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ANALYSIS OF BOND STRENGTH BETWEEN SILICONE AND POLY(METHYLMETHACRYLATE) IN CRANIOFACIAL PROSTHETIC APPLICATIONS

BY

JOHN IVAN WORONUK ©

A thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfilment of the requirements
for the degree of MASTER OF SCIENCE

in

ORAL BIOLOGY

FACULTY OF DENTISTRY

Edmonton, Alberta

SPRING 1995

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Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "Analysis of Bond Strength Between Silicone and Poly(methylmethacrylate) in Craniofacial Prosthetic Applications" submitted by John Ivan Woronuk in partial fulfillment of the requirements for the degree of Master of Science in Oral Biology.

Dr. T. McGaw

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Gary Faulkner
Dr. G. Faulkner

Dr. S. Wylie

Date: April 18, 1995

DEDICATION

This thesis is dedicated to my wife and our family with the sincere hope that in their lives they may find the joy and stimulation from their chosen fields that academic pursuits have provided [illegible] me. I must express my appreciation to each of my grandchildren for their love, patience and understanding when I was unable to fulfill the role of a typical grandfather.

TRACT

The silicone/poly(methylmethacrylate) bond common to many craniofacial prosthetic appliances frequently fails from stresses that resemble peel forces. This study measured the variables associated with the development of the bond between A2186 silicone (Factor II, Lakeside, Arizona, U.S.A. and commercial batch PMMA Acrylite®FF (Chemacryl Plastics Ltd., Rexdale, Ontario, Canada) through a peel test. The variables considered were the surface character of the PMMA (3); the wash methods prior to priming (2); the primers used (3); and the primer time (2). The results seemed to show that a smooth PMMA surface washed with methanol followed by an immediate distilled water rinse, primed with 92-023 primer (Dow Corning, Midland, Michigan, U.S.A.) and a 3 hour primer reaction time prior to the application of silicone dough produced the strongest bond.

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Numerous people have contributed to the completion of this document; some through encouragement and patience amongst whom I must single out my wife and family and others through sharing their knowledge and dedication to academic pursuits. To this latter group I am particularly indebted and I list their names in acknowlegement.

Dr. John Wolfaardt, whose guidance and supervision, his unparallelled dedication to the advancement of craniofacial and maxillofacial rehabilitation made this work applicable, exciting and possible.

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Dr. Rex Holland, who patiently guided me through the formalities of research and defense.

Dr. Simon Wylie, whose interest in this endeavor prompted him to accept the position of External Examiner in the thesis defense.

Mr. Phillip Coss, anaplastologist [illegible] our Craniofacial Osseointegrated Maxillofacial Prosthetic Unit (COMPRU) whose frustrations with adhesion failures prompted this investigation.

Mr. John Pinchbeck, my student corroborator who did much of the laboratory work and collected the volumes of data. His patience and critical analysis with the sometimes mundane repetition of procedures was remarkable.

Mr. William Winters from the Alberta Research Council who set up the testing equipment and did the preliminary "runs".

The staff at COMPRU: Trudy, Val, Betty and Pips and my own secretaries Donna and Lynne whose assistance in searches, in filing and in maintaining a constant cooperative atmosphere made my work pleasant.

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CHAPTER 1

BACKGROUND INFORMATION

1.1.1 Introduction

The need for significantly higher bond strengths between silicones used for facial prostheses and poly(methylmethacrylates) (PMMA) used as substructures became evident when craniofacial osseointegrated implants were used to successfully retain facial prostheses. The retention mechanics of structures attached to osseointegrated titanium implants permitted facial prostheses to gain high levels of retention. Bond failures occurred when the forces applied to remove the prostheses exceeded the bond strength.

The silicone prosthesis is bonded to PMMA and may constitute the visible part of the facial replacement (Figures 1 and 2). The PMMA substructure is a necessary constituent designed to contain retention elements that provide a firm support for silicone components.

Figures 1 and 2: Indicates debonding failure on an ear prosthesis. Note that the failure is not readily apprarent (figure 1) and requires careful examination to detect debonding along the margin between the PMMA and the silicone.

During placement and removal of the prostheses, the bond interface is subjected to forces that may cause the bond to fail. Failure is represented by either partial or total debonding of the silicone from the PMMA.

