ADHESION OF SILICONE HYDROGEL TO SILICATE SUBSTRATES

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By

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ABSTRACT

The challenge of demolding during the cast molding process of silicone hydrogel contact lenses can be addressed with the application of hydrophobic coatings on the surface of lens mold. In particular, the adhesion between silicone hydrogel and silicate substrates was minimized by applying silane modification on the surface of silicate substrates. Peel tests were conducted to measure the adhesive strengths between silicone hydrogel and surface modified glass substrates. Water contact angle measurement and X-ray photoelectron spectroscopy (XPS) were utilized to characterize the surface properties of silane treated glass substrates.

Silicone hydrogel was obtained by curing macromer mixture under UV for 6 minutes, with UV intensity of 95.0 mW/cm^2. The obtained silicone hydrogel had a modulus of 0.87±0.09 MPa, within the same range of commercial contact lenses. And the hydrogel with a UV curing time of 6 minutes was unable to be peeled off from clean glass substrates. The effects of silane type and concentration on coating effectiveness were investigated and the most effective types of silane were found to be triethoxyphenylsilane (TEPhS) and octyltriethoxysilane (OTES), with an optimal concentration of 5 wt%. The peel strength between silicone hydrogel and silicate substrates was reduced to below 15.5 N/m with the application of TEPhS and OTES coatings. However, these silane coatings were not durable enough. Silane coupling agents need to be reapplied before each curing process of silicone hydrogel.

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To mom and dad, thank you for letting me be the person I am today. I can never tell you enough how much I love you and how proud I am to be your daughter. Mom and dad, I love you and always will!

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

ATMS	Allyltrimethoxysilane
BTMS	Isobutyl(trimethoxy)silane
CE-PDMS	Chain-Extended polydimethylsiloxane vinylic macromer
CTAB	Cetrimonium bromide
DC 1173	2-Hydroxy-2-methylpropiophenone
DCDMS	Dichlorodimethylsilane
DMA	N,N-Dimethylacetamide
DMCOS	Chloro(dimethyl)octylsilane
EGDMA	Ethylene glycol methacrylate
FAS	1H,1H,2H,2H-Perfluorodecyltrimethoxysilane
FTES	1H,1H,2H,2H-Perfluorooctyltriethoxysilane
GLYEO	3-Glycidoxypropyl triethoxysilane
HDTMS	Hexadecyltrimethoxysilane
HEMA	Hydroxyethyl methacrylate
LBL	Lay-by-Layer
MMA	Methacrylic acid
OTES	Octyltriethoxysilane
PMMA	Poly(methyl methacrylate)
Poly(HEMA)	Poly(2-hydroxyethyl methacrylate)
PTES	n-Propyltriethoxysilane
PTFE	Polytetrafluoroethylene
PVAm	Poly(vinyl amine)

RGPs	Rigid gas permeable contact lenses
SDS	Dodecyl sulfate
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TEOS	Tetraethylorthosilicate
TEPhS	Triethoxyphenylsilane
TMMS	Trimethoxymethylsilane
TMPTMA	Trimethylolpropane trimethacrylate
TRIS	Tris(trimethylsiloxy)silyl
TRIS-AAm	N-[Tris(trimethylsiloxy)-silylpropyl]acrylamide
UV	Ultraviolet
VP	Vinyl pyrrolidone
XPS	X-Ray photoelectron spectroscopy

Chapter 1 Introduction

Contact lenses are medical devices worn directly on the surface of the eye. As alternatives to eyeglasses for vision correction, contact lenses have many benefits over eyeglasses. They provide a wider and more stable field of view as well as less vision obstructions and distortions. Moreover, contact lenses are not affected by weather conditions and are less likely to cause eye injury, making them ideal for sports and outdoor activities. In addition to vision correction, contact lenses are applied to therapeutic usage and cosmetic purpose [1].

The concept of contact lens was first illustrated by Leonardo da Vinci in 1508. He proposed that the optics of human eye could be altered by placing the cornea directly in contact with water [2]. However, it was not until 1887 when the first contact lens was manufactured from glass [3-5]. Since then, the materials used for producing contact lenses have been improved from glass to plastic, and to silicone hydrogel [6,7].

According to the Food and Drug Administration's classification, there are two general categories of contact lenses: soft contact lenses and rigid gas permeable contact lenses (RGPs) [8]. Soft contact lenses are made of a cross linked polymeric material named hydrogel. Hydrogel is hard and brittle under dehydrated state. It absorbs water and becomes soft and gel-like when hydrated. Soft contacts are easy to adjust and comfortable to wear. Rigid gas permeable contact lenses are made of a durable plastic that allows oxygen transmission and contains little water. Compared with soft contacts, rigid gas permeable contacts provide clearer vision and higher durability, while they are less comfortable to wear and require longer adaptation period.

Silicone hydrogel contact lenses are the latest development in soft contacts. They are designed to address the challenge of extended and overnight wear. Silicone hydrogel contacts are superior to conventional hydrogel contacts in many ways, including higher oxygen permeability, increased comfort, extended wear as well as decreased risk of eye infection [7].

The most commonly applied manufacturing method for soft contacts, including silicone hydrogel contacts, is cast molding process [9-11]. In this process, liquid macromer mixture is injected into the hollow cavity formed by two parts of mold and polymerized into solid hydrogel, which is then released from the mold. Nevertheless, some of the contact lens material is still attached to the mold making it difficult to separate two mold halves, which results in damage to contact lenses as well as reduced efficiency and increased cost in the long run.

To address the challenge of demolding, both mechanical and chemical methods are utilized. In particular, the basic idea of chemical approach is to apply a hydrophobic coating on the surface of silicate mold. A typical example is to modify the surface of silicate mold with silane coupling agents. The hydrolyzable alkoxy groups of silane are able to covalently bond with the hydroxyl groups at the surface of silicate substrate, and the organic side chain of silane alters the surface properties of treated substrate [12]. Thus, the wetting properties of silicate mold surface can be easily adjusted by varying the type of silane. And the adhesion between silicone hydrogel and silicate substrates is minimized in this way.

Chapter 2 Literature Review

2.1 Soft Contact Lenses and Manufacturing Processes

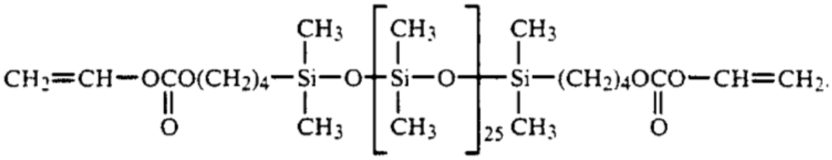
According to their compositional materials, soft contact lenses can be categorized to two types, silicone hydrogel contact lenses and conventional hydrogel contact lenses. The first commercially available soft contact lens was invented by Wichterle in 1971. It was made of poly(2-hydroxyethyl methacrylate) (poly(HEMA)) hydrogel material [3-5,13]. The introduction of poly(HEMA) hydrogel as contact lens material was highlighted to be the beginning of soft contact lenses era. Since then, a broad range of hydrogel polymers have been designed as soft contact lens materials [6].

High water content of conventional hydrogel contact lenses provides softness and good oxygen permeability, however, it could also cause or aggregate the dehydration problem of contact lenses [14-17]. During the wear of hydrogel contact lenses, the water at anterior surface of lens slowly evaporates, which breaks the equilibrium of water content in hydrogel material and leads to the water diffusion from posterior surface to anterior surface of contact lens. Dehydration of hydrogel contact lenses is unfavourable to extended and continuous wear because it cannot only affect the fitting and comfort of contact lenses, but also give rise to the dry eye problem [18]. Thus, hydrogel lens material with low dehydration rate is desired in soft contact lens design. In the work of Doughty et al. [19], the relationships between water content and dehydration of both conventional and silicone hydrogel contact lenses were investigated by *in vitro* studies. The water diffusion rate of hydrogel lens material and its water content were found to be closely proportional.

Oxygen permeability (Dk) is another key factor of contact lenses. It quantifies the ability of contact lens material to let oxygen pass through its bulk [20,21]. High oxygen permeability is desired for the comfortable and continuous wear of contact lenses. Oxygen permeability of conventional hydrogel contact lenses have been demonstrated to negatively relate to their water content [22]. Consequently, high water content of conventional hydrogel lenses leads to reduced oxygen permeability and increased dehydration rate, which are detrimental to contact lens continuous wear.

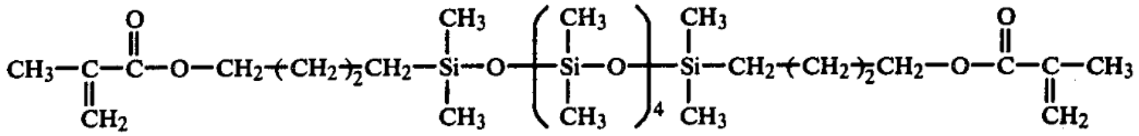
To address the challenge of overnight and extended wear, silicone hydrogel contact lenses with high oxygen permeability were introduced. A significant advantage of silicone is that it allows higher oxygen transmission than water. With the application of silicone hydrogel as contact lens material, the oxygen permeability of lens is no longer restricted by its water content, making the extended wear of contact lens possible.

Silicone hydrogel formulation is prepared with at least one silicone containing monomer, examples of which are as follows [23-25]:



$$CH_2{=}CH{-}O\underset{\underset{O}{\|}}{C}O(CH_2)_4{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\left[\underset{CH_3}{\overset{CH_3}{Si}}{-}O\right]_{25}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}(CH_2)_4O\underset{\underset{O}{\|}}{C}O{-}CH{=}CH_2$$

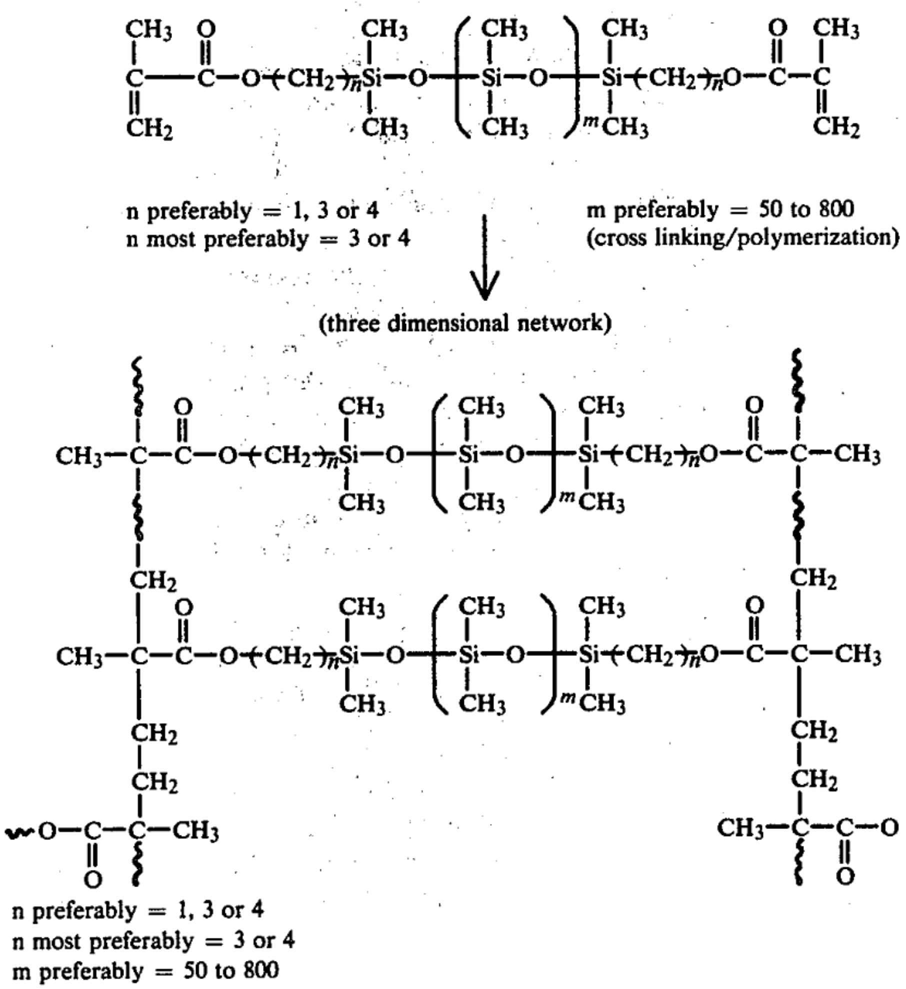
(I)



$CH_3-C(=CH_2)-C(=O)-O-CH_2(CH_2)_2CH_2-Si(CH_3)_2-O-[Si(CH_3)_2-O]_4-Si(CH_3)_2-CH_2(CH_2)_2CH_2-O-C(=O)-C(=CH_2)-CH_3$

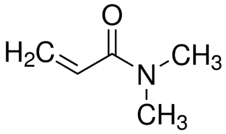
(II)

Three dimensional silicone hydrogel is obtained by the polymerization of silicone containing monomers [26]:



(III)

With the aim of improving wettability and on-eye movement of contact lenses, hydrophilic co-monomers such as N,N-dimethylacrylamide (DMA) are incorporated. The water content in contact lenses becomes adjustable with the addition of hydrophilic co-monomers, leading to the increase of comfort and performance of contact lenses. Structure of DMA is as follows:



(IV)

In addition to silicone containing macromer, hydrophobic co-monomers are introduced into the polymer system to enhance the mechanical properties and to lower the cost by partially replacing the expansive polysiloxane macromer. Monomers with tris(trimethylsiloxy)silyl (TRIS) group are commonly used as hydrophobic co-monomers, structure of which is as follows:

$$CH_2{=}C(CH_3)\text{-}C(O)\text{-}Z\text{-}X''\text{-}Si[OSi(CH_3)_3]_3 \qquad \text{(V)}$$

wherein, X” is alkylene linking group;

Z is N, O or S.

Composition of a representative silicone hydrogel formulation is as follows [27]: 32 wt% chain-extended polydimethylsiloxane vinylic macromer (CE-PDMS), 21 wt% N-[tris(trimethylsiloxy)-silylpropyl]acrylamide (TRIS-AAm), 23 wt% N,N-dimethylacetamide (DMA), 1 wt% 2-hydroxy-2-methylpropiophenone (DC 1173), and 23 wt% 1-propanol. This formulation is prepared by dissolving silicone-containing macromer CE-

PDMS, hydrophilic co-monomer DMA, hydrophobic co-monomer Tris-AAm and photo-initiator DC 1173 in 1-propanol solvent sequentially.

Soft contact lenses are mainly manufactured by three methods, spin casting, lathe cutting and cast molding. In spin casting process, liquid macromer mixture is injected into the mold, then the centrifugal force is utilized to form the inside curve of lens, while the outside curve is shaped by the curvature of mold. Ultraviolet (UV) light is applied to cure the lens. After polymerization, lens is polished to achieve the surface smoothness (**Figure 2.1.1**) [28-30].

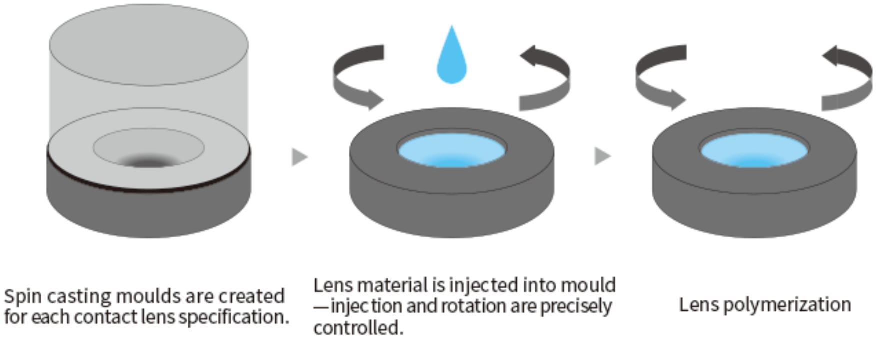


Figure 2.1.1 Soft contact lens spin casting process [31].

Lathe cutting is a method used for manufacturing both soft contact lenses and rigid gas permeable contact lenses. In this process, solid lens material is put on a rotating mount, and the lens is shaped with a cutting tool controlled by computer. Soft contact lens product is obtained after polishing and hydrating processes (**Figure 2.1.2**) [32-34]. Spin casting and lathe cutting provide enhanced comfort and precision of contact lenses, nevertheless, the high requirements for time, technology and resources restrict these methods from large-scale manufacture.

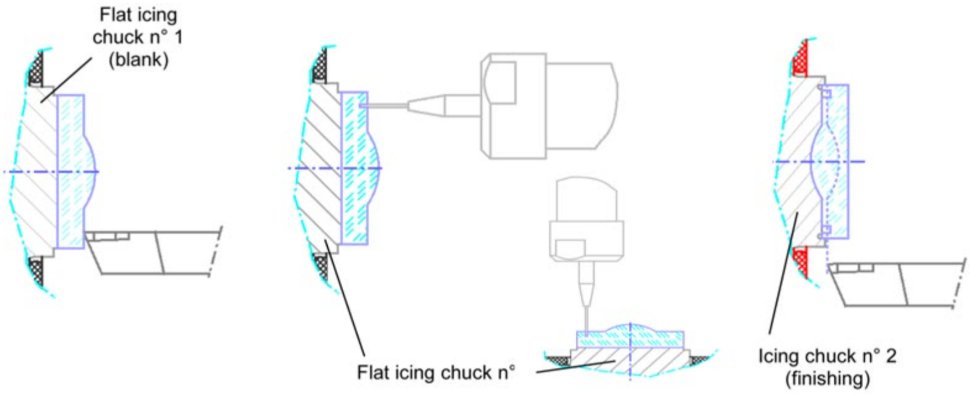


Figure 2.1.2 Soft contact lens lathe cutting process [35].

Cast molding is the most cost-efficient method to produce soft contact lenses in large quantities. The mold for soft contact lens cast molding process consists of two sections, a female mold half and a male mold half (**Figure 2.1.3**). In the cast molding process, liquid macromer mixture is injected into the cavity formed by two mold halves. UV light is applied to solidify the lens material. After polymerization, contact lens is released from the mold (**Figure 2.1.4**). Polypropylene, polystyrene and thermoplastic polyolefin resin are commonly used mold materials for cast molding process [36-38]. However, there are deficiencies of theses materials, including poor processibility and surface distortions during the cast molding process. To overcome these deficiencies, U.S. Pat. 8480227 disclosed a mold composed of a quartz female mold half and a glass male mold half [27]. This mold design improved the efficiency of polymerization by applying quartz as female mold half. Since quartz does not absorb UV radiation, UV is able to go thorough quartz female mold without any loss.

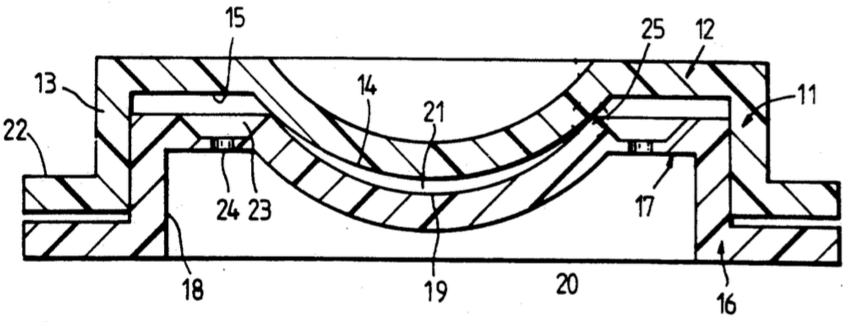


Figure 2.1.3 Mold for soft contact lens cast molding process [39].

