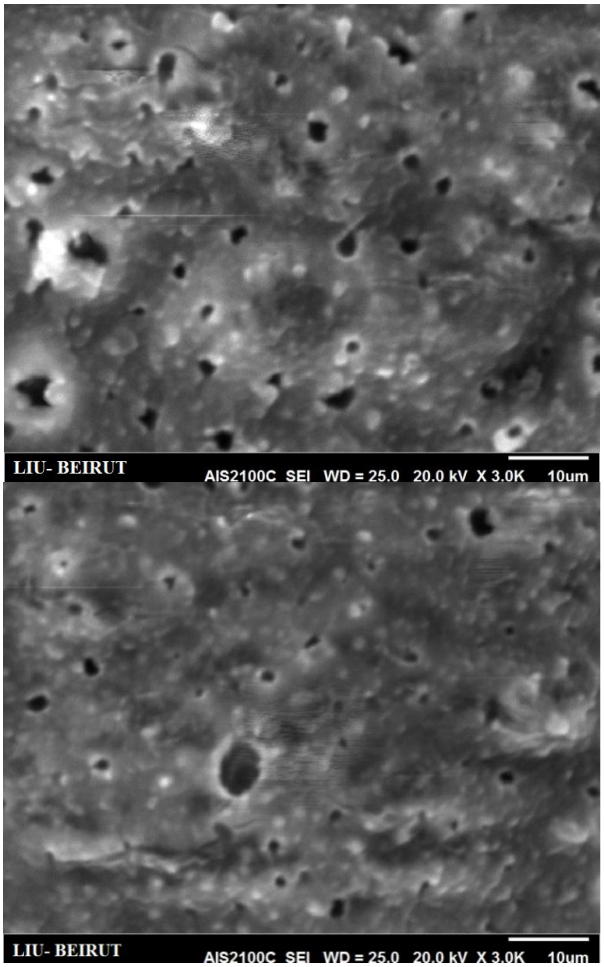


Figure 5.5: Picture taken by the SEM for porous PMMA from different angles

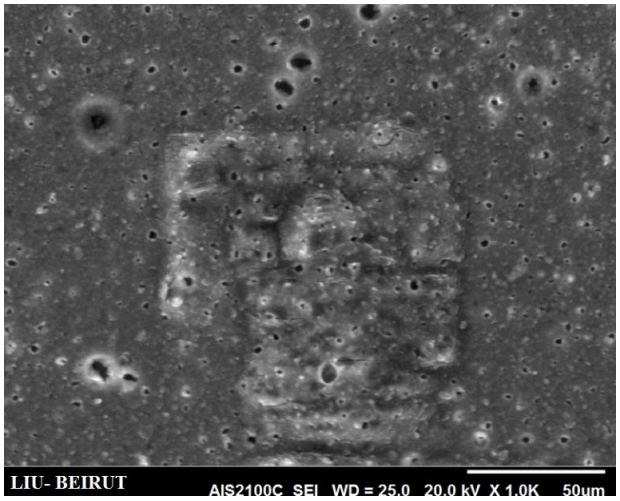


Figure 5.6: SEM image of porous PMMA at 50µm

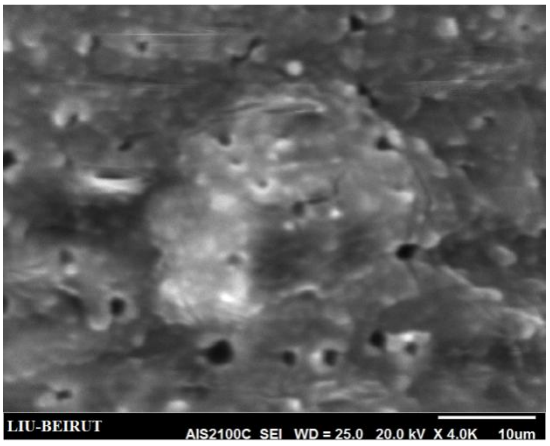


Figure 5.7: SEM image of porous PMMA at 10µm

The size of the pores showed in the Figure 3.21 ranges among nm and 2,5µm which is analogous with the size of the pores of the silicon chip that it was intended to complement it. All along; in the Figure 3.22 the distance measured amongst the pores of PMMA was 2,5µm over and above 20,8µm that is again approving the morphology of silicon pores. In the after scanned presented image, the pores were not arranged in a coordinated manner and not uniform; they were pores of diverse size guaranteeing again that these pores are the complement of the silicon template.