Partial debonding creates a space between the silicone and the PMMA substructure. The space may be inaccessible to conventional hygiene and provide an area for microbial growth. The extension of yeast colonization on silicone surfaces

Lemon, 1994). The proximity of these organisms to the skin surface is cause for concern. Yeast invasion of silicone surfaces appears to adversely affect certain properties of the material.

Any degree of debonding may constitute a total failure of the prosthesis and necessitate the reconstruction of the entire prosthesis. Repair methods have not provided adequate bond strength or a microbial seal.

The relatively recent development of the craniofacial osseointegration approach has provided a new challenge to the performance of facial prosthetic materials. Efforts to date appear not to have succeeded in producing predicable high bond strengths between silicones and PMMA appropriate to this application.

1.1.2 Objectives

The objective of the present research was to test the effect of several variables on the bond strength created by bonding A2186™ (Factor II, Lakeside, Arizona, U.S.A.) silicone to AcyliteFF® (Chemacryl Plastics Limited, Rexdale, Ontario, Canada), a bulk cured poly(methylmethacrylate) through a peel test. The variables chosen for this study were related to the surface character of the PMMA, whether:

1. smooth and clear, sanded or sandblasted;
2. cleansed with methanol and water, or trichloroethylene;
3. primers applied, A4040 (Dow Corning, Midland, Michigan, U.S.A.), 92-023 (Dow Corning) or A304 (Factor II, Lakeside, Arizona, U.S.A.), or none;
4. the application of the bonding agent was followed immediately by silicone application or allowed to remain in contact with the PMMA for 3 hours before the application of the silicone.

The data gathered were analyzed to determine any statistically significant comparative results from various treatments of the PMMA surface and from different primers. The experiment and the interpretation of the results were designed to separate the independent effects of each variable upon the bond strength and to evaluate any interaction effects of variable combinations upon the bond strength.

1.1.3 Hypothesis

The final bond strength tested under conditions of controlled temperature and barometric pressure between AcryliteFF and A2186 silicone is unrelated to:

1. The physical surface character of the PMMA substrate: (1) smooth (as available from its manufacturer); (2) sanded; (3) sand blasted.
2. The material and method used to cleanse the surface of the PMMA prior to the application of a bonding agent or silicone: (1) trichloroethylene (1,1,1-tichloroethane); (2) methanol followed by distilled water.
3. The choice of primer of the three types selected: (1) A4040; (2) 92-023; (3) A304 ; (4) none (control).
4. The length of time the bonding agent is allowed to affect the PMMA surface prior to the application of the silicone elastomer:
   (1) immediate (constitutes a period as brief as possible, a time of approximately 10 minutes);
   (2) 3 hours.

A null hypothesis was selected to protect an unbiased research objective.

1.2.1 Literature search

A search of the literature through Medline, Health and Inspec was carried out. Key words used were silicones and adhesives, craniofacial prostheses, osseointegration and facial prostheses, bonding silicones, bonding silicones to poly(methylmethacrylates), PMMA, silicones and primers, maxillofacial prostheses/ all subheadings, adhesives (explode), silicone-elastomers/ all subheadings, polymers (explode), tensile strength/ all subheadings, silicones (explode), poly(methylmethacrylates)(explode)/all sub-headings.

Readings at the Scott Medical and Cameron libraries at the University of Alberta were directed at developing an understanding of bond mechanics, bond forces and statistical analysis.

1.2.2 Literature description

The literature search began with a review of the standards established by American Standard for Testing Materials (ASTM) for testing peel resistance of adhesives. Four publications were appropriate to this research:

1. Designation D1876 - 72 (Reapproved 1983)

2. Designation D903 - 949 in Rees (Reapproved 1983)

3. Designation D1781 - 1876 in Rees (Reapproved 1986)

4. Designation D 907 - 91B.

Designation D907 - 91B titled Standard Terminology of Adhesives. The terminology used in this paper will follow the definitions accepted by this standard except where authors provide modifications to such definitions.

1.2.3 Definitions of Adhesion

ASTM defines adhesion as the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action or both (ASTM designation D907 - 91B).. Phillips (1982) states that there is adhesion when unlike molecules are attracted and cohesion when molecules of the same kind are attracted. Andrews (Andrews and Kinloch, 1973) states that current literature defines adhesion as the difference in surface free energies between the separated surfaces and the intact surface.