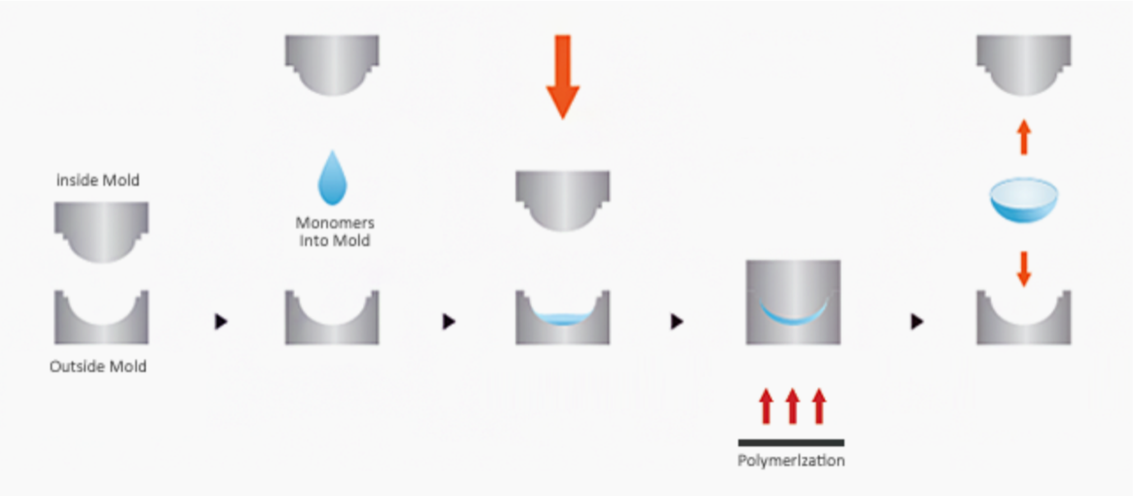


Figure 2.1.4 Soft contact lens cast molding process [40].

Quartz and glass are silicate substrates. Quartz is pure, crystalline silicon dioxide or silica, while glass is impure, amorphous compound containing silica. Surface of clean silicate substrate is hydrophilic, chemical structure of which is shown in **Figure 2.1.5**.

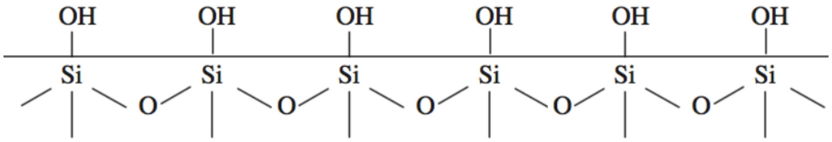
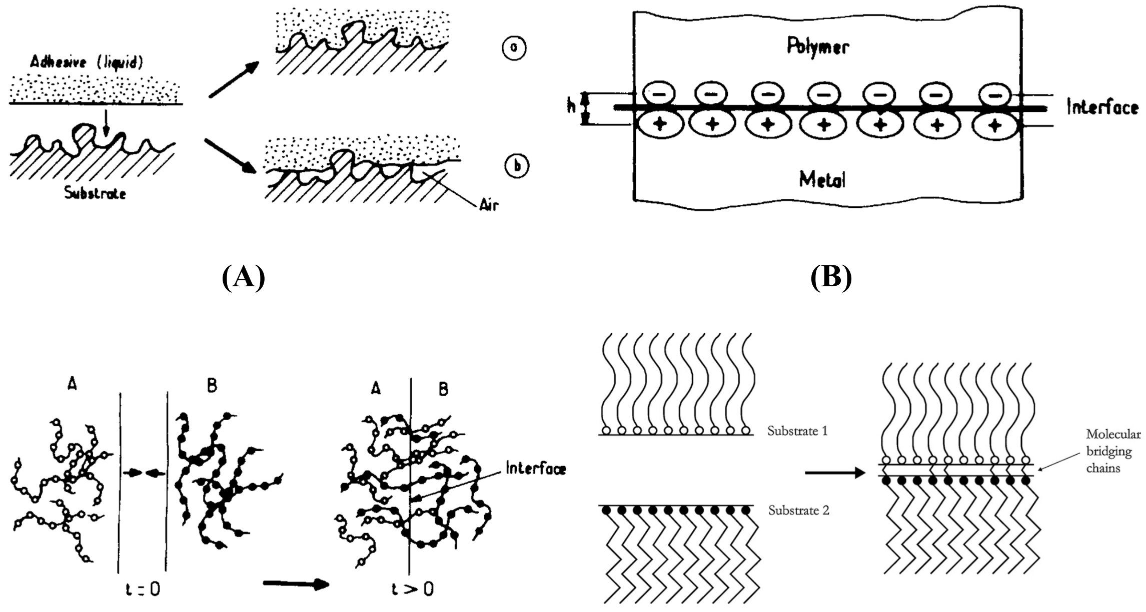


Figure 2.1.5 Chemical structure of silicate substrate.

2.2 Adhesion Mechanisms of Silicone Hydrogel

Adhesion is the tendency of two dissimilar surfaces to cling to one another, in contrast, cohesion refers to the intermolecular forces that hold the same substance together [41]. The interaction between hydrogel lens material and mold substrate is adhesion.

There are four main mechanisms of adhesion: mechanical interlocking, electronic theory, diffusion theory and adsorption theory [42-45]. Each theory has its applying circumstance and limitation. Due to the complexity of adhesion phenomenon, actual adhesion mechanism is normally a combination of several theories with one or two in domain. Mechanical interlocking proposes that the interlocks of polymer into the irregularities of substrate are the main source of adhesion. Surface roughness of substrate is the key of this theory. Moreover, enhanced adhesion is obtained only if the polymer is in liquid state and of good wetting. Electronic theory states that the formation of an electrical double layer at the polymer/metal interface has a contribution to the adhesion. While in diffusion theory, molecular diffusion across the polymer interface is believed to be the main reason of adhesion. Compatibility of polymers and sufficient mobility of polymer chain segments are the fundamental requirements of diffusion theory. Adsorption theory is the closest model of the adhesion between silicone hydrogel and glass substrate. It is also the most broadly applicable mechanism of adhesion. According to adsorption theory, adhesion is the result of secondary bonds, such as Van der Waals forces and hydrogen bonds, at polymer/substrate interface, with the condition that polymer and substrate are in intimate contact (**Figure 2.2.1**).



(A) **(B)**

(C) **(D)**

Figure 2.2.1 Mechanisms of adhesion: (A) mechanical interlocking; (B) electronic theory; (C) diffusion theory; and (D) adsorption theory [44,45].

As described in Section 2.1, the most commonly applied manufacturing method for silicone hydrogel contacts, is cast molding process. In this process, liquid macromer mixture is injected into the hollow cavity formed by two mold halves and polymerized into solid hydrogel, which is then removed from the mold. However, a particular problem during cast molding process is that liquid macromer mixture is supplied in excess. As placing the mold halves together, the overfilled macromer mixture is expelled from the mold cavity and rests between the flanges of mold halves. After polymerization process, this excess macromer mixture forms an annular ring around the cured contact lens, which resists the separation of two mold halves [53,56-69]. Adhesion of excess cured lens material to the flanges of mold halves could be explained by adsorption theory. Expelled liquid monomers completely fill the space in between the flanges of two mold halves, allowing intimate contact of lens material to the flanges. Consequently, the excess solid lens material is able to adhere to the surfaces of the mold flanges by secondary bonds, such as Van der Waals forces.

A typical silicone hydrogel contact lens is polymerized from siloxane macromer PDMS, hydrophilic co-monomer DMA, and hydrophobic co-monomer TRIS-AAm [27]. PDMS forms the fundamental structure of three-dimensional network and is the key to silicone hydrogel behaviours. The incorporation of hydrophilic component DMA is to adjust the water content and to improve the comfort of contact lens. TRIS-AAm is added with the aim of enhancing mechanical properties and lowering the cost. To understand the role of siloxane-containing macromer PDMS in adhesion, a series of work have been done.

Yoon et al. [46-50] synthesized a series of poly(imidesiloxane) copolymers with variation of dimethylsiloxane (PDMS) content from 0 to 30%, and investigated their adhesive properties to titanium and graphite composites. Lap shear tests were conducted at room temperature, samples for which were prepared by melt laminating polyimide and poly(imidesiloxane) copolymer films between the titanium adherends. Enhanced adhesive bond strengths were observed with the introduction of PDMS (**Figure 2.2.3**). The improvement of adhesive strength was found to relate to the increase of ductility and flexibility of polymers with the incorporation of siloxane.

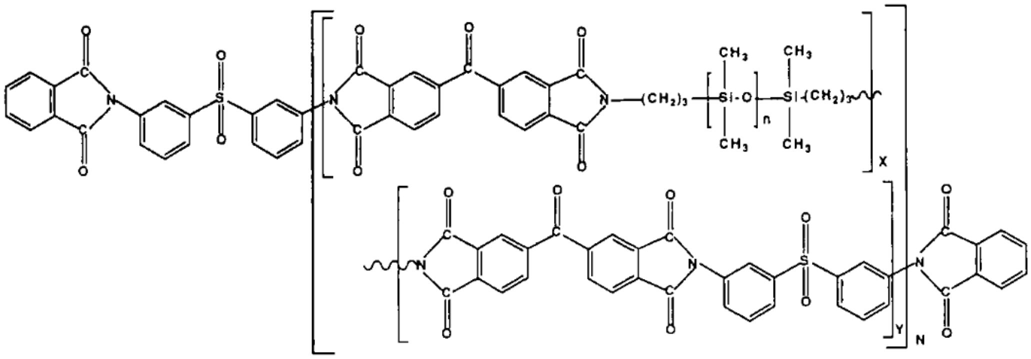


Figure 2.2.2 Chemical structure of poly(imidesiloxane) copolymers [47].

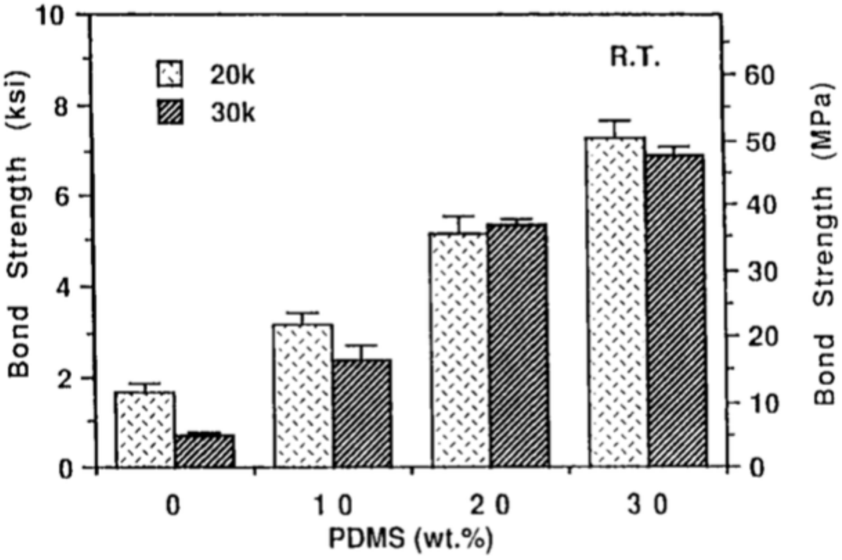


Figure 2.2.3 Adhesive bond strengths of poly(imidesiloxane) copolymers with various contents of PDMS [47].

Further studies of Novák, Igor, et al. [51]. revealed the effect of surface structure on adhesive performances of poly(imidesiloxane) copolymers. Pure polyimide, and poly(imadesiloxane) copolymers containing 10 wt%, 20 wt%, 30 wt% and 33wt% siloxane were prepared. Their surface morphology and wettability were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and contact angle measurement. The surface roughness and hydrophobicity were found to increase with the incorporation of siloxane (**Figure 2.2.4**). Adhesive properties of poly(imadesiloxane) copolymers were measured by peel tests and lap shear tests. An almost linear decrease of adhesive strengths was observed with the increase of siloxane content (**Figure 2.2.5**).

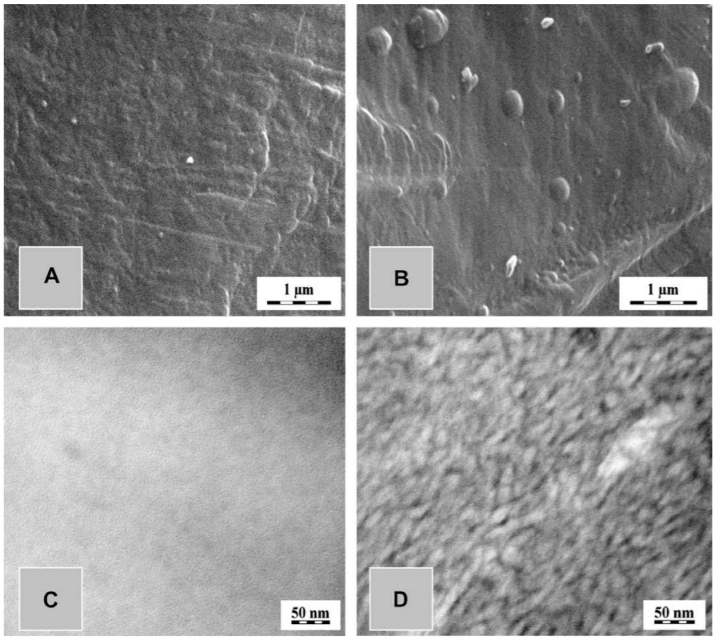


Figure 2.2.4 SEM images of (A) polyimide and (B) poly(imadesiloxane) copolymer containing 30 wt% siloxane; and TEM images of (C) polyimide and (D) poly(imadesiloxane) copolymer containing 30 wt% siloxane [51].

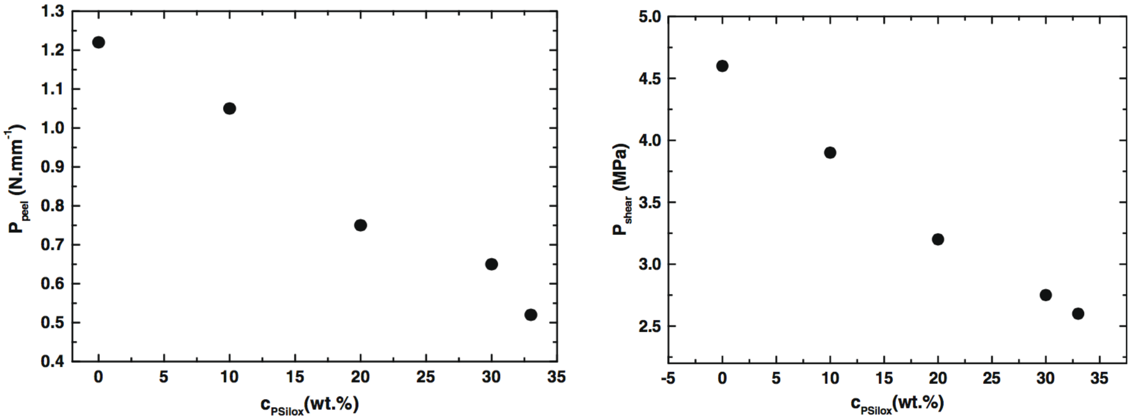


Figure 2.2.5 Peel strengths and lap shear strengths of poly(imidesiloxane) copolymers with various siloxane contents [51].

The relationship between siloxane segment length and adhesive properties of poly(imidesiloxane) copolymers was investigated by Mahoney et al. [52]. Poly(imidesiloxane) copolymers containing multiple ratios of G-1 (PDMS with segment length of 1 repeat unit) and G-9 (PDMS with segment length of 9 repeat units) were synthesized with total PDMS concentration of 10 wt%. Adhesive strengths of copolymer films to Ni/Fe alloy substrates were measured by peel tests. Among all synthesized poly(imidesiloxane) copolymers, the one containing 10 wt% G-1 showed the highest peel strength, while peel strengths of the others were equivalent. These results were consistent with the Si/N ratios measured by X-ray photoelectron spectroscopy (XPS) (**Figure 2.2.6**). The results can be explained by the distinct thickness of PDMS layer at polymer surface. Sample containing 10 wt% G-1 had a thinner layer of PDMS at surface, whereas the others containing longer siloxane segment lengths tended to segregate to the polymer surface, leading to the formation of thicker layers and higher concentrations of PDMS at surface.

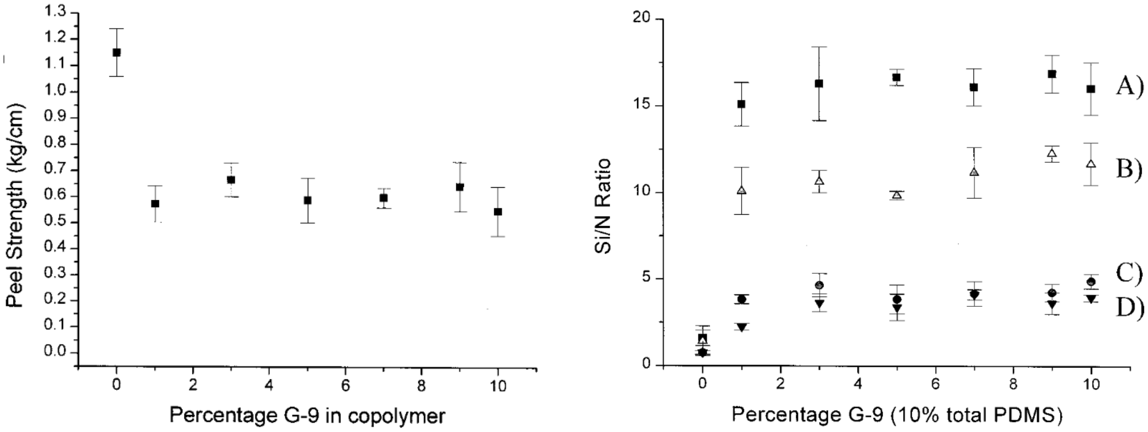


Figure 2.2.6 Peel strengths and Si/N ratios of poly(imidesiloxane) copolymers [52].

2.3 Common Approaches to Minimizing Adhesion between Contact Lens and Mold

As discussed in Section 2.1, the most commonly applied manufacturing method for soft contact lenses, including silicone hydrogel contacts, is cast molding process. Mold for this process consists of two sections, a female mold half and a male mold half (**Figure 2.1.3**). A particular problem during demolding is that liquid macromer mixture is supplied in excess. As placing the mold halves together, the overfilled macromer mixture is expelled from the mold cavity and rests between the flanges of mold halves. After polymerization process, this overfilled macromer mixture forms an annular ring around the cured contact lens, which resists the separation of two mold halves [53, 56-69]. To overcome this problem, both mechanical and chemical methods are utilized.

2.3.1 Mechanical Methods for Minimizing Adhesion

U.S. Pat. No. 5,820,895 disclosed a method for reducing the adhesion between hydrophilic soft contact lens and male mold half by heating the back curve of mold [53]. A heating probe was applied to heat the outside of male mold half, as a result, a temperature gradient was created between male mold half and contact lens through the heat transfer process. The temperature gradient caused differential extension of the contact lens surface and the surface of male mold half, leading to the decrease of interfacial adhesion. Soft contact lens formulation in this method was prepared from hydrophilic macromer (meth)acrylate ester, an alkyl (meth)acrylate co-monomer, and a cross-linking co-monomer, as described in U.S. Pat. No. 5,039,459 [54]. Polypropylene or polystyrene was used as mold material [55]. In addition to conductive heating probe, hot air stream, laser irradiation, microwave energy and ultrasonic energy were applied to achieve the temperature gradient [56-64].