5.2 Development of Porous PDMS

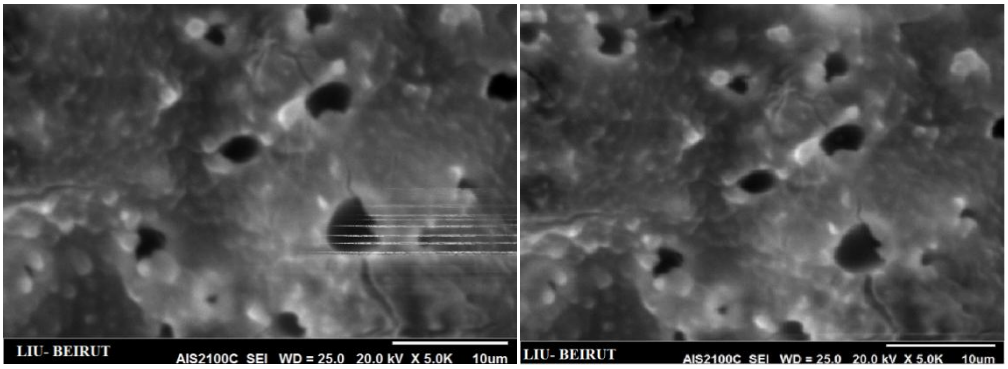
In this part of the research PDMS and Gluteraldehyde were mixed based on the ratio (V_{PDMS}: $V_{Gluteraldehyde}$) that is (1:11) where 2 ml of PDMS were cured with 22 ml of the curing reagent and whisked for 25 minutes. Just after air bubbles starts evaporation the porous PMMA developed earlier was dropped on the mixture experiment and left for 36 hours at room temperature. This is considered to be stage G on the diagram of the generic recipe. Once cured the two polymers were peeled out from each other. The taken off PDMS has the same texture as the silicon sample. A picture of the developed PDMS sample after being peeled from the surface of porous PMMA is shown in figure 4.8.

Figure 5.8: On the left the mold PMMA, on the right the completing porous cured PDMS similar to silicon

Figure 5.9: PDMS sample size compared with the top of the pen

5.2.1 PDMS Morphology and Microstructure Properties Analysis

After detaching the PDMS from the top of the PMMA after 3 days, the sample was treated with copper. Then, the sample's pores were inspected by means of SEM. The PDMS porosity was measured at the same scale 10µm but with different magnifications value; one is set at 5kV, one at 3kV and one at 20kV. The pores sizes altered between few nm all along to 2µm. The remarkable point to be taken into consideration is that the sample under study has the same texture as well as the porosity of that of the silicon sample. The below figures show a non-uniform and non-coordinated repartition of the pores morphology that again the case of the silicon chip.