1.2.4 Adhesive and Bond Theories

There are several theories that explain bonding. Veysey and French discuss four such theories:

1. Mechanical interlocking theory states that adhesion may be created by or enhanced by interlocking the silicone to the PMMA.
2. The diffusion theory describes adhesion as a mutual diffusion of polymer molecules across the interface. This presumes a degree of solubility to the macromolecules of the polymer chain.
3. The electronic theory states that unlike materials have different electronic bond structures and a balanced condition is achieved by electron transfer. This presumes a doubled electron charge at the interface and thereby creates an adhesion.
4. The absorption theory suggests that if sufficient intimate intermolecular contact is achieved at the interface, the materials will adhere due to surface forces acting between atoms. This theory raises the possibility of chemisorption where actual ionic covalent bonds may operate across the interface.

Cohesive forces provide the strongest bonds but since the PMMA substrate and the silicone normally have differing surface molecular structures, cohesive interfacial bonding may not be possible. The adhesion that is possible at the interface of these polymers may be created by van der Waals forces in combination with mechanical interlocking. The adhesion may be dependent on the surface characteristics of the substrate in accordance with the absorption and mechanical theories referred to above.

1.2.5 Surface of substrate (PMMA) research

Some literature states that the surface preparation of the substrate affects the bond strength. Amin (Amin, Fletcher and Ritchie, 1981) and Kawano (Kawano, Dootz, Koran and Craig, 1992), reported that bond strength of silicones bonded to unprimed PMMA in denture lining was greatest using smooth PMMA substrate surfaces. The testing was performed after the test samples were immersed in water for a period of time and compared to a control of non-immersed samples. The results in both tests showed uniformity.

Udagama (1987) reported on testing several polymers for their capacity to bond with silicone. Ethyl methacrylate, polyvinyl butyrate, methyl methacrylate, polyvinyl acetate, corrugated polyethylene, polyvinyl chloride and polyurethane were bonded to silicone. The researchers chose to treat the substrate with either hot acetone or to heat the substrate after acetone application. The results showed that polyurethane provided the best base for this facial prosthetic application. However, all applications failed either from bond failure or from discoloration within a relatively short period of time.

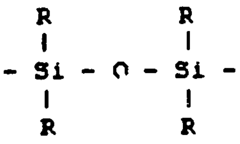
Inconsistent results from previous research indicate that the nature of the surface of the substrate is a variable that deserves further evaluation. Tests have shown that the surface character of the PMMA substrate affects the bond (Soulong and Setchell, 1991; Davis, Moser and Brinsden, 1976). These tests bonded dental impression silicone to impression tray material and did not clearly parallel the objectives of the current research. McMordie and King (1989), in evaluating primers used for bonding silicone to denture base material, chose to sand the surface before primer application. The paper does not indicate the reasons for this preference.

1.2.6 Properties of silicones in facial prosthetics

Silicones used in facial prosthesis construction must exhibit the necessary properties of tissue compatibility, skin-like texture as well as ease in laboratory prostheses manufacture. Some room temperature vulcanizing (RTV) addition and condensation type silicones appear to satisfy these conditions. They are usually available in two components which are mixed together as base and catalyst.

Most dual mix RTV silicones are catalyzed by metallic salts of carboxy acids. The terminal end of the polymer chain is usually an -OH group which is reactive and capable of uniting with adjacent polymer chains through the process of end linking, thus rapidly producing long chains. The process can be accelerated by the addition of heat. Cross-linking is achieved by the addition of initiators such as tetraethoxy silane. Various fillers usually of very fine silica are added to give the final consistency to the silicone.

The vulcanized silicone product has a chemical structure with unreactive methyl groups forming the terminal ends of most of the R branches.



$$-\underset{\substack{|\\ R}}{\overset{\substack{R\\ |}}{Si}}-O-\underset{\substack{|\\ R}}{\overset{\substack{R\\ |}}{Si}}-$$

The low reactivity of the R groups of the silicone oxygen backbone in this type of silicone is responsible for the low surface energies which make the material difficult to bond to other substances.