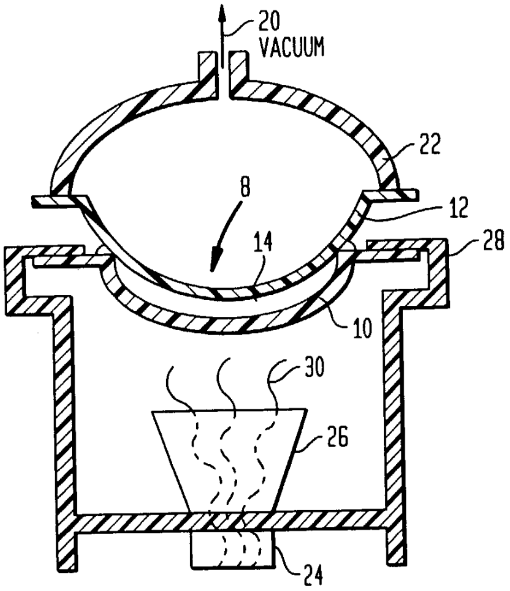
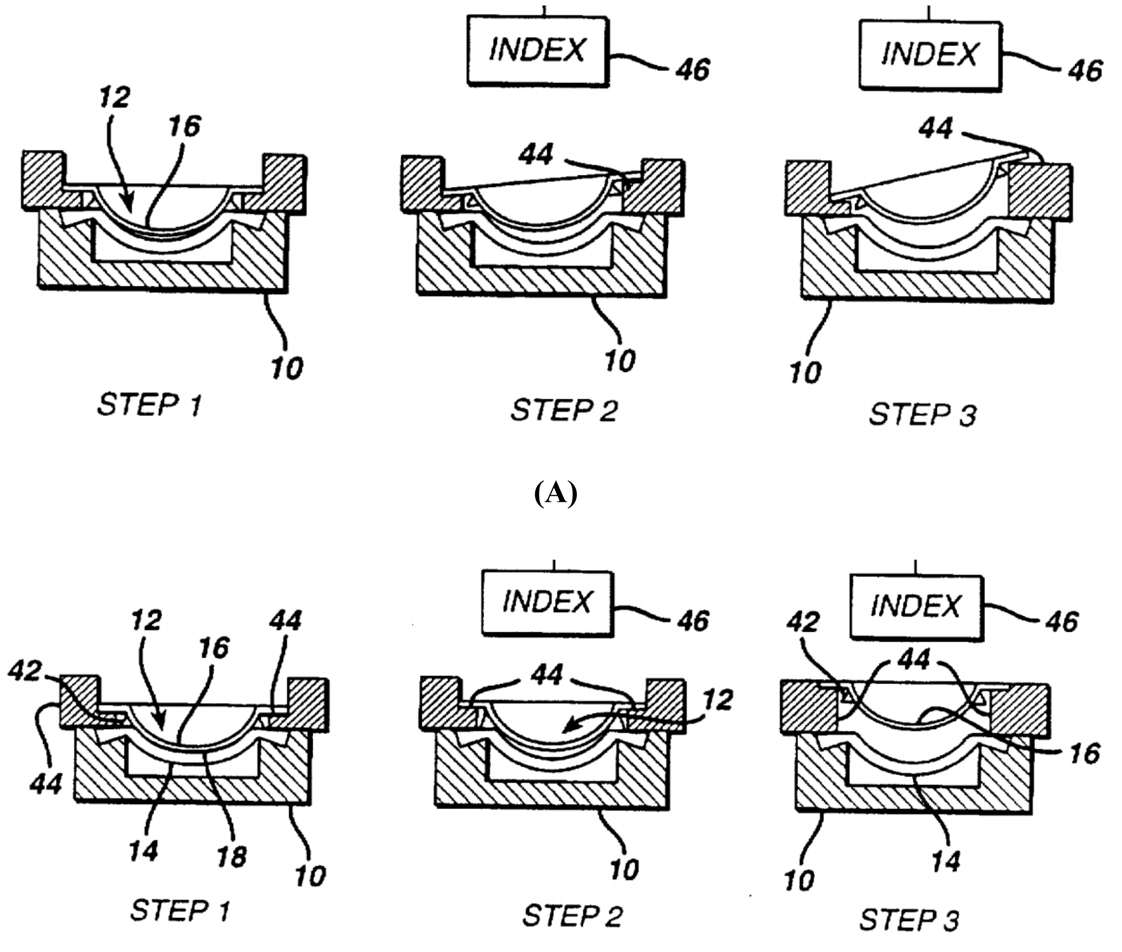


Figure 2.3.1 Process of demolding with the application of microwave energy [61].

A method utilizing mechanical leverage to address the demolding problem was revealed in U.S. Pat. No. 5,935,492 [64]. The mechanical leverage was applied to the male mold half particularly. In detail, a restraining force was put to one edge of male mold half, while a rotational force was applied to the other edge in order to vertically lift the mold half. Mold used in this method was made from polystyrene. Hydrophilic soft contact lens was prepared from poly(HEMA). A similar method was disclosed in U.S.

Pat. No. 5,693,268 [65]. In this method, at least one separating wedge was employed between the surrounding flanges of mold halves (**Figure 2.3.2**).



(A)

(B)

Figure 2.3.2 Process of demolding with the application of separating wedge on (A) one side or (B) double sides between flanges of mold halves [65].

In addition, corona treatment was applied on the surface male mold half to facilitate demolding [67,68]. Corona treatment increased the adhesion between male mold half and excess lens material, as disclosed in U.S. Pat. No. 5,326,505 [67]. In particular, corona treatment was applied on the surface of male mold half before the injection of liquid macromer mixture into the mold cavity. After polymerization process, the excess polymerized material adhered to male mold half while the cured contact lens was removed with female mold half. Hydrophilic soft contact lens was prepared from hydroxyethyl methacrylate (HEMA), methacrylic acid (MMA), ethylene glycol methacrylate (EGDMA) and trimethylolpropane trimethacrylate (TMPTMA) monomers. Mold was made from polystyrene.

Main ideas of mechanical methods for reducing adhesion between contact lens and mold are summarized in **Table 2.3.1**.

Table 2.3.1 Summary of mechanical methods for minimizing adhesion between contact lens and mold.

Method	Main Idea	References
Heating [53,56-64]	A conductive heating probe, hot air stream, laser irradiation, microwave energy, or ultrasonic energy was applied on the back curve of male mold half to cause a temperature gradient between contact lens and mold half, resulting in differential extension of contact lens surface and the surface of male mold half.	U.S. Pat. No. 5,820,895 U.S. Pat. No. 5,294,379 U.S. Pat. No. 5,417,557 U.S. Pat. No. 5,770,119 U.S. Pat. No. 5,850,107 U.S. Pat. No. 5,815,238 U.S. Pat. No. 5,648,024 U.S. Pat. No. 10/365,251 U.S. Pat. No. 10/982,232 U.S. Pat. No. 10/117,545
Mechanical leverage [53,65-67]	A mechanical leverage was applied on the male mold half to rotationally lift it from the female mold half.	U.S. Pat. No. 5,935,492 U.S. Pat. No. 5,693,268 U.S. Pat. No. 5,358,672 U.S. Pat. No. 5,820,895
Corona treatment [68,69]	Corona treatment was applied on the surface of male mold half to enhance its adhesion to excess cured lens material, facilitating the removal of contact lens with female mold half.	U.S. Pat. No. 5,326,505 U.S. Pat. No. 5,158,718

2.3.2 Chemical Methods for Minimizing Adhesion

U.S. Pat. No. 4,159,292 disclosed a method to control the removal of poly(HEMA) hydrogel contact lens from a resinous mold [70]. In particular, resinous particles such as polyamide, polyethylene, polypropylene, polymethylpentene or polycarbonate particles were selected to make the lens mold. Those particles were treated by release agents such as silicone oil, polyvinyl alcohol, steric acid, fluorocarbons or waxes. Then heat and pressure was applied to fuse the coated resinous particles into the shape of lens mold.

However, the layer formed by conventional release agents was relatively thick and uneven, which may alter the surface shape of contact lens and cause the loss of contact lens precision. To facilitate the demolding without altering the surface character of contact lens, a fluorocarbon film with thickness of 1nm was applied (**Figure 2.3.3**) [71]. The chemical adsorption of this thin film was achieved by immersing the poly(methyl methacrylate) (PMMA) mold in 1H,1H,2H,2H-perfluorodecyltriethoxysilane ($CF_3(CF_2)_7(CH_2)_2Si(OCH_3)_3$) for one hour, following ultrasonic cleaning in chloroform, acetone and water sequentially and air-drying.

Chemical compositions of release agents and mold materials are summarized in Table **2.3.2**.

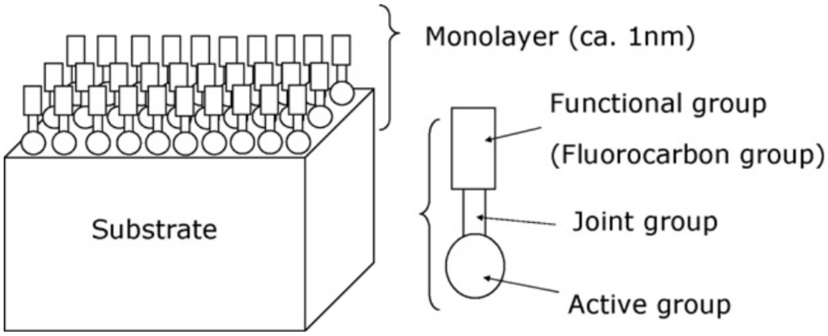


Figure 2.3.3 Chemical adsorption of fluorocarbon film on resinous lens mold [71].

Table 2.3.2 Summary of chemical methods for minimizing adhesion between contact lens and mold.

Release Agent	Mold material	Reference
Silicone oil Polyvinyl alcohol Steric acid or Fluorocarbons	Polyamide Polyethylene Polypropylene Polymethylpentene or Polycarbonate	U.S. Pat. No. 4,159,292 [70]
1H,1H,2H,2H-Perfluorodecyltriethoxysilane	Poly(methyl methacrylate) (PMMA)	Yamamoto et al. [71]
Polytetrafluoroethylene (PTFE)	Poly(methyl methacrylate) (PMMA)	Guo et al. [72]

2.4 Silane Coupling Agents and Surface Modification of Silicate Substrates

Silane coupling agents are commonly used for glass surface modification. A general structure of silane is R_{4-n}—Si—$(R'X)_n$ (n = 1, 2), where R is alkoxy group, R' is alkyl spacer, and X is organic functional group. The hydrolyzable alkoxy substituents of silane are able to covalently bond with the hydrophilic substrate, and the organic side chain alters the surface properties of treated substrate. During the hydrolysis process, the alkoxy substituents of silane are hydrolyzed and then react with the hydroxyl groups at the surface of hydrophilic substrate to form —Si—O—Si— bonds (**Figure 2.4.1**) [73,74]. Silanes are recognized as efficient surface modification agents for two reasons. First, the covalent bonds between silane and glass substrate are stable, which guarantee the durability of coating. Second, by applying silanes with various organic side chains, the treated substrates can experience wide range of surface properties, from hydrophilic to hydrophobic.

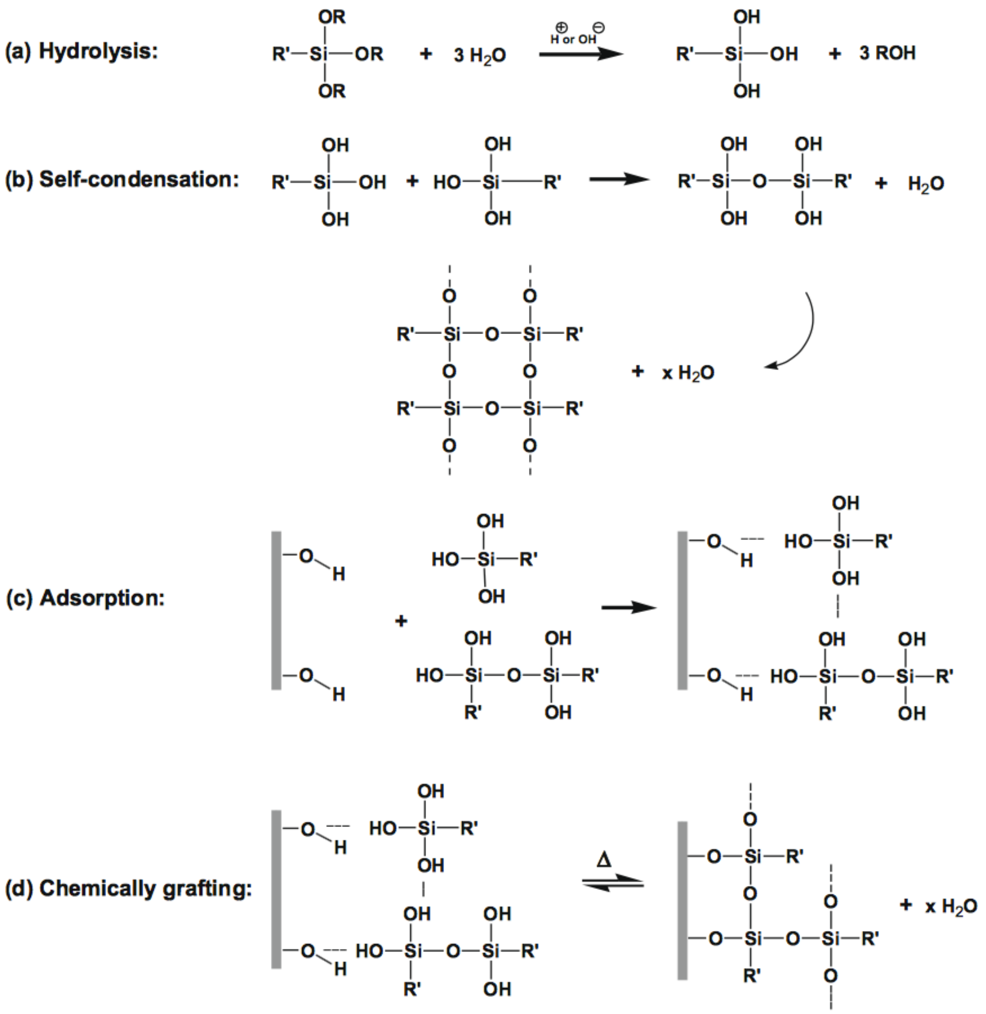


Figure 2.4.1 Interaction of silanes with silicate substrates during hydrolysis process [73].

Yoshino et al. [75] synthesized a series of silane coupling agents with variation of fluorocarbon side chain length. These silane coupling agents were used to modify the surface of glass substrates. Contact angle of water and oleic acid on glass substrate treated with $(CH_3O)_3SiCH_2CH_2(CF_2)_nCF_3$, $(CH_3O)_2Si(CH_3)CH_2CH_2(CF_2)_nCF_3$, $(CH_3O)_3SiCH_2CH_2(C_6H_4)(CF_2)_nCF_3$ and $(CH_3O)_3SiCH_2CH_2(C_6H_4)(CF_2)_nCF_3$ (n = 3, 5, 7, 9) was measured (**Figure 2.4.2**). The contact angle of treated glass substrate was found to increase with the growth of fluorocarbon side chain length. The proposed surface structure of silane treated glass was shown in **Figure 2.4.3**.

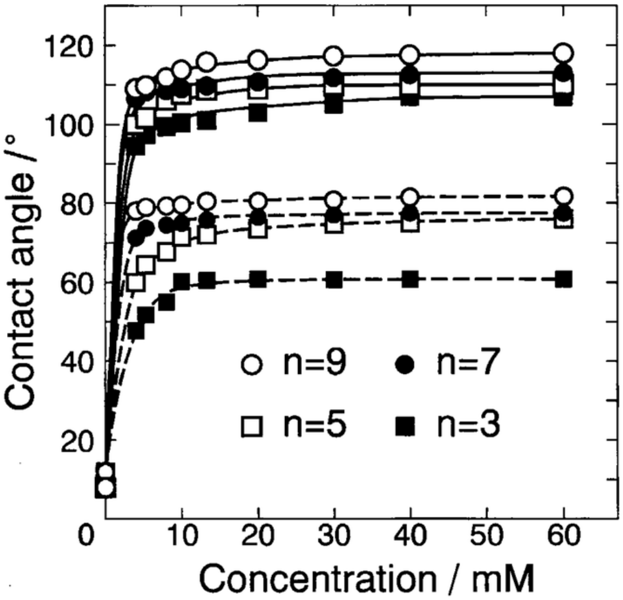


Figure 2.4.2 Contact angle of water and oleic acid on glass substrate treated with $(CH_3O)_3SiCH_2CH_2(CF_2)_nCF_3$ (n = 3, 5, 7, 9) [75].