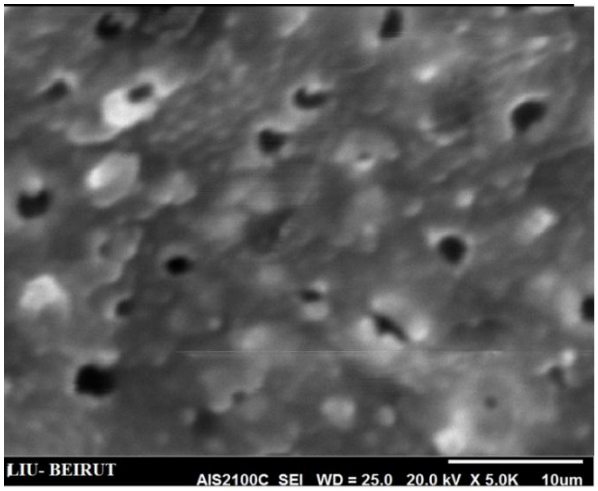


Figure 5.10: PDMS SEM images at 5 KV

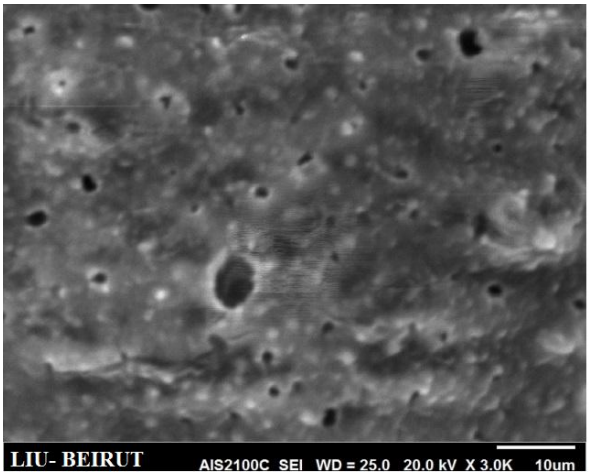


Figure 5.11: PDMS SEM images at 3 KV

5.3 Novelty of the Generic Recipe: Results of Comparison with Typical Applied Porous Polymer Fabrication

Previous curing official process for PMMA and PDMS polymers supplied by Sigma Aldrich were lacking existence. The experimental procedures for curing them were prepared using the Sylgard 184 Silicone Elastomer Kit that is a ready package with a clear instruction for curing parameters. In this research we were able to develop the curing parameters for both polymers PMMA and PDMS that may be applied for polymers obtained from any supplier.

The other novelty of this work was the easiness in the procedure and the accessibility to pores morphology. Previously each porous manufacturing technique use to necessitate a special manufacturing process. The old applied manufacturing were either gas foaming, phase separation including immersion precipitation, chemically and thermally induced phase separation, small liquid drops templating, bio-continuous micro-emulsion templating, colloid crystal templating, templating via self-assembled structures or molecular imprinting. Each of these methods necessitates a special temperature, pressure, equipments all along to cross-linker. The costs encountered with these techniques are very high. While the proposed generic recipe coast are very low since no equipments and special machine are needed.

The process is just straight forward consisting of two micro-molding steps while other techniques necessitate many phase for developing the porous polymer.

This technique offers accessibility to the pores morphology and size which is in nano-scale.

Table 5.1: Table showing the compared factors of the generic recipe proposed and typical methods

Methods for porous polymer development / factors to be compared	Generic Recipe	Other Techniques Applied
Costs	LOW COST	HIGH COST/EXPENSIVE
Equipments	Porous Silicon chip used as a scaffold	Each one necessitates special machine and equipments
Time of manufacturing	Two to three days	Long time of manufacturing
Environment	Chemistry lab	Specially equipped laboratories
Type of polymers	Any type of polymers	Special type of polymers
Manufacturing Process	Very easy, straight forward based on two-micromolding processes	Very complicated
Pores size	Nano-scale	Depends on the method applied
Pressure factor	Not taken into consideration	An important factor that defines the porosity morphology

Pressure is another factor to be taken into consideration during the fabrication of the porous polymer. Each of the processes used for fabrication of porous polymer are conducted at a different pressure in order to obtain the required porosity. For the generic recipe, the pressure factor will be neglected; the pores within the surface of the polymer could be formed at a specific pressure. Hence, no need for complicated calculations in order to achieve a pressure to volume ratio within the surface of the structure

Previous methods intend to develop porous polymers with a porosity size and shape depends on the application and manufacturing technique. In the proposed novel generic recipe the porosity morphology depends on one factor: the porosity morphology of the porous silicon scaffold. The generic recipe is just a straight forward method composed of two micro molding steps that does not necessitate a special environment nor expensive equipments.

CHAPTER 6
CONCLUSION

6.1 Conclusion

In this thesis it was aimed to develop a method or more critically a generic recipe that can be applied to specific polymers to texture their surface with any intended porous structure. This porous structure is achieved by two processes the first one when complementing the pores of silicon chip that worked out as a template and that the final polymer will have the same identical pores. The second step is to complement the obtained polymer.

This method helps to dispense the usage of the methods widely used to develop pores structure on any polymer's surface. Another advantage is that this procedure costs are less than any of the typical applied method. Also it does not need any electrolyte or machine just the silicon template.

The curing recipes were under construction and trials, experiments done and applied proved that the best recipe for curing PMMA was the usage of 25 mg of PMMA under powder form and 7 ml of Dichloromethane at 126°C for 2 min in the oven. This recipe has resulted usage and applications.

The curing of PDMS was achieved via application of the recipe with a ratio (V_{PDMS}: $V_{Gluteraldehyde}$) (1:11) at room temperature for three days where the curing reagent was Glutaraldehyde. The resulting cured polymer was on the level of the expectations from both clearance (transparency) and flexibility characteristics. This cured polymer on top of porous PMMA resulted with a conventional porous PDMS stamped with similar pores to those of the silicon template.

The aim and intentions that enthusiast toward the thought of this procedure is that silicon when implanted into the human body may present some compatibility issue while the three mentioned polymers has been proved to be compatible. And lots of newly diverging applications in biomedical are inducing the use of PDMS.