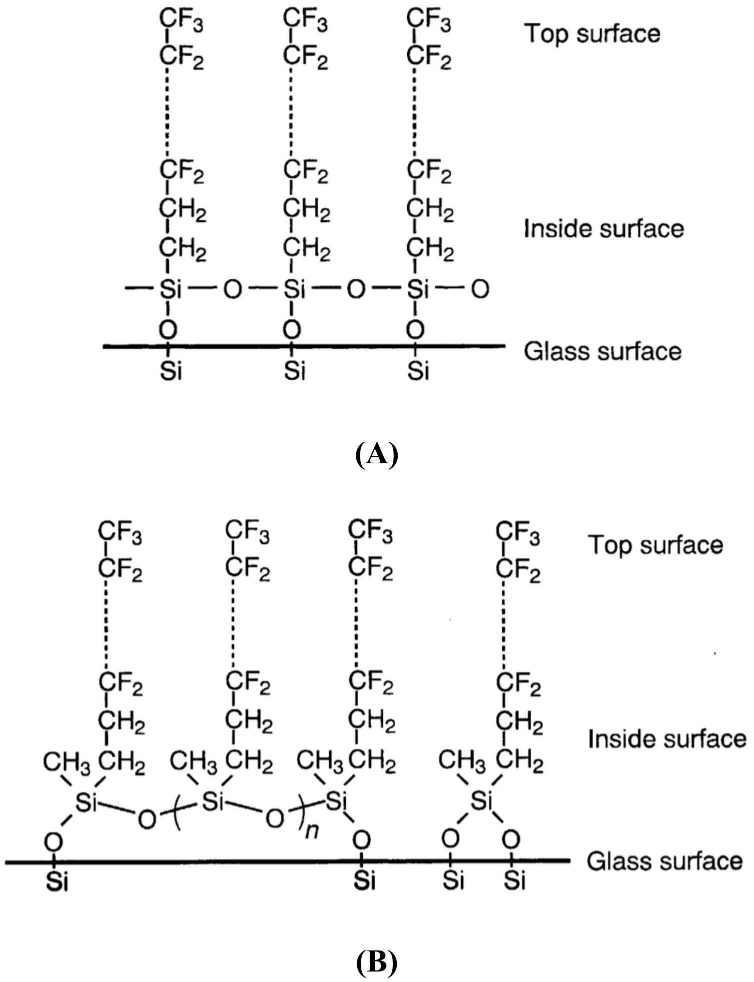
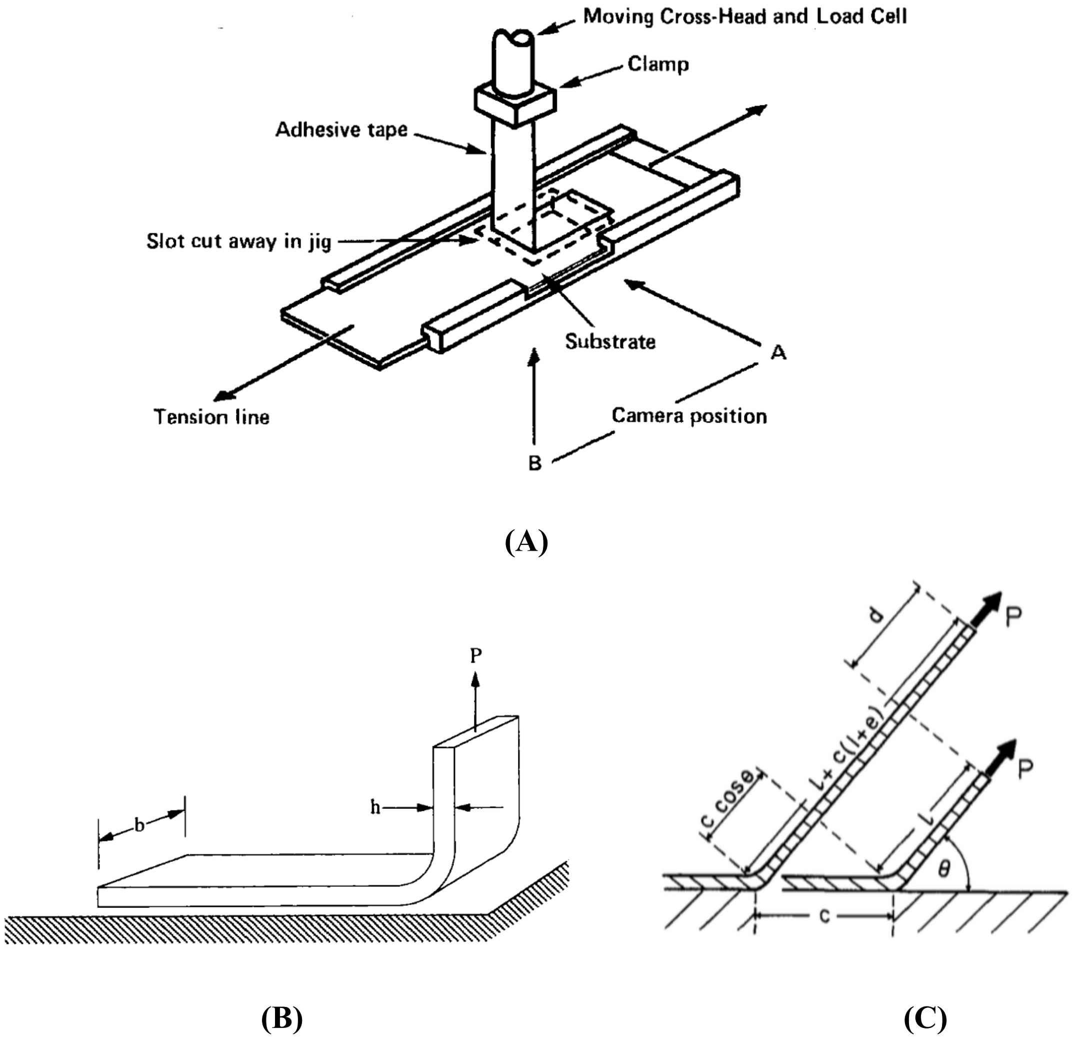


Figure 2.4.3 Schematic of glass surface modified with fluoroalkylsilanes (A) $(CH_3O)_3SiCH_2CH_2(CF_2)_nCF_3$ and (B) $(CH_3O)_2Si(CH_3)CH_2CH_2(CF_2)_nCF_3$ [75].

2.5 Peel Test

Peel test is a commonly used technique for adhesion measurement. It provides quantitative values of adhesion between adhesive and substrate. Specimen for peel test is prepared by attaching adhesive tape on a rigid substrate, and the peel force is measured as peeling the adhesive tape off the substrate (**Figure 2.5.1**).



(A)

(B) **(C)**

Figure 2.5.1 Schematic of peel test [76,80].

There are multiple parameters that affect peel force, including peel angle, peel rate, as well as mechanical properties and thickness of the adhesive tape. When the adhesive tape is inextensible in tension, and the peel angle is no less than 45˚, the relationship between peel strength P/b and peel angle θ is as follows [77-86]:

$$\frac{P}{b} = \frac{G_c}{1 - \cos\theta} \qquad \text{(VI)}$$

wherein, P is peel force;

b is width of adhesive tape;

Gc is critical adhesive energy per unit area;

and θ is peel angle.

When the adhesive tape is extensible and the peel angle is less than 45˚, an elastic term must be included, and a quadratic equation of peel strength P/b was obtained:

$$G_c = (1 - \cos\theta)\frac{P}{b} + \frac{P^2}{2b^2Eh} \qquad \text{(VII)}$$

wherein, Gc is critical adhesive energy per unit area;

θ is peel angle;

P is peel force;

b is width of adhesive tape;

E is modulus of elastic adhesive tape;

and h is thickness of the tape.

To verify the above equations, Kendall et al. [77,78] measured a series of peel strengths and peel angles with constant adhesive energy R = 5 N/m and peel rate v = 80 μm/s. The relationship between peel strength and peel angle is shown in **Figure 2.5.2**.

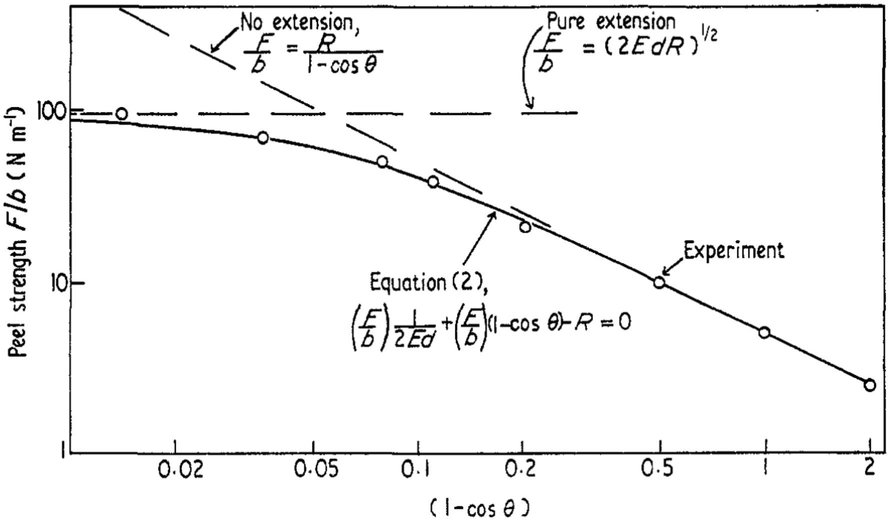


Figure 2.5.2 The relationship between peel strength and peel angle [78].

In the work of Williams et al. [86], The force of peeling 3M commercial tape from a PTFE substrate was tested with variation of peel angle. Peel tests were conducted with constant critical adhesive energy, peel rate, elastic modulus and thickness of the adhesive tape. Peel force was found to decrease with the increase of peel angle, whereas the adhesive energy showed clear increase (**Figure 2.5.3**).

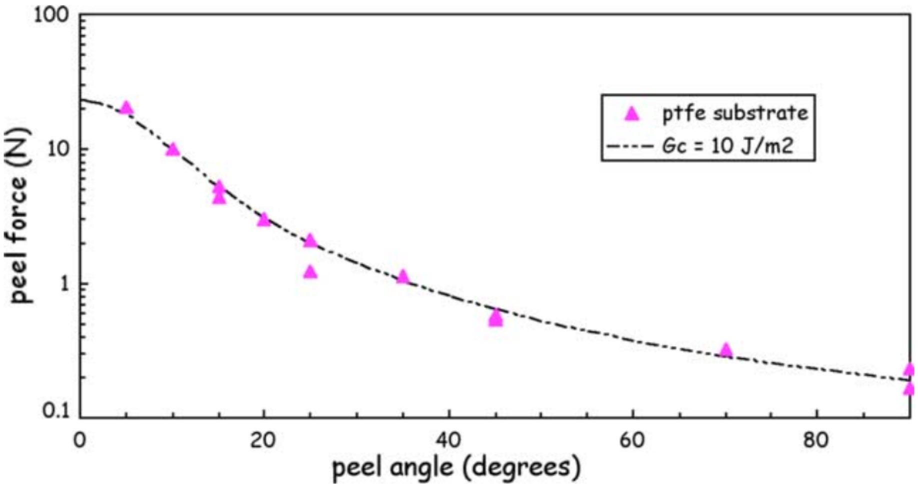


Figure 2.5.3 Effect of peel angle on peel force [86].

Peel rate and ambient temperature are parameters that influence the peel strength by altering the mechanical properties of adhesive tape. Peel tests are normally conducted under room temperature. Peel rate is given as follows:

$$v = \frac{v_{\text{ch}}}{[(1-\varepsilon_1)(1+\varepsilon_2)-\cos\theta]} \quad \text{(VIII)}$$

wherein, v is peel rate;

v_{ch} is the rate of cross head;

ε_1 is pre-strain of adhesive tape;

and ε_2 is strain of adhesive tape in the peel arm.

The relationship between peel rate and peel angle is shown in **Figure 2.5.4**.

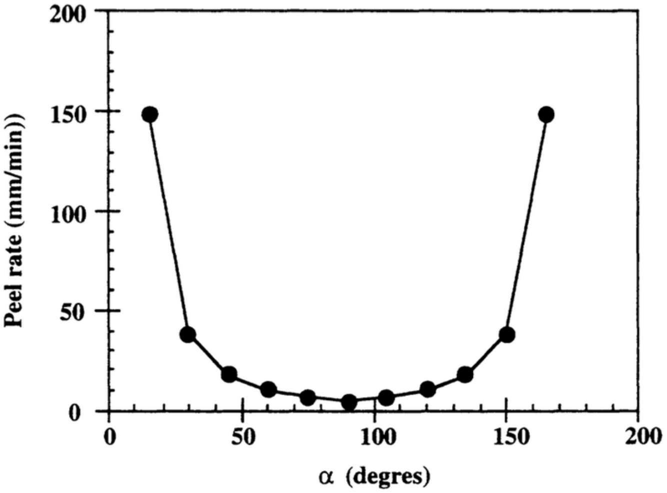


Figure 2.5.4 The relationship between peel rate and peel angle [87].

Williams et al. [86] investigated the effect of peel rate on peel force by varying the rate of cross head from 0.5 mm/min to 20 mm/min. Adhesive samples were made from aluminum, cellophane and PVC tapes, and the peel tests were conducted at room temperature. Results showed that peel rate barely affected the mechanical properties and peel forces of aluminum and cellophane tapes, while the PVC tape become slightly stiffer with the increase of peel rate, leading to a slight increase of peel force.

In the work of Gent et al. [82], poly(ethylene terephthalate) films with various thicknesses were prepared, and adhesive strengths of these films were tested by peeling them off the rubber-coated metal substrates. The relationship between peel force and tape thickness is shown in **Figure 2.5.5**. When an adhesive tape was relatively thin, the contribution of plastic yielding to peel force was negligible. When the adhesive tape was thick enough, it become too rigid to experience plastic yielding. Within certain range of tape thickness, plastic yielding had a noticeable effect on peel force, and there existed a critical point of thickness at which the plastic yielding had the greatest contribution to peel force.

Peel tests are normally combined with surface characterization methods, such as X-ray photoelectron spectroscopy (XPS), and contact angle measurement to fully investigate the properties of adhesive joints.

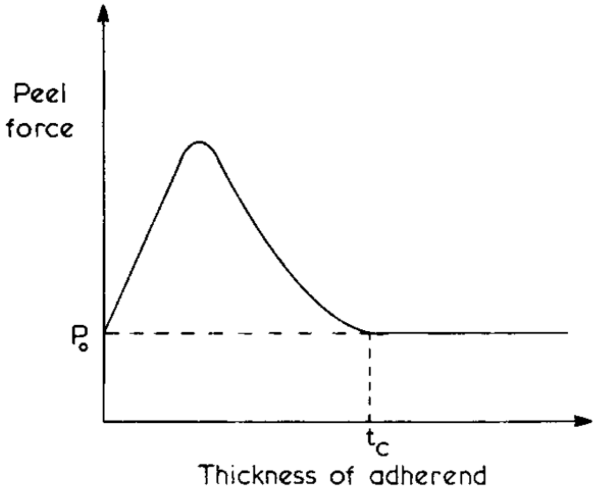


Figure 2.5.5 Effect of adhesive tape thickness on peel force [82].

2.6 Objectives

The most commonly applied manufacturing method for soft contact lenses, including silicone hydrogel contacts, is cast molding process. In this process, liquid macromer mixture is injected into the hollow cavity formed by two mold halves and polymerized into solid hydrogel, which is then released from the mold. A particular problem during demolding is that liquid macromer mixture is supplied in excess. As placing the mold halves together, the overfilled macromer mixture is expelled from the mold cavity and rests between the flanges of mold halves. After polymerization process, this excess macromer mixture forms an annular ring around the cured contact lens, which resists the separation of two mold halves [53, 56-69]. To overcome the demolding problem, both mechanical and chemical methods are utilized (**Table 2.3.1**, **Table 2.3.2**). However, only a few patents can be found, and most of which are related to mechanical methods. Moreover, contact lenses tested in the patents are conventional hydrogel lenses made of poly(HEMA), and the mold material is polypropylene or polystyrene.

The aim of this study is to minimize the adhesion between silicone hydrogel and silicate substrates with the application of silane modification on the surface of glass substrates. Various surface modification agents were applied to treat glass slides, and peel tests were conducted to measure the adhesive strengths between silicone hydrogel and surface modified glass substrates. Water contact angle measurement and XPS were utilized to characterize the surface properties of coated glass substrates.

The effect of UV curing time on tensile properties of silicone hydrogel was investigated to produce silicone hydrogel with high modulus. The effectiveness and efficiencies of silane, layer-by-layer adsorbed and sol-gel coatings were investigated to determine the most advantageous method for minimizing the adhesion between silicone hydrogel and glass substrates. The effects of silane type and concentration on coating effectiveness were also investigated to find the most effective silane type and the optimal silane concentration. In addition, the coating durability was tested by curing and peeling silicone hydrogel multiple times on silane treated glass substrates.

Chapter 3 Experimental Procedures

3.1 Preparation of Surface Modified Silicate Substrates

3.1.1 Pretreatment of Glass Slides with Piranha Solution

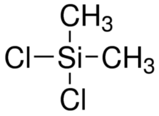
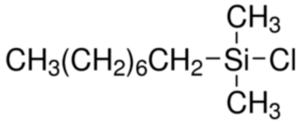
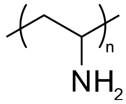
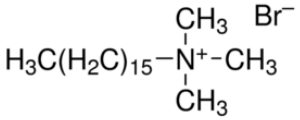
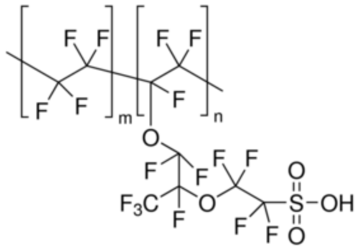
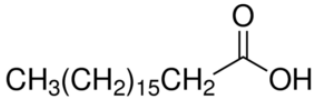
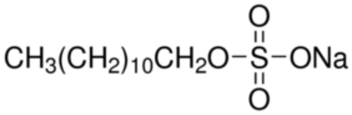
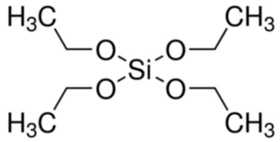
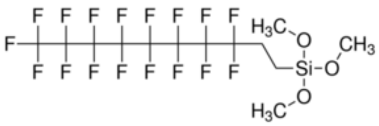
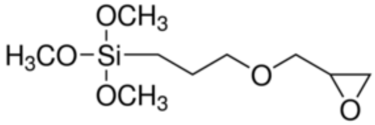
Piranha solution is applied to pretreat the glass slides (VWR plain micro slides, length × width × thickness 75mm × 25mm × 1mm). It is a mixture of 70 wt% sulphuric acid and 30 wt% hydrogen peroxide. Piranha solution is capable of removing most organic matter, and hydroxylate the surface of glass slides, making it extremely hydrophilic [88]. Glass slides treated by Piranha solution are referred to clean glass slides. The procedure is as follows:

1) Sonicate (Branson B3510 ultrasonic cleaner, Branson Ultrasonics) up to 20 glass slides in Milli-Q water (Barnstead Nanopure, Thermo Scientific) for 60 minutes.
2) Take glass slides out of Milli-Q water, and dry them under a stream of nitrogen. Treat one slide each time.
3) Ensure proper PPE (a lab coat, goggles, double gloves, and work in fume hood).
4) Place a glass petri dish bottom (Pyrex petri dishes, O.D. × H 100 mm × 15 mm) on stirrer hotplate (VMS-C7 Stirrer Hotplate, VWR International), then place a 300 mL beaker on top of glass petri dish bottom and add 75 mL 30% hydrogen peroxide to the beaker.
5) Add 175 mL sulphuric acid to hydrogen peroxide very slowly.

6) Place glass slides into the solution one by one slowly. Heat the solution to around 100 ˚C. It should be bubbling. Place a glass petri dish cover (Pyrex petri dishes, O.D. × H 100 mm × 15 mm) on top of beaker. Leave the solution on heat until bubbles decrease, which may take 3 hours.
7) After use, cool the solution to room temperature in a clearly labelled open container for several hours, preferably overnight, in the fume hood.
8) Dilute the solution 4 times with Milli-Q water. Carefully place it to waste collection bottle and ensure there is no heat generated or reactions occurring.
9) Rinse slides with Milli-Q water for no less than 5 times.
10) Dry slides under a stream of nitrogen and perform surface treatment within 2 hours.
11) Store slides in methanol if no surface treatment is to take place.

After the pretreatment with Piranha solution, clean glass slides are modified by three methods, including silane coupling agents, layer-by-layer adsorption, and sol-gel methods. The information on surface modification agents used here is summarized in **Table 3.1.1**.

Table 3.1.1 Information on surface modification agents.

Chemical Name	Abbreviation	Chemical Structure	Supplier
Dichlorodimethylsilane	DCDMS	 $Cl-\overset{CH_3}{\underset{Cl}{Si}}-CH_3$	Sigma-Aldrich
Chloro(dimethyl)octylsilane	DMCOS	 $CH_3(CH_2)_6CH_2-\overset{CH_3}{\underset{CH_3}{Si}}-Cl$	Sigma-Aldrich
Poly(vinyl amine)	PVAm		BASF
Cetrimonium bromide	CTAB	 $H_3C(H_2C)_{15}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3\ Br^-$	Sigma-Aldrich
Nafion	Nafion		Sigma-Aldrich
Stearic acid	Stearic acid		Sigma-Aldrich
Sodium dodecyl sulfate	SDS	 $CH_3(CH_2)_{10}CH_2O-\overset{O}{\underset{O}{S}}-ONa$	Sigma-Aldrich
Tetraethylorthosilicate	TEOS		Sigma-Aldrich
1H,1H,2H,2H-Perfluorodecyltrimethoxysilane	FAS		Sigma-Aldrich
3-Glycidoxypropyl triethoxysilane	GLYEO		Sigma-Aldrich

3.1.2 Surface Modification of Glass Slides with Silane Coupling Agents

Treat clean glass slides with dichlorodimethylsilane (DCDMS):

1) Immerse clean glass slides in 10 wt% DCDMS solution (10 wt% DCDMS in pure chloroform) for 2 hours, in 10 wt% DCDMS solution for 15 minutes, and in 5 wt% DCDMS solution (5 wt% DCDMS in pure chloroform) for 15 minutes, respectively.
2) Rinse the slides with chloroform, methanol and Milli-Q water for no less than 5 times sequentially.
3) leave the slides to air-dry.

Treat clean glass slides with chloro(dimethyl)octylsilane (DMCOS):

1) Immerse clean glass slides in 25×10^{-3} M DMCOS solution (25×10^{-3} M DMCOS in pure hexane), and in 2.5×10^{-3} M DMCOS solution (2.5×10^{-3} M DMCOS in pure hexane) for 15 minutes, respectively.
2) Rinse the slides with hexane, acetone and Milli-Q water for no less than 5 times sequentially.
3) leave the slides to air-dry.

3.1.3 Surface Modification of Glass Slides via Layer-by-layer Adsorption

First layer is created by poly(vinyl amine) (PVAm, Lupamin 5095, MW 50,000, BASF). Second layer is created by cetrimonium bromide (CTAB), Nafion (MW 70,000, Sigma-Aldrich), stearic acid, dichlorodimethylsilane (DCDMS) and sodium dodecyl sulfate (SDS), respectively. The procedure is as follows:

1) Immerse glass slides in 0.01 wt% PVAm solution overnight. Then rinse the slides with Milli-Q water, and dry the slides under a stream of nitrogen.
2) Immerse PVAm treated glass slides (obtained in step 1) in 0.2 wt% CTAB solution overnight. Then rinse the slides with Milli-Q water, and dry the slides under a stream of nitrogen.
3) Immerse PVAm treated glass slides (obtained in step 1) in 5 wt% DCDMS solution (5 wt% DCDMS in pure chloroform) for 15 minutes. Then rinse the slides with chloroform, methanol, and Milli-Q water sequentially. Dry the slides under a stream of nitrogen.
4) Immerse PVAm treated glass slides (obtained in step 1) in a 500 mg Nafion solution (500 mg Nafion in 80% methanol and 20% water) overnight. Then rinse the slides with Milli-Q water, and dry the slides under a stream of nitrogen.
5) Immerse PVAm treated glass slides (obtained in step 1) in 1wt% stearic acid solution (1 wt% stearic acid in acetone) overnight. Then rinse the slides with acetone and Milli-Q water sequentially. Dry the slides under a stream of nitrogen.

6) Immerse PVAm treated glass slides (obtained in step 1) in a 1 wt% SDS solution overnight. Then rinse the slides with Milli-Q water, and dry the slides under a stream of nitrogen.

3.1.4 Surface Modification of Glass Slides by Sol-Gel Methods

Tetraethylorthosilicate (TEOS) is applied as a silica sol. Hydrophobic materials such as 1H,1H,2H,2H-Perfluorodecyltrimethoxysilane (FAS), Hexadecyltrimethoxysilane (HDTMS) and Octyltriethoxysilane (OTES) are used to produce gel. To make more cross-linkable sol, 3-glycidoxypropyl triethoxysilane (GLYEO) is added as a co-curser. For comparison, one silica sol is prepared with only TEOS. The procedure is as follows:

1) Dissolve 5 mL TEOS and FAS with the FAS/TEOS mol ratio of 1:10 in 25 ml ethanol.
2) Mix the solution with an ammonium hydroxide/ethanol solution (6 mL 28% ammonium hydroxide in 25 mL ethanol), and stir the mixture intensively at room temperature for 12 hours.
3) Sonicate (Branson B3510 ultrasonic cleaner, Branson Ultrasonics) the milky mixture for 30 minutes to produce a homogeneous suspension.
4) Dip glass slides in the obtained solution for 12 hours, then leave the slides to air-dry.
5) Use 6 mL 0.01 N hydrogen chloride solution to replace the ammonium hydroxide/ ethanol solution in step 2, to achieve acidic hydrolysis.

3.2 Preparation of Silicone Hydrogel

3.2.1 Preparation of Macromer Mixture

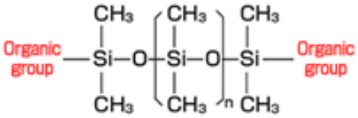
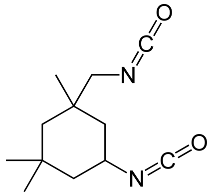
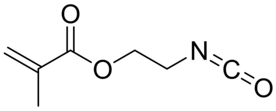
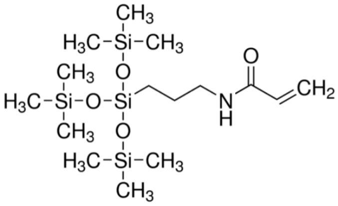
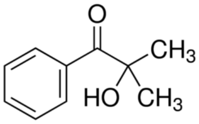
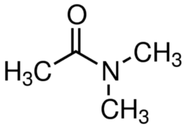
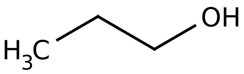
The silicone hydrogel formulation is supplied by Alcon. The ingredients are formulated in the following order for safety, accuracy, and to reduce the possibility of 1-propanol evaporation during the formulation: CE-PDMS, TRIS-AAm, DC 1173, DMA and 1-Propanol. Chemical structures of the ingredients are shown in **Table 3.2.1**. Normally a 20g batch size in a 20 mL vial is prepared each time. The procedure is as follows:

1) Take all chemicals out of the refrigerator and allow them to reach room temperature by placing them on the bench for a minimum of 60 minutes.
2) Prepare a water bath with stir plate (VMS-C7 Stirrer Hotplate, VWR International) and set temperature to 40°C.
3) Place a 20 mL vial on balance (XP6002S toploading balance, Mettler Toledo) and add 6.4g CE-PDMS directly to vial.
4) Tare the balance and add 4.2g TRIS-AAm directly to the vial.
5) Tare the balance and add 0.2g DC 1173 directly to the vial.
6) Tare the balance and add 4.6g DMA directly to the vial.
7) Tare the balance and add 4.4g 1-propanol directly to the vial.
8) Place a stir bar into the vial, close vial with lid and wrap the neck of the vial with Parafilm M® film. Place the formulation in the water bath and cover loosely with foil.

Mix the formulation in a water bath at 40˚C and ensure stirring speed is between 300-400 rpm for 3 hours.

9) Remove the vial from water bath and let it cool at room temperature for at least one hour.
10) Obtain another vial and filter the contents of the first vial batch-wise into the second vial using a 5 μm blunt fill needle with filter (REF 305211, BD PrecisionGlide) and a 3 mL syringe (REF 309657, BD PrecisionGlide). Close the vial with lid and wrap neck of vial with Parafilm M® film.
11) Formulation can be stored for up to 7 days at ambient conditions as long as it stays in motion.

Table 3.2.1 Information on ingredients of macromer mixture.

Chemical Name	Abbreviation	Chemical Structure	Supplier
Chain-extended polydimethylsiloxane vinylic macromer	CE-PDMS	IEM-PDMS-IPDI-PDMS-IPDI-PDMS-IEM  PDMS (KF-6001, MW 2,000 and KF-6002, MW 3,000, Shin-Etsu)  IPDI  IEM	Alcon
N-[Tris(trimethyl-siloxy)-silylpropyl]acrylamide	TRIS-AAm		Alcon
2-Hydroxy-2-methylpropiophenone	DC 1173		Sigma-Aldrich
N,N-Dimethylacetamide	DMA		Sigma-Aldrich
1-Propanol	1-Propanol		Sigma-Aldrich

3.2.2 Injection of Macromer Mixture into Mold

Silicone hydrogel casting mold is composed of metal base, polyethylene (PE) bottom, glass slide, PE spacer, PE film, quartz slide and PE top. Since silicone hydrogel does not adhere to PE, PE film is applied to produce silicone hydrogel with one side adhered to glass slide. Both quartz slide and PE film do not adsorb UV, so UV light is able to go thorough quartz slide and PE film without any loss. Screws are used to fix these parts together. Macromer mixture is injected into the spacer layer between quartz slide and glass slide (**Figure 3.2.1-Figure 3.2.3**). The procedure is as follows:

1) Place solid polyethylene bottom onto metal mold.
2) Place treated glass slide on top of PE bottom in appropriate position.
3) Place PE spacer on top of glass slide.
4) Place a PE film over the PE spacer, then place a quartz slide on top of it.
5) Place thick PE on top. Fasten wing nuts onto mold. Be cautious not to break the slides.
6) Inject the macromer mixture into the spacer layer with a 3 mL syringe (REF 309657, BD PrecisionGlide) and a needle (REF 305145, BD PrecisionGlide). Ensure there is no air bubble.

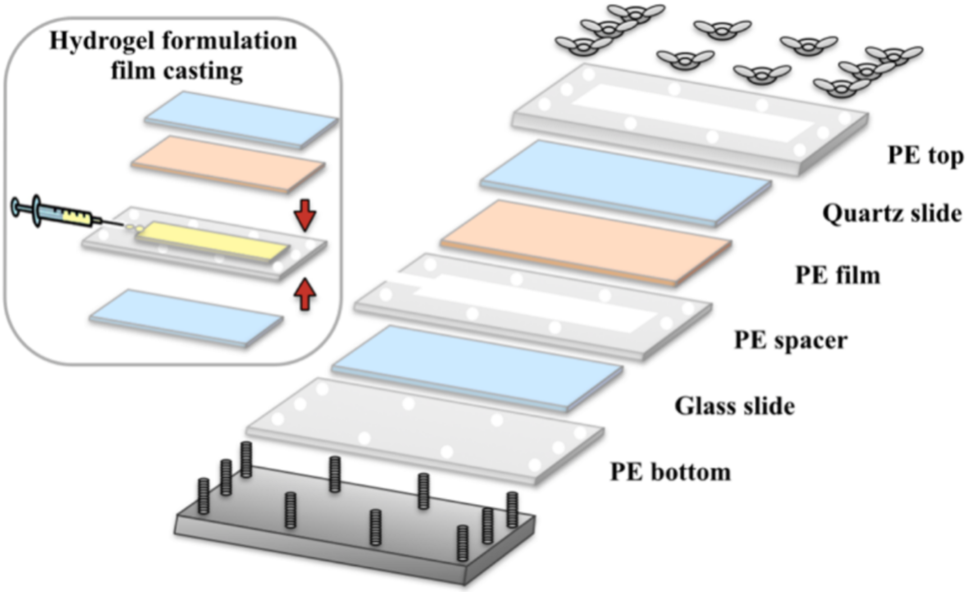


Figure 3.2.1 Schematic of silicone hydrogel casting mold and injection of macromer mixture into mold.

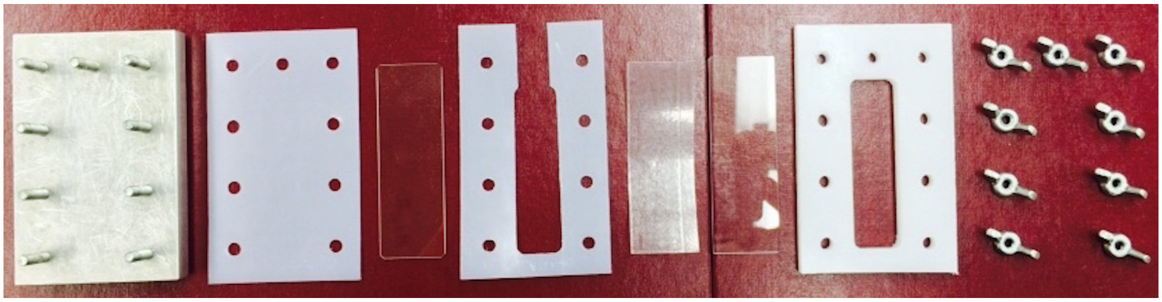


Figure 3.2.2 Silicone hydrogel casting mold.

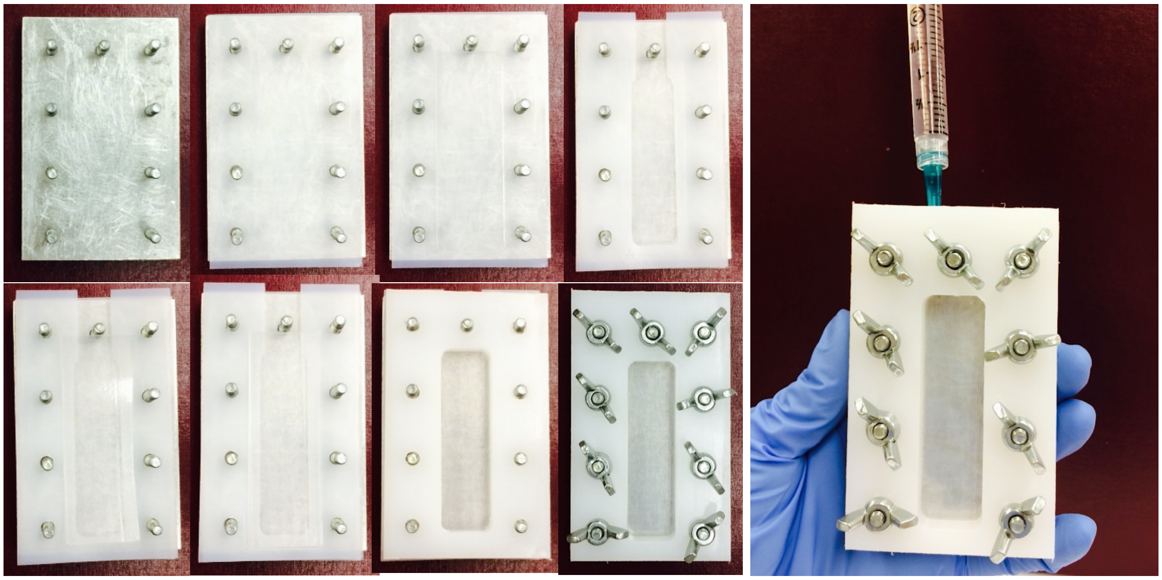


Figure 3.2.3 Assembly of casting mold and injection of macromer mixture into mold.

3.2.3 Polymerization Process

Silicone hydrogel is obtained by curing macromer mixture under UV light (Cure Zone UV Flood Curing System, CON-TROL-CURE, UV Process Supply, Inc.) for 6 minutes, with UV intensity of 95.0 mW/cm^2 (**Figure 3.2.4**).

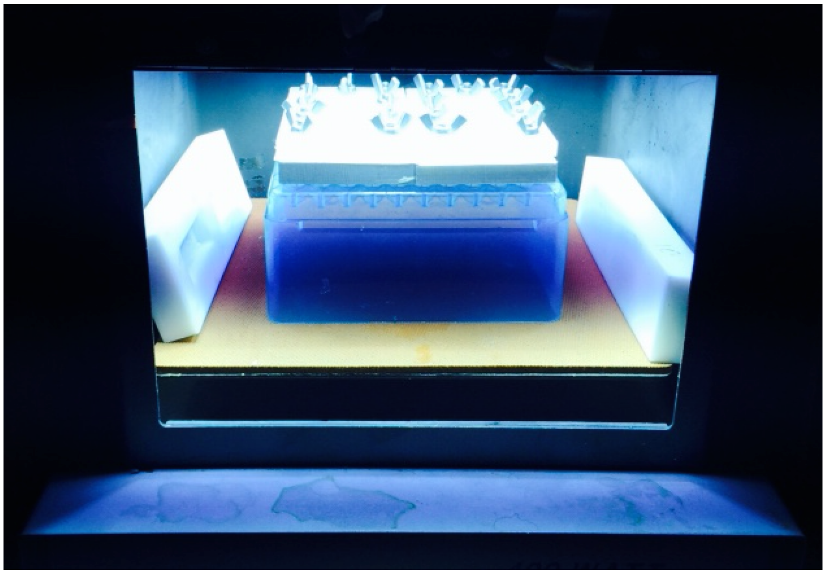


Figure 3.2.4 Polymerization process under UV light.

3.2.4 Release of Silicone Hydrogel from Mold

Adhesive joint of silicone hydrogel and glass substrate is released from the mold for peel test (**Figure 3.2.5**). The dimension of silicone hydrogel is 65 mm × 18 mm × 0.2 mm (length × width × thickness) . The procedure is as follows:

1) Unfasten the wing nuts, remove PE top, and take the rest of the layers off the metal base at once.
2) Remove quartz slide.
3) Carefully dislodge the PE + double-sided tape + PET top with a knife and peel it off the hydrogel.

4) Carefully remove the PE spacer. Ensure the edge of the hydrogel remain intact and attached to the glass slide.
5) Peel hydrogel off glass slide for 1 cm in length with a knife.
6) Attach the adhesive joint on flat bed of Instron (Instron 4411 Universal Testing System, Instron Co.) with 3M commercial tape. Ensure the peeled part of the hydrogel facing forward.

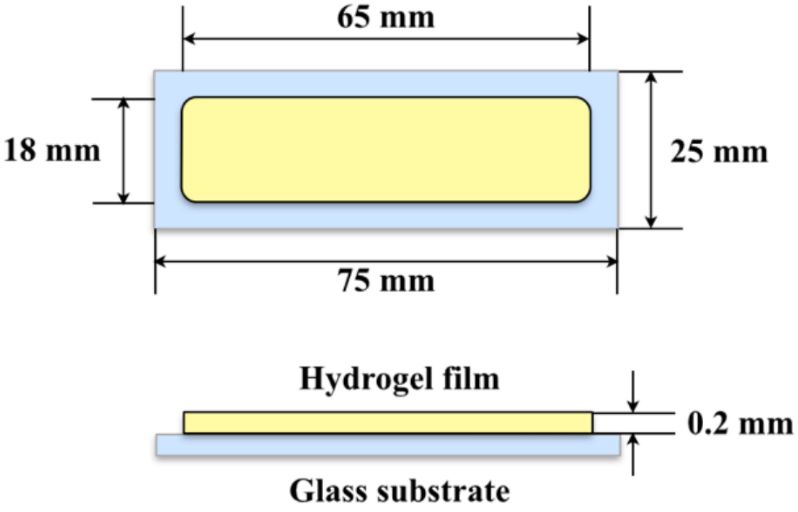


Figure 3.2.5 Specimen for peel test.

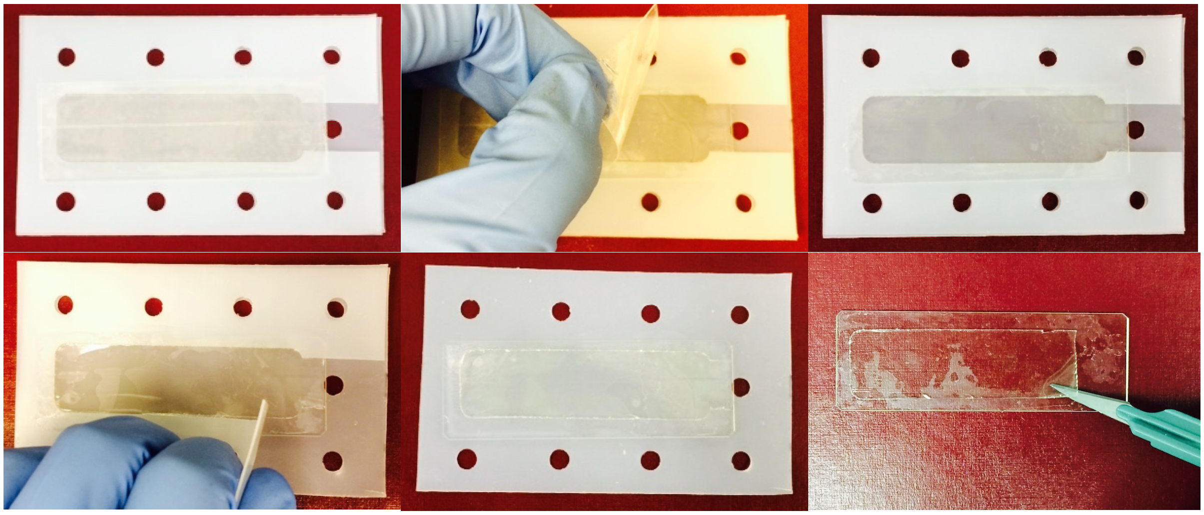


Figure 3.2.6 Release of silicone hydrogel and glass substrate from mold.