The applied process was a simple, direct forward and flexible based on the fact that developed porous polymers may owe several pores morphology and the morphology may

be changed as the application demands. This porosity alteration may be achieved simply by changing the matrix of porous silicon chip. These samples may be used in all biomedical domains and applications related to biomedical field; from contact lenses against UV lights to polymeric uterus and many other applications that will help to improve the human life.

As a conclusion; PDMS, PMMA and PDMS are good candidates for several biomedical application and porous structure of these polymers will make an innovation in the biomedical world. This proposed generic method is very easy to be applied and very less costing compared to other applied methods.

6.2 Recommendation and Future Work

Infertility is fundamentally the inability to conceive offspring. The causes of infertility either sex refer to some DNA damage, hypothalamic-pituitary factors, environmental factors, and other general factors such as diabetes mellitus, thyroid disorders, and adrenal disease. In vitro fertilization (López-Saucedo et al., 2014) provides a solution for the formation of a zygote where an egg is fertilized by sperm outside of the body. Microporous polymers will serve as a substrate for in vitro fertilization providing a large surface for multiple trials due to the large number of pores within the polymer surface.

Each microporous polymer will reflect a culture medium that consists of carbohydrates, macromolecules, amino acids, vitamins, and antibiotics. The sperm and the ovum may be placed selectively in the same pore. Upon fertilization the early embryos (zygote) have a simple physiology and maintain low levels of oxidative metabolism. Amino acids are important regulators of mammalian pre-implantation development. Carboxylic acids and amino acids are used as energy sources prior to the embryonic genome. Moreover, macromolecules like proteins maintain the stability of the cell membrane while vitamins play a role as antioxidants. The pores within the polymer are regularly supplemented with antibiotics to prevent bacterial contamination. The osmotic pressure of the medium should resemble the osmotic pressure of the oviduct fluid. Similarly, the PH must be between 7.2 and 7.4. Under these conditions, the zygote will then be transferred to the mother’s uterus (Lebrun, Camargo, and Correa, 1988).

Other application may be the polymeric uterus. Female infertility problems that a good number of woman face every single year around the world, is frequently associated with complications occurring in the ovaries, fallopian tubes all along with uterus. Once fertilization takes place and zygote develops; the latter will be pushed along the Fallopian tube up until attaining the uterine lining where it will find a place in the uterine wall to implant itself. This place will stands as nourishment place throughout the whole period of pregnancy. In case of any problems falling in this uterus section due to any factor associated to the uterine tissue, the pregnancy will be threatened. The developed recipe of porous polymer will solve the problem where it's going to be used a nourishment source for the damaged cellular parts of the uterus.

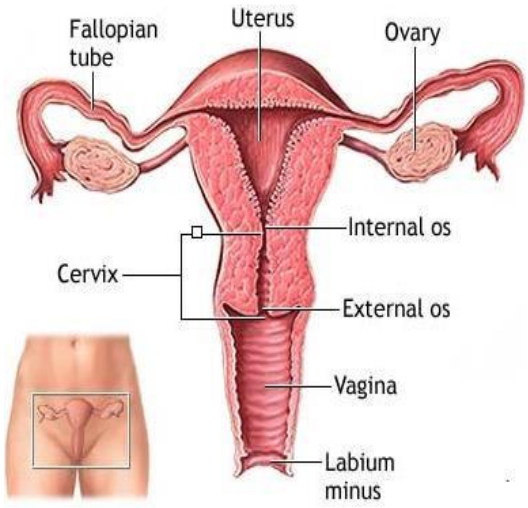


Figure 6.1: Anatomical representation of the uterus (Elias, Markovits, Reshef, van der Zee, and Cohen, 1990)

Subsequent to any accident at the cellular level, a sample of the uterus may be prepared by means of the liquid polymers; an entire polymeric uterus surface may be fabricated duplicating the normal female uterus throughout the application of the generic recipe developed throughout this work. Applying the upper steps of the previous general recipe synchronically, the first step considers curing the liquid polymer over a biopsy of the patient uterus treated in a specific container respecting all hygiene, purity, temperature among other factors confirming the expanse of the natural human uterus. Once cured, the

polymeric surface will be peeled off gently to form the uterus complementing template. This latter sample will be complemented in turns by curing the chosen polymer on its surface. Once cured, the obtained polymer is just a copy sample textured with the female cells porosity ready to be implanted in the mother female. Knowing that each polymer has a specific period of degradation, the choice of the implanted polymer must be very critic to exceed the ten months in the aim of covering the whole period of pregnancy.

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