3.3 Tensile Properties of Silicone Hydrogel

Tensile test (Instron 4411 Universal Testing System, Instron Co.) is conducted to measure the tensile property of silicone hydrogel. In particular, silicone hydrogel tapes with UV curing time from 1 minute to 20 minutes are prepared and their tensile properties are tested. The variation of applied load with extension of hydrogel tape is recorded.

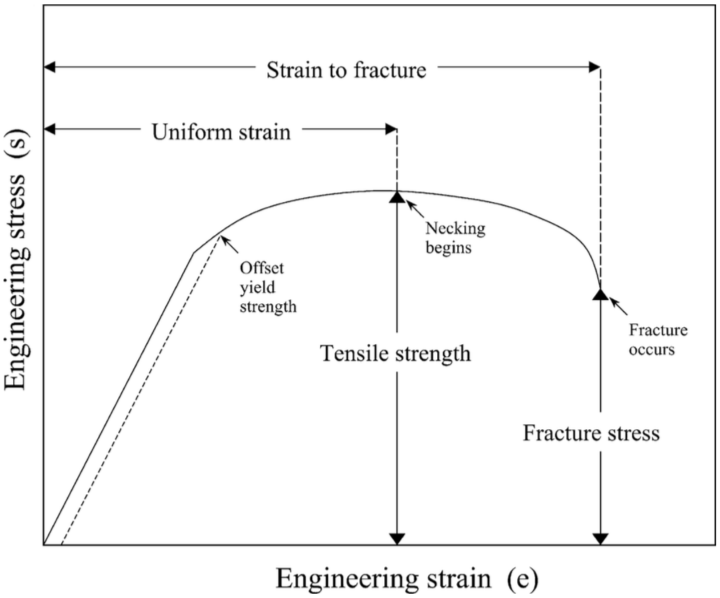


Figure 3.3.1 Schematic of stress-strain curve [88,89].

To obtain the modulus of silicone hydrogel tape, tensile stress is calculated from the average applied load per unit area of the hydrogel cross section:

$$\sigma = \frac{P}{A} \tag{IX}$$

wherein, σ is stress;

P is applied load;

A is original cross sectional area.

Tensile strain is calculated from the change of length divided by the original length of hydrogel:

$$\varepsilon = \frac{\delta}{L} \tag{X}$$

wherein, ε is strain;

δ is change of length;

L is original length.

Schematic of stress-strain curve is shown in **Figure 3.3.1**. The slope of the initial linear portion of stress-strain diagram is the elastic modulus or Young's modulus of silicone hydrogel:

$$E = \sigma / \varepsilon \tag{XI}$$

wherein, E is elastic modulus or Young's modulus.

3.4 Adhesive Properties of Silicone Hydrogel to Surface Modified Glass Slides

The adhesive strength of silicone hydrogel to glass substrate is measured by peel test (Instron 4411 Universal Testing System, Instron Co.). The test is conducted at room temperature of 25ºC, with crosshead rate of 50 mm/min. The variation of applied force with displacement is recorded. 1 N and 50 N load cells are used (**Figure 3.4.1**, **Figure 3.4.2**). The procedure is as follows:

1) Ensure the 50 N or 1 N load cell is in use.
2) Insert flat bed and rod. Ensure the 3M commercial tape on flat bed is sticky.
3) Rotate Instron clips to be in-line with the peeled part of the silicone hydrogel.
4) Jog the clips down and place the peeled part of hydrogel between the clips with a tweeze. Fasten the clips.
5) Tighten the string connecting flat bed to the rod.
6) Open computer software and start new experiment in "DATA" folder.
7) Use the standard peel method (peel rate 50 mm/min).
8) Press "IEEE 448" button on Instron 4411 to turn red light off.
9) Press "BAL", "ENTER", and "GL RESET" buttons sequentially.
10) Press "IEEE 448" button to turn red light back on.
11) Start experiment. Input the width of sample (18mm) into software.

12) When sample is peeled, click "Stop" at software. Choose two cursors on plot (first one at the beginning, second one at the end of the flat region of obtained plot). Note that though the plot may be noisy, the general trend is horizontal. Record average load and peel strength.

13) Save the results into "OUTPUT" folder.

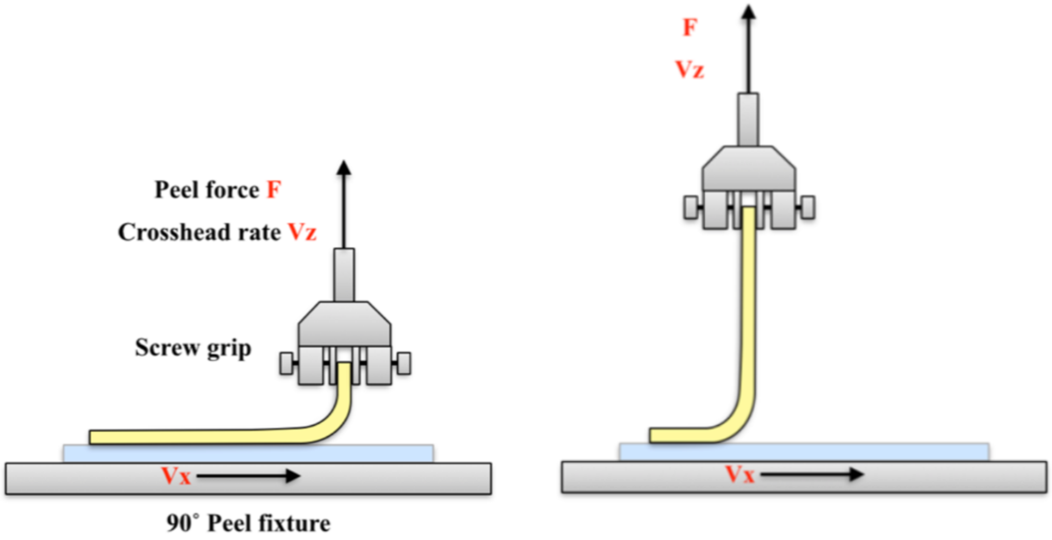
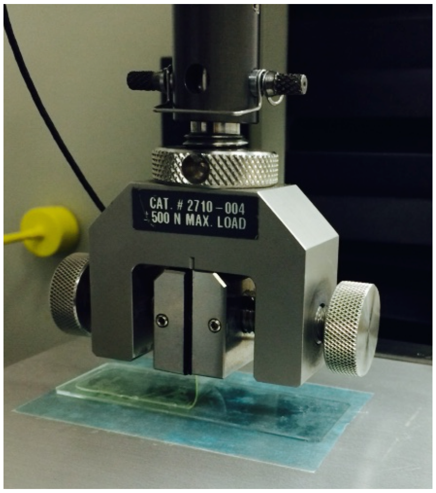
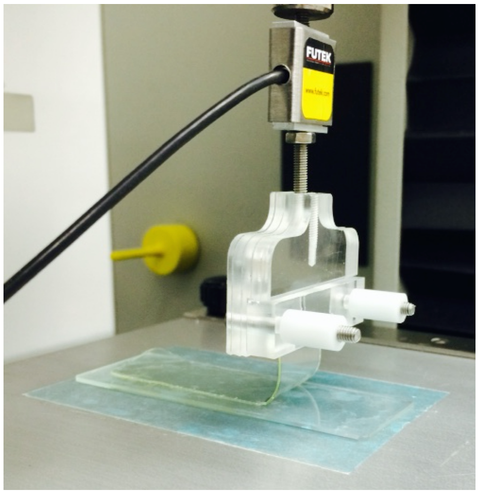


Figure 3.4.1 Schematic of 90º peel test.

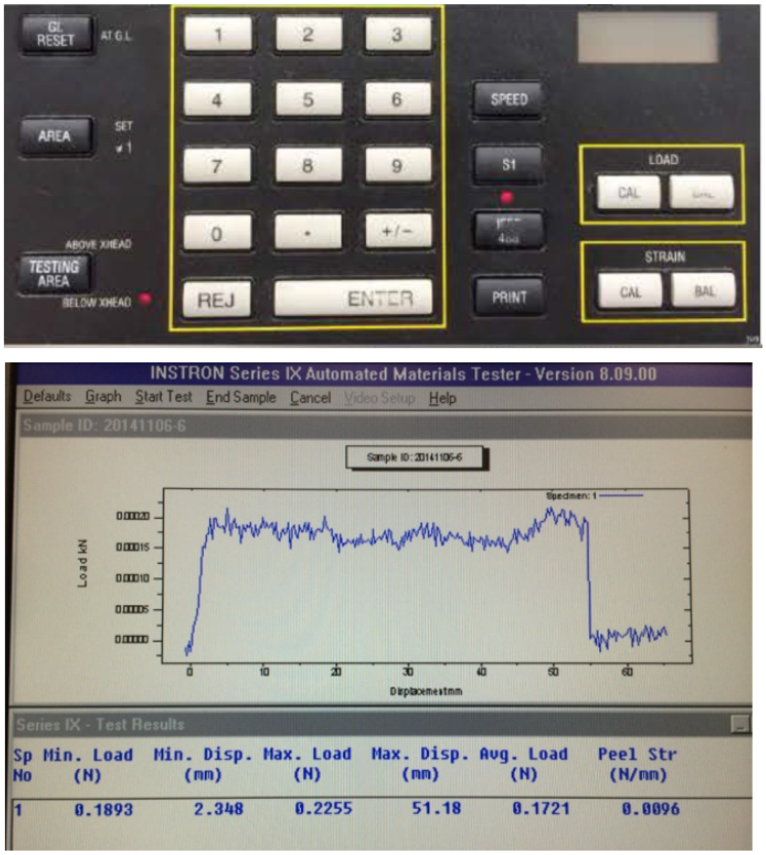
(A) 90˚ Peel test



(B) 50N Load cell and grip



(C) 1N Load cell and grip



```
Sp Min. Load  Min. Disp. Max. Load  Max. Disp. Avg. Load   Peel Str
No    (N)        (mm)       (N)        (mm)       (N)       (N/mm)

1     0.1893     2.348     0.2255      51.18     0.1721     0.0096
```

(D) Test results

Figure 3.4.2 90° Peel test. Glass substrates tested here were treated with 1H,1H,2H,2H-perfluorodecyltrimethoxysilane.

3.5 Contact Angle Measurement of Surface Modified Glass Slides

Drop shape analysis system (DSA 10, Krüss) is applied to measure the water contact angle of surface modified glass slides. The measurement is conducted at room temperature. Advancing contact angle is recorded.

3.6 Elemental Analysis of Surface Modified Glass Slides

Elemental analysis of surface modified glass slides is conducted by X-ray photoelectron spectroscopy (XPS, Physical Electronics, Inc.).

Chapter 4 Results and Discussions

4.1 Effect of UV Curing Time on Tensile Properties of Silicone Hydrogel

Silicone hydrogel samples with UV curing time from 1 minute to 20 minutes were prepared and their tensile properties were tested. The variation of applied load with extension of hydrogel tape was recorded. Tensile stress was calculated from the average applied force per unit area of the hydrogel cross section. Tensile strain was calculated from the change of length divided by the original length of hydrogel. The slope of the initial linear portion of stress-strain diagram is the modulus of silicone hydrogel.

The relationship between silicone hydrogel modulus and UV time is plotted in **Figure 4.1.1**. Silicone hydrogel had a high modulus of 0.87±0.09 MPa when cured under UV for 6 minutes. While the modulus properties of silicone hydrogel were relatively low (0.60-0.74 MPa) under at other UV curing time. Therefore, silicone hydrogel is prepared by curing under UV for 6 minutes. UV intensity at this time is 95.0 mW/cm^2 (400 × 1000 mW ÷ (6.5 cm×1.8 cm×6×60) = 95.0 mW/cm^2). The appropriate UV time was also verified by the peel test results. Adhesive joints of silicone hydrogel and clean glass substrates with various UV curing time were prepared, and peel tests were conducted to measure their adhesive strengths. When cured under UV for 6 minutes, the obtained silicone hydrogel was unable to be peeled off from clean glass substrates. In contrast, hydrogel samples prepared under other UV time were easily peeled off from the substrates.

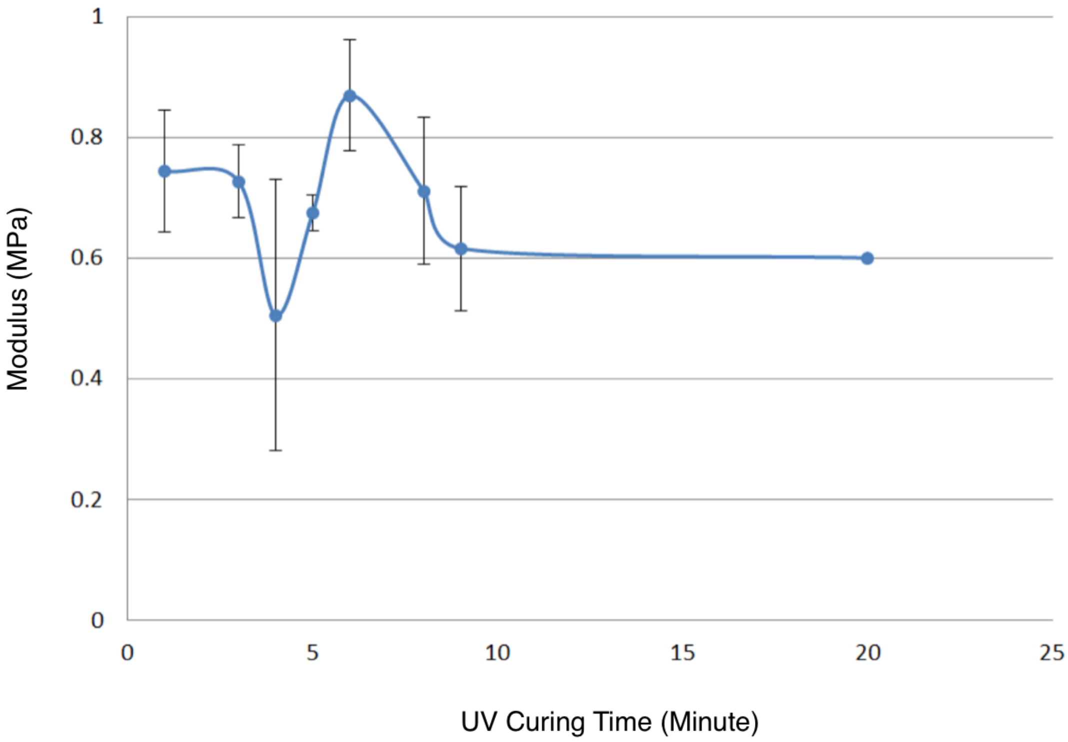


Figure 4.1.1 The relationship between silicone hydrogel modulus and UV curing time. Each measurement was replicated five times. Error bars represent standard deviation of the mean.

Tranoudis et al. [89] studied the tensile properties of hydrogel contact lenses made from various materials. The values of tensile strength, elongation at break and Young's modulus are shown in **Table 4.1.1**. Contact lens made of vinyl pyrrolidone (VP) and MMA copolymer had the highest modulus of 1.59±0.12, the one made of HEMA and VP copolymer had the lowest modulus of 0.36±0.07 MPa.

Table 4.1.1 Tensile properties of hydrogel contact lenses made from various materials [89].

Material	Tensile strength (kg/cm^2)	Elongation-at-break (%)	Young's modulus (kg/cm^2)
HEMA/VP 40%	2.59 ± 0.83	56.33 ± 15.04	7.01 ± 0.44
HEMA/VP 55%	1.81 ± 0.93	52.40 ± 27.91	3.72 ± 0.68
HEMA/VP 70%	4.01 ± 0.81	81.50 ± 23.74	5.87 ± 1.52
VP/MMA 55%	5.87 ± 2.48	43.33 ± 17.65	16.25 ± 1.18
VP/MMA 70%	3.40 ± 1.16	81.00 ± 31.41	5.04 ± 0.95
HEMA 40%	2.71 ± 1.27	43.00 ± 24.30	8.80 ± 0.49
HEMA/MAA 55%	1.23 ± 0.59	18.00 ± 5.16	5.92 ± 1.51
HEMA/MAA 70%	1.52 ± 0.47	21.60 ± 10.62	7.83 ± 1.10

In the work of Kim et al. [90], contact lenses made of pure poly(HEMA) and copolymer of HEMA and methacrylic acid (MA) were immersed in 0.15 M saline solution (0.15 M saline in sodium chloride), then their elastic modulus properties were measured. The modulus of poly(HEMA) contact lens with 38% water content was 1.34 ±0.13 MPa, and the modulus of poly(HEMA/MA) contact lens with 55% water content was 0.47±0.04 MPa.

Compared with the values of commercial contact lenses, modulus of silicone hydrogel is within the same range of contact lenses, and the modulus of silicone hydrogel with UV curing time of 6 minutes (0.87±0.09 MPa) is moderate.

4.2 Efficiencies of Silane, Lay-by-Layer Adsorbed and Sol-Gel Coatings

Clean glass slides were modified via three methods, including silane modification, layer-by-layer adsorption and sol-gel methods. Specimens for peel tests were prepared by cast-molding silicone hydrogel on surface modified glass slides under UV for 2 minutes. Peel tests were conducted at peel rate of 50 mm/min, with peel angle of 25-45º. Peel angle between silicone hydrogel and clean glass slide is shown in **Figure 4.2.1**. Peel Strengths between silicone hydrogel and silane modified, layer-by-layer adsorbed and sol-gel modified glass slides are shown in **Figure 4.2.2**-**Figure 4.2.4**. Structures of chemicals used here can be found in **Table 3.2.1**.

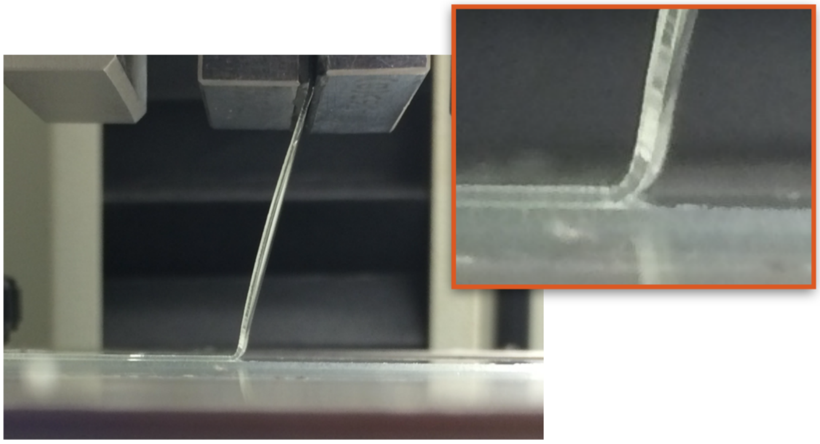


Figure 4.2.1 Peel angle between silicone hydrogel and clean glass slide (45º).

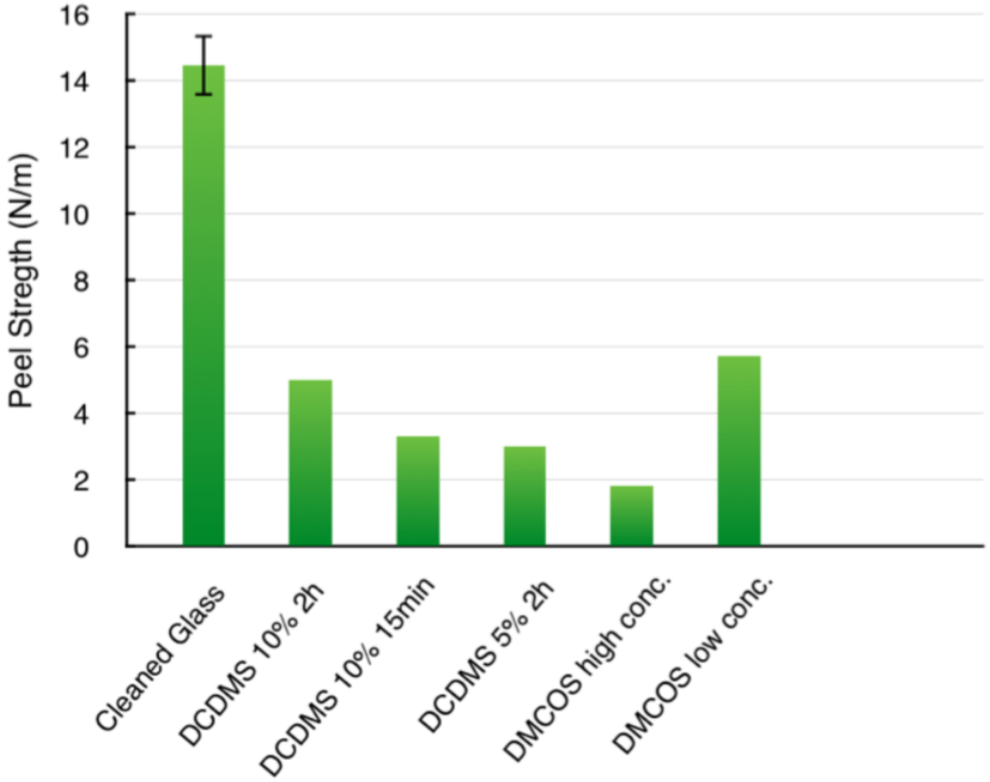


Figure 4.2.2 Peel Strengths between silicone hydrogel and silane modified glass slides. Peel tests were conducted at peel rate of 50 mm/min, with peel angle of 25-45º. Each measurement was replicated five times. Error bars represent standard deviation of the mean.

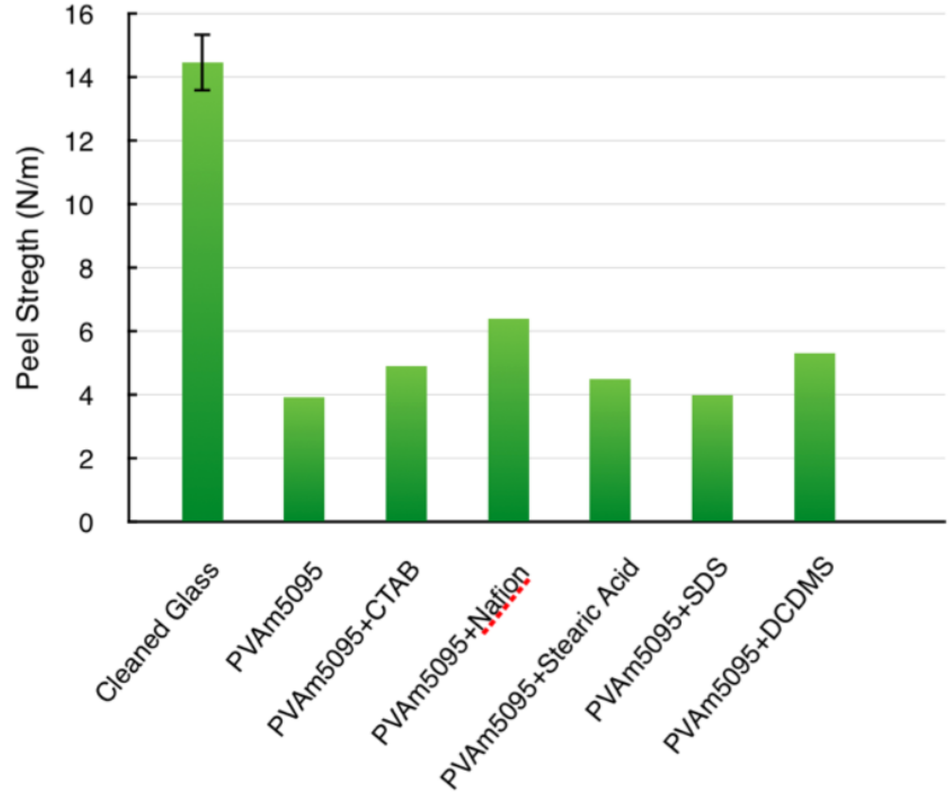


Figure 4.2.3 Peel Strengths between silicone hydrogel and layer-by-layer adsorbed glass slides. Peel tests were conducted at peel rate of 50 mm/min, with peel angle of 25-45º. Each measurement was replicated five times. Error bars represent standard deviation of the mean.

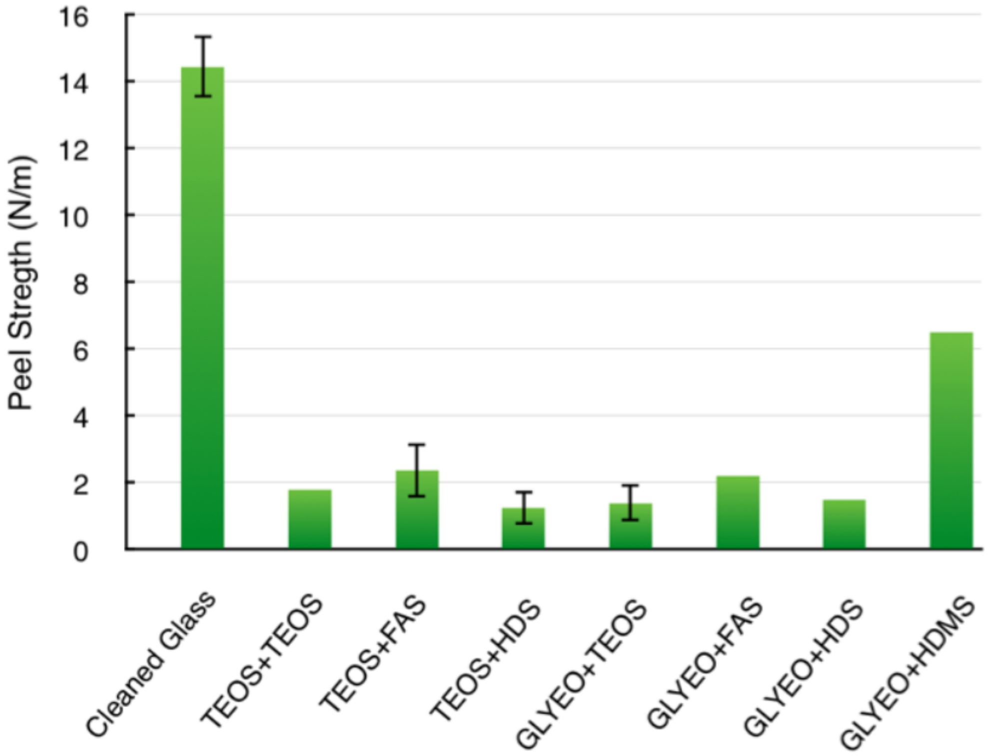


Figure 4.2.4 Peel Strengths between silicone hydrogel and sol-gel modified glass slides. Peel tests were conducted at peel rate of 50 mm/min, with peel angle of 25-45º. Each measurement was replicated five times. Error bars represent standard deviation of the mean.

Peel strength between silicone hydrogel and clean glass slide was 14.2±0.6 N/m, and it decreased to below 6 N/m with the application of surface treatment on glass slides. Therefore, coatings prepared by silane modification, layer-by-layer adsorption and sol-gel methods all reduced the adhesion between silicone hydrogel and glass substrates. To compare the effectiveness and efficiencies of three types of coatings, the surface smoothness, transparency and trapped air bubbles of coatings, treatment time required for each coating, as well as peel strengths are listed in **Table 4.2.1**.

Silane coatings and layer-by-layer adsorbed coatings were optically smooth, transparent, and there were no trapped air bubbles. In contrast, sol-gel coatings were optically rough and opaque, moreover, chemicals from sol-gel coatings adhered to the silicone hydrogel surface after peeling the hydrogel off from the coated substrates, which were detrimental to the surface properties of contact lenses. It took 15 minutes to 2 hours to prepare a silane coating on glass slides, while layer-by-layer adsorption and sol-gel treatment could take up to 24 hours. DMCOS coating and TEOS+FAS coating reduced the peel strength between silicone hydrogel and clean glass slides from 14.2±0.6 N/m to 2 N/m, whereas PVAm+SDS coating only reduced the peel strength to 4 N/m.

In conclusion, silane coatings are more efficient than layer-by-layer adsorbed coatings and sol-gel coatings in minimizing adhesion between silicone hydrogel and glass substrates. Two hours are enough to prepare a coating. And the obtained silane coatings are optically smooth, transparent and with no trapped air bubbles. With the application of DMCOS coatings, peel strength can be reduced from 14 N/m to 2 N/m.

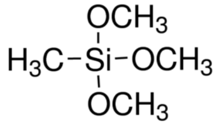
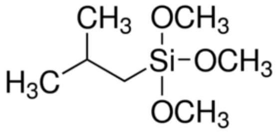
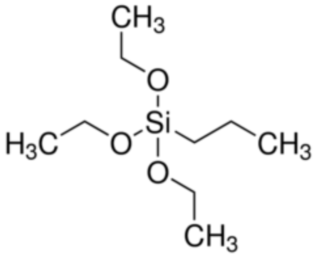
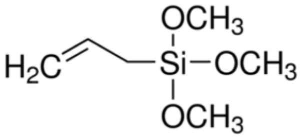
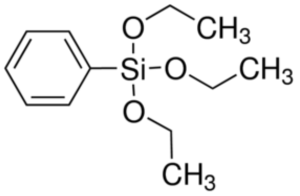
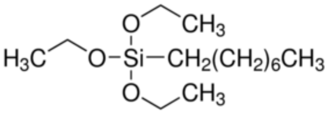
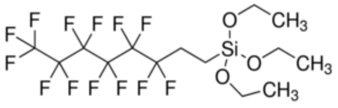
Table 4.2.1 Comparison of silane, lay-by-layer adsorbed and sol-gel coatings.

Coatings	Smoothness	Transparency	Trapped Air Bubbles	Treatment Time	Peel Strength (N/m)
Silane coatings	Optically smooth	Transparent	No	15 minutes-2 hours	2-6
Layer-by-Layer adsorbed coatings	Optically smooth	Transparent	No	24 hours	4-6
Sol-Gel coatings	Optically rough	Opaque	No	24 hours	2-6

4.3 Effects of Silane Type and Concentration on Coating Effectiveness

Silanes with various organic functional groups were applied to modify the surface of glass slides. Structures of silane coupling agents used here are shown in **Table 4.3.1**. In particular, 5 wt% silane solutions (5 wt% silane in 1-propanol) were prepared, and clean glass slides were dipped in silane solutions for 2 hours, then the slides were rinsed by Milli-Q water and left to air-dry. Specimens for peel tests were obtained by cast-molding silicone hydrogel on silane modified glass slides under UV for 6 minutes, with UV intensity of 95.0 mW/cm^2. Peel tests were conducted at peel rate of 50 mm/min, with peel angle of 25-45°. Peel Strengths between silicone hydrogel and glass slides treated with various silanes are shown in **Figure 4.3.1**. Water contact angle on silane treated glass slides was measured, as seen in **Figure 4.3.2**.

Table 4.3.1 Information on silane coupling agents.

Chemical Name	Abbreviation	Chemical Structure	Supplier
Trimethoxymethylsilane	TMMS		Sigma-Aldrich
Isobutyl(trimethoxy)silane	BTMS		Sigma-Aldrich
n-Propyltriethoxysilane	PTES		Sigma-Aldrich
Allyltrimethoxysilane	ATMS		Sigma-Aldrich
Triethoxyphenylsilane	TEPhS		Sigma-Aldrich
Octyltriethoxysilane	OTES		Sigma-Aldrich
1H,1H,2H,2H-Perfluorooctyltriethoxysilane	FTES		Sigma-Aldrich

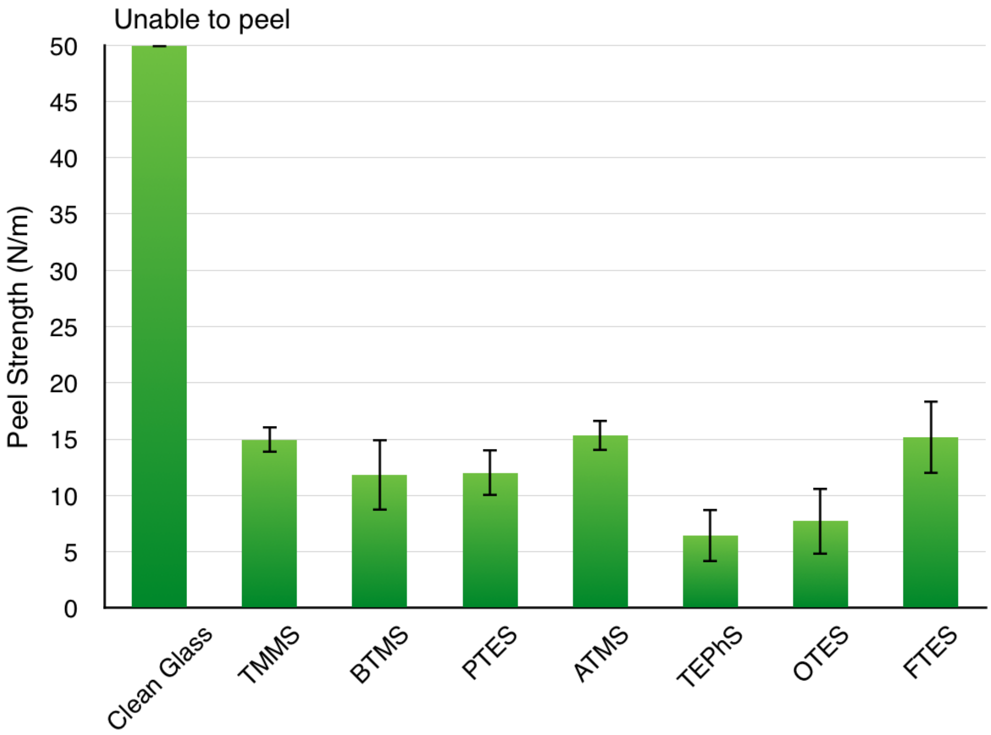


Figure 4.3.1 Peel Strengths between silicone hydrogel and silane treated glass slides. Peel tests were conducted at peel rate of 50 mm/min, with peel angle of 25-45º. Each measurement was replicated five times. Error bars represent standard deviation of the mean.

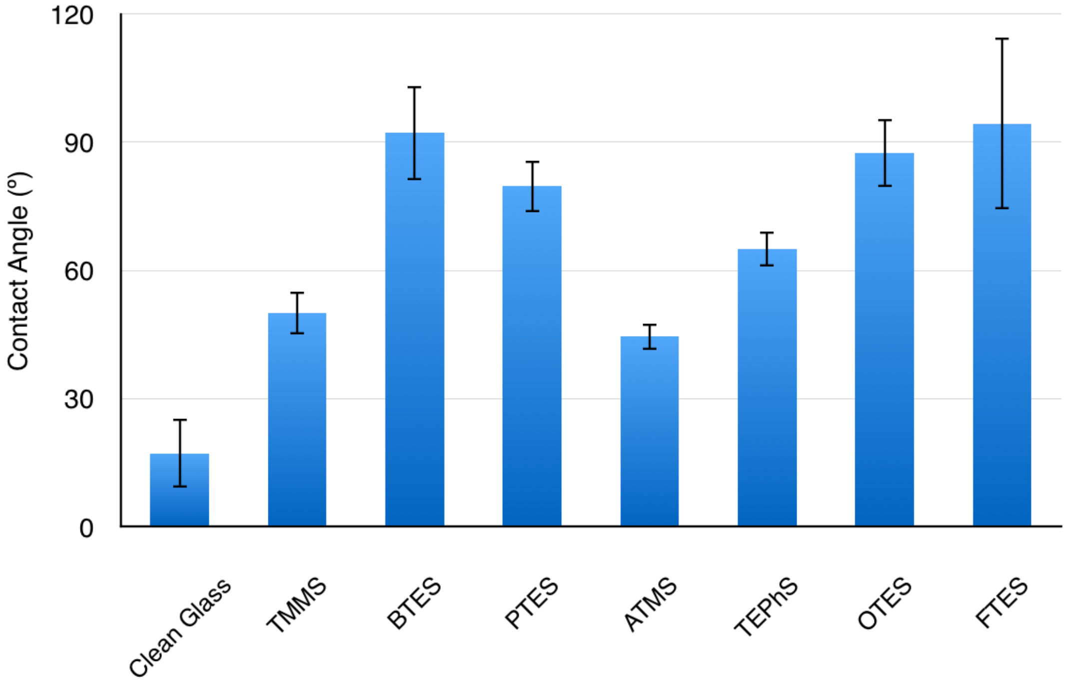


Figure 4.3.2 Water contact angle on silane treated glass slides. Contact angle here refers to advancing contact angle. Each measurement was replicated three times. Error bars represent standard deviation of the mean.

Table 4.3.2 Comparison of various silane coatings.

Chemical Abbreviation	Organic Functional Group	Peel Strength (N/m)	Contact Angle (º)
TMMS	$-CH_3$	14.9±1.2	50.1±5
BTMS	$-CH_2CH(CH_3)_2$	11.6±3.2	92.2±11
PTES	$-CH_2CH_2CH_3$	12.1±2.0	79.7±6
ATMS	$-CH_2CH=CH_2$	15.3±1.4	44.5±3
TEPhS	$-C_6H_5$	6.4±2.4	65±4
OTES	$-CH_2(CH_2)_6CH_3$	7.7±3.0	87.5±8
FTES	$-CH_2CH_2(CF_2)_5CF_3$	15.2±3.3	94.4±20

When cured under UV for 6 minutes, the obtained silicone hydrogel completely adhered to clean glass substrates and was unable to be peeled off. With the application of silane coatings, silicone hydrogel was easily peeled off from the glass substrates, and the peel strength was reduced to below 15.5 N/m (**Figure 4.3.1**). Thus, silane coatings are effective to reduce the adhesion between silicone hydrogel and glass substrates.

Comparing the peel strengths between silicone hydrogel and glass slides treated with various silanes, with the application of TEPhS and OTES coatings, peel strength between silicone hydrogel and clean glass slides was reduced to 6.4±2.4 N/m and 7.7±3.0 N/m respectively (**Table 4.3.2**). Thus, TEPhS and OTES are the most effective silanes to minimize the adhesion between silicone hydrogel and glass substrates among 7 types of silanes tested here. Factors that influence the effectiveness of a silane coating consist of the organic functional groups, the distribution of silane molecules on substrates, the degree of silane molecules coverage, and the unreacted hydroxyl groups [91]. Compared with the organic functional groups of other silanes, the phenyl groups ($-C_6H_5$) of TEPhS and the octyl groups ($-CH_2(CH_2)_6CH_3$) of OTES could shield the surface of glass substrates more effectively and leave less uncovered hydroxyl groups at the surface. Therefore, the TEPhS and OTES coatings are more effective to reduce the adhesion between silicone hydrogel and glass substrates.

Water contact angle quantifies the wettability of a surface. A surface with greater water contact angle is more hydrophobic. As shown in **Figure 4.3.2** and **Table 4.3.2**, with the application of BTMS, PTES, OTES and FTES coatings, the water contact angle on glass slides increased from 17º to 90º, and the surface wettability of glass slides altered from hydrophilic to hydrophobic accordingly. The relationship between peel strength and contact angle is shown in **Figure 4.3.3**. A decreasing trend of peel strength was found as the contact angle of silane treated glass slides increased. However, the influence of contact angle on peel strength was not notable enough. The surface wettability of silane coated glass slides can not be taken as the main factor affecting coating effectiveness.

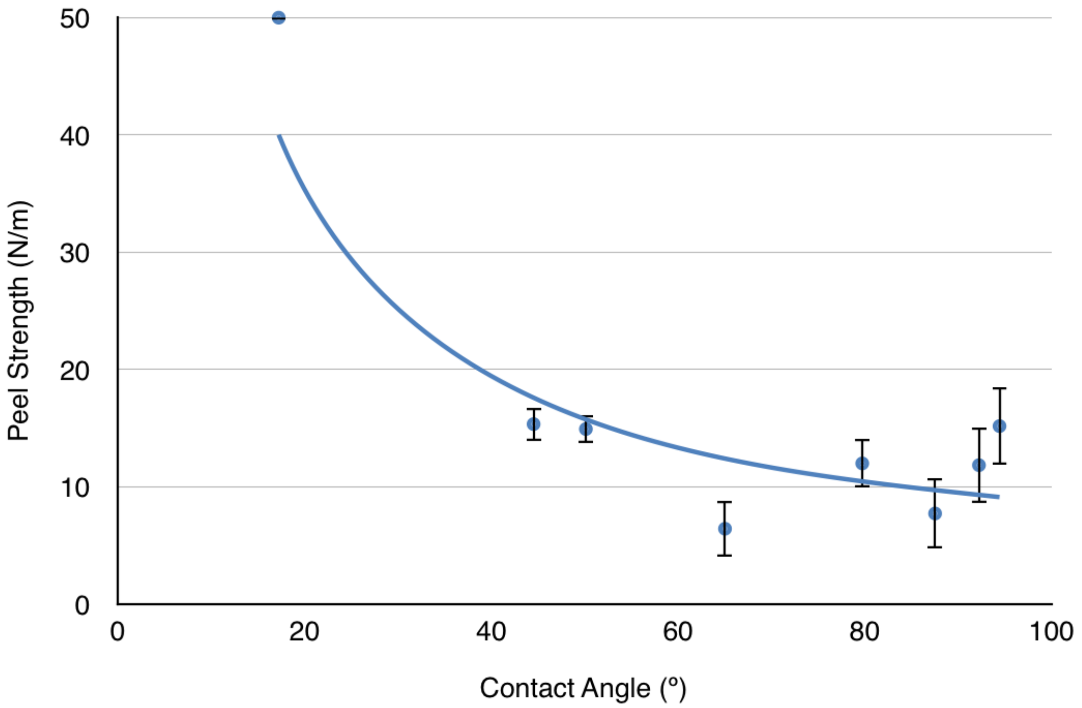


Figure 4.3.3 The relationship between peel strength and contact angle.

In addition to silane type, silane concentration is another factor that influences the coating effectiveness. To investigate the effect of silane concentration, silane solutions with multiple concentrations were applied to treat the glass slides, and peel tests were conducted to measure the adhesive strengths between silicone hydrogel and silane treated glass slides. In particular, TEPhS and OTES solutions were prepared by dissolving 1 wt %, 5 wt% and 10 wt% TEPhS and OTES in 1-propanol respectively. Clean glass slides were dipped in silane solutions for 2 hours. Then the slides were rinsed by Milli-Q water and left to air-dry. The optimal silane concentration was 5 wt% for both TEPhS and OTES solutions (**Figure 4.3.4**). The reason is that when silane is at relatively low concentration, silane molecules react with the hydroxyl groups and distribute loosely at the surface of substrates; as silane concentration increases, silane molecules are able to react with each other to form two dimensional network of silane (**Figure 4.3.5**). There exists an optimal silane concentration, at which the surface of substrates is fully occupied by silane molecules, and further increase of silane concentration cannot affect the silane adsorption at the surface of substrates [92].

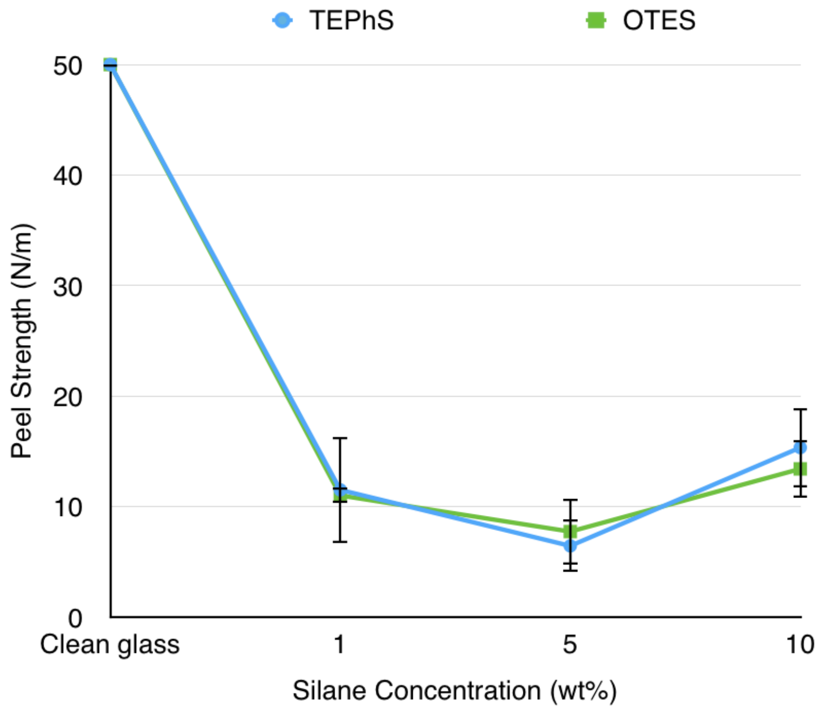


Figure 4.3.4 The relationship between peel strength and silane concentration. Peel tests were conducted at peel rate of 50 mm/min, with peel angle of 25-45°. Each measurement was replicated three times. Error bars represent standard deviation of the mean.

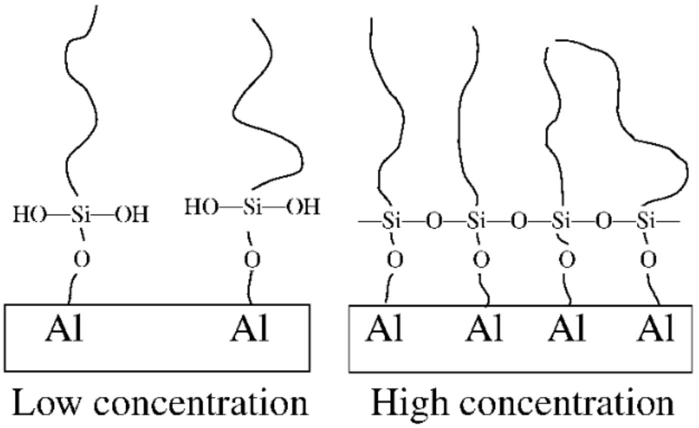


Figure 4.3.5 Schematic of silane adsorption on the surface of aluminum substrate at low and high concentrations [92].

4.4 Durability of Silane Coatings

The durability of silane coatings was tested by curing and peeling silicone hydrogel on silane treated glass slides five times. In particular, silicone hydrogel was cured on a coated glass slide and peeled off, then another silicone hydrogel was cured on the same glass slide and peeled off. This cycle of curing and peeling was repeated five times. And the glass slide was not treated by solvent after each cycle of curing and peeling. Clean glass slides and glass slides with three types of silane coatings, including TEPhS, OTES and FTES coatings were tested here. Peel strengths between silicone hydrogel and silane treated glass slides at first and fifth cycle of curing and peeling are shown in **Figure 4.4.1**. Water contact angle on silane treated glass slides before and after five cycles of curing and peeling was measured, as seen in **Figure 4.4.2**. The atomic concentration (%) at the surface of silane modified glass substrates was measured by X-ray photoelectron spectroscopy (XPS) (**Table 4.4.1**).

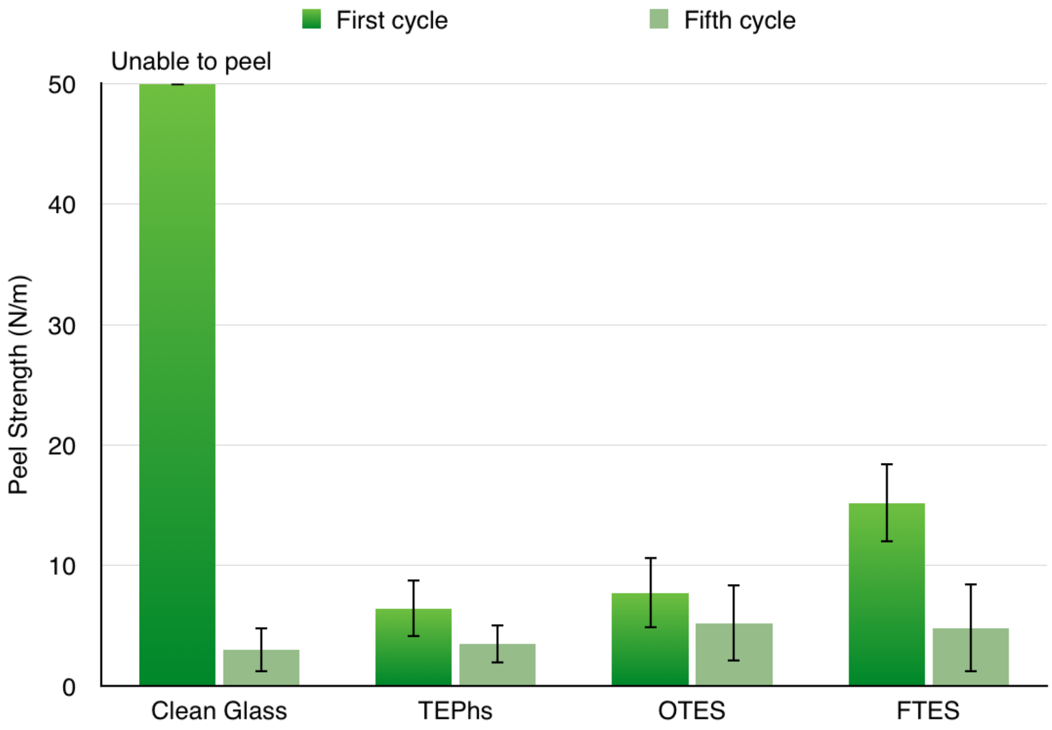


Figure 4.4.1 Peel Strengths between silicone hydrogel and silane treated glass slides at first and fifth cycle of curing and peeling. Peel tests were conducted at peel rate of 50 mm/min, with peel angle of 25-45º. Each measurement was replicated five times. Error bars represent standard deviation of the mean.

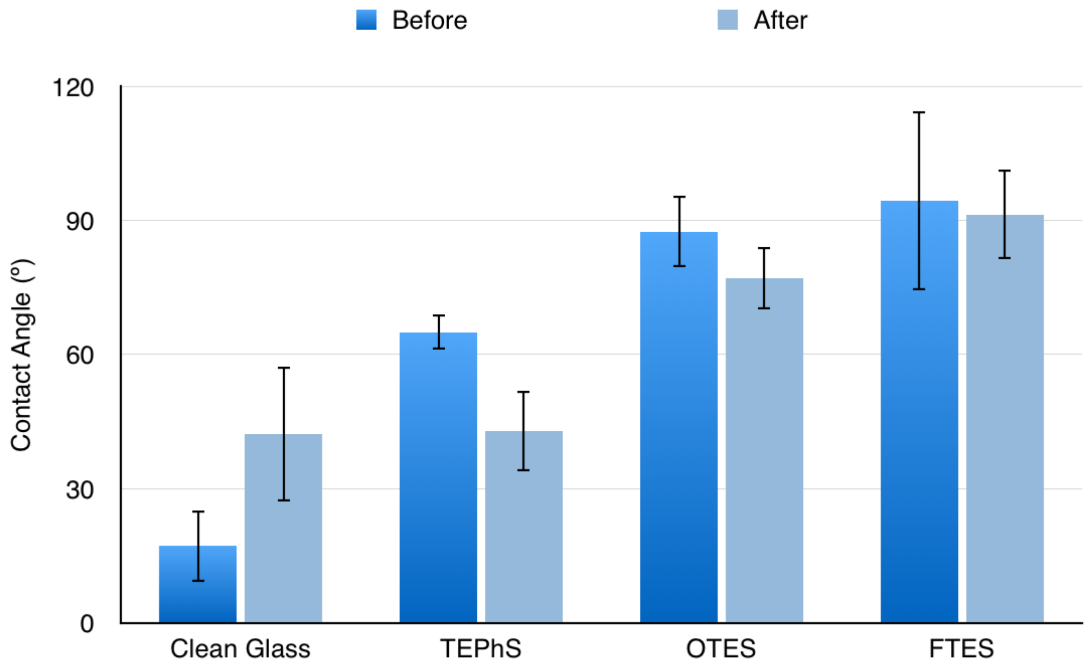


Figure 4.4.2 Water contact angle on silane treated glass slides before and after five cycles of curing and peeling. Contact angle here refers to advancing contact angle. Curing and peeling were performed five times. Each measurement was replicated three times. Error bars represent standard deviation of the mean.

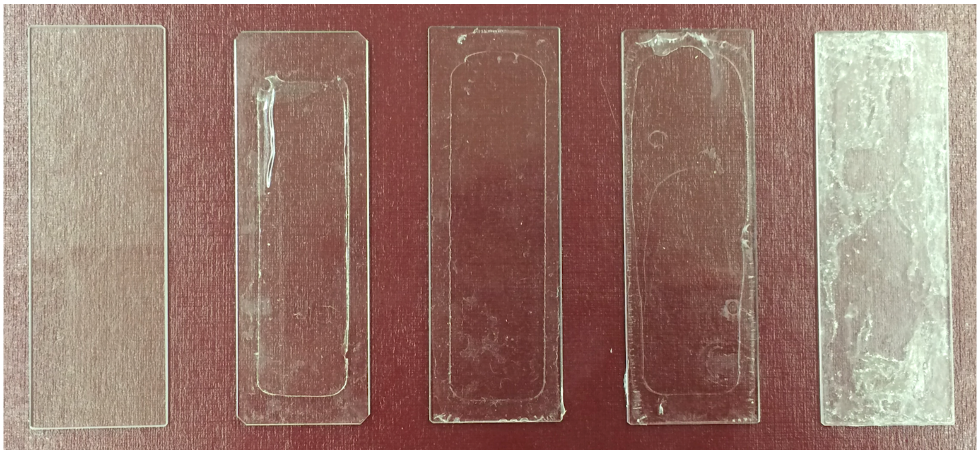


Figure 4.4.3 (A) Clean glass slide; (B) Silicone hydrogel and glass slide after first curing; (C) Glass slide after first peeling; (D) Glass slide after second peeling; (E) Glass slide after fifth peeling.

Compared with peel strengths between silicone hydrogel and silane treated glass slides at first cycle of curing and peeling, the peel strengths at fifth cycle decreased to below 5 N/m, which indicates the adhesion between silicone hydrogel and glass substrates reduced as the cycle of curing and peeling increased. However, after first cycle of curing and peeling, excess hydrogel material was left on the surface of glass substrates, and an annular ring was formed, which was unfavourable to the curing process of silicone hydrogel (**Figure 4.4.3**). Thus, the glass slides need to be treated by 1-propanol solvent to remove the excess hydrogel material, and the silane coatings need to be reapplied before the curing process of silicone hydrogel.

Table 4.4.1 Atomic concentration (%) at the surface of silane modified glass substrates before and after curing and peeling silicone hydrogel on them. Curing and peeling were performed five times.

Sample	**Before**					**After**				
	C	**N**	**O**	**Si**	**F**	**C**	**N**	**O**	**Si**	**F**
Clean glass	30.46	1.97	44.5	23.07	0	52.29	5.26	26.25	16.20	0
OTES	55.40	1.91	26.36	16.09	0	57.23	1.97	23.06	17.73	0
FTES	32.36	0	18.88	11.39	37.38	35.77	1.29	9.52	6.02	47.40

After five cycles of curing and peeling silicone hydrogel, a decrease of water contact angle was found on the surface of silane treated glass slides, indicating that the surface of glass slides became less hydrophobic. It can be explained by the variation of surface chemistry after curing and peeling silicone hydrogel on glass slides. As seen from **Table 4.4.1**, the atomic concentration at the surface of OTES treated and FTES treated glass slides slightly altered after peeling hydrogel on them. There are two possible reasons for the variation of surface chemistry, one is that some of the silane chemistry adhered to silicone hydrogel and was removed as peeling silicone hydrogel off from the glass substrates, the other reason is that the excess liquid monomers were left on the surface of glass substrates. In contrast to the contact angle decrease of silane modified glass slides, the contact angle of clean glass slides showed an increase after curing and peeling silicone hydrogel on them. It could result from the excess liquid monomers which were left on the surface of clean glass slides.

To summarize, the adhesion between silicone hydrogel and glass substrates reduced as the cycles of curing and peeling increased. However, after first cycle of curing and peeling, excess hydrogel material was left on the surface of glass substrates, and an annular ring was formed, which was unfavourable to the curing process of silicone hydrogel. Thus, the glass slides need to be treated by 1-propanol solvent to remove the excess hydrogel material, and the silane coatings need to be reapplied before the curing process of silicone hydrogel.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

The following conclusions can be drawn from this study:

Silicone hydrogel was obtained by curing macromer mixture under UV for 6 minutes, with UV intensity of 95.0 mW/cm^2. The obtained silicone hydrogel had a modulus of 0.87±0.09 MPa, within the same range of commercial contact lenses. And the hydrogel with a UV curing time of 6 minutes was unable to be peeled off from clean glass substrates.

Triethoxyphenylsilane (TEPhS) and octyltriethoxysilane (OTES) are the most effective silanes to minimize the adhesion between silicone hydrogel and glass substrates among 7 types of silanes tested in this study. The silane coatings were optically smooth, transparent and with no trapped air bubbles. And the peel strength between silicone hydrogel and glass substrates can be reduced to below 15.5 N/m with the application of TEPhS and OTES coatings. The optimal silane concentration was 5 wt% for both TEPhS and OTES solutions.

The durability of octyltriethoxysilane (OTES) and 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FTES) coatings was tested. The adhesion between silicone hydrogel and glass substrates reduced as the cycle of curing and peeling increased. However, after first cycle of curing and peeling, excess hydrogel material was left on the surface of glass substrates, and an annular ring was formed, which was unfavourable to the curing process of silicone hydrogel. Thus, the glass slides need to be treated by solvent to remove the excess hydrogel material, and the silane coatings need to be reapplied before the curing process of silicone hydrogel.

5.2 Recommendations

Heat treatment should be applied on silane coated glass slides to improve the stability and durability of silane coatings. Silane heat treatment could help eliminate water, propanol from the surface of glass slides, and facilitate the formation of covalent bonds between silane coatings and hydrophilic substrates [93,94]. In the work of Yoshino et al. [75], glass slides were heated in the oven at 150 ºC for 2 hours after reacting with fluoroalkylsilanes at 47 ºC for 2 hours. While in the work of Metwalli, E., et al. [95], silane coated glass slides were baked at 110 ºC for 15 minutes.

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