Bonds dependent upon interatomic forces are more difficult to achieve when crosslinked elastomers are employed (Ahagon and Gent, 1975). The selection of silicones for craniofacial prostheses where bonding to PMMA is essential, would be better served by long chain polymers. These polymers provide more free radicals, primarily silanols, to form bonds with the adjacent substrate. Cross-linked silicone polymers provide the necessary elasticity essential to facial prostheses but lack the end silanols that are effective bond producing radicals.

Sandrik and Vacco (1983) compared the bond strength of addition and condensation type impression silicones. Their findings indicated that addition type silicones provided a higher tensile bond strength than the condensation type. Addition type silicones are generally vulcanized at room temperature (RTV). They consist of two separate components that are mixed together to initiate the vulcanization process. These components are usually a silanol terminated gum, which constitutes the first part and a catalyst as well as a cross-linking agent comprising the second component (Saunders, 2nd Edition).

Condensation type silicones may also be room temperature vulcanizing. Several catalysts are capable of initiating the condensation process from which ethanol is the usual byproduct. The production of a soluble byproduct may affect the dimensional stability and where that property is an essential factor, condensation type silicones may be inappropriate (Phillips, 1982).

Sanchez (Sanchez, Moore, Cruz and Chappel, 1992) compared the physical properties of polydimethyl siloxanes used in facial prostheses. This study compared a traditional MDX 4210 to the newer A-2186 silicone. The latter was found to have greater tear resistance, tensile strength, and elongation. The physical properties of A-2186 includes RTV convenience and appears to be biologically compatible with human tissue.

1.2.7 The primers

The purpose of primers is to improve the adhesive bond between two substances. Primers are chemical substances that coat the surfaces of substrates and act as coupling agents in preparation for adhesion. Their formulation depends upon the specific substances with which they interface (bond specific).

Primers are low viscosity liquids containing reactive silanes such as tetra (2-methoxy) silane (Raymond, 1977; Hulterström. An appropriate primer would generate surface free radicals that would allow intermolecular bonding to occur between the primer and the adherend. Cohesive bonds may develop when matching surface molecules occur at the bond interface. Numerous primers have been formulated that purport to improve the bond between silicone and poly(methylmethacrylate) (see **2.2.4**).

The formulation of most primers is protected under patent. New Product Information bulletins issued with primers used in the present study state that they are silane couplers and may contain naphtha, a flammable solvent. Such solvents act as carriers for chemicals that provide the necessary radicals for bonding. They may also act as wetting agents to enhance the distribution of the bonding agents over the surface of the adherend with minimum application.

Singer (Singer, Mitchell and Pelleu, 1988) peel-tested the bond strength of silicone elastomers bonded to polyurethane and reported that without primers, no measurable bonding occurred. This study reported significant variance in bond strength with different primers and different silicone elastomers. Under some test conditions, <u>unzipping</u> occurred. This phenomenon was described as <u>a sudden releasing of the bond during force build-up prior to peeling or during the peeling process</u>. In some tests, following unzipping, peeling forces tended to remain at a low level. In other tests, peel forces regained or exceeded their initial level. The researchers offered no explanation for these observations.

1.2.8 Contaminants to the bond surface

Water constitutes a contaminant to the bonding surface. It negatively affects silicone polymerization which results in lowering the bond strength. Platinum or other metalic salts act as catalysts are used in addition type silicones to initiate vulcanization. This process involves the mixing of the catalyst with a hydrogen terminated silane base. The platinum and the silane become inactivated in the presence of water (Braden and Wright, 1983).

Some silicones are highly water sorbent. Enlarged silicone volume can cause strain to the bond interface. The work of Braden and Wright (1983) measured the degree of absorption of water by silicones after polymerization. They noted that with some silicones, ethanol was a byproduct of polymerization and was rapidly extracted by water. The metallic salt produced in RTV vulcanization also dissolved in water. This process caused some silicones to lose more than 7% of their soluble materials. On removal from water, these materials were lost to the silicone and potentially affected dimensional stability.

Kahn (Kahn, Martin and Collard, 1989) reported similar findings with addition type silicones bonded to Triad ™ (Dentsply

International Corp., York, Pa., U.S.A.) a visible light cured PMMA resin. Testing bond strength followed storage in water for varying periods of time. The results showed a progressive bond weakening as a function of time of immersion. Such findings may indicate a characteristic of some condensation and addition type silicones. Water at the silicone-PMMA junction during vulcanization may be a contaminant.

The current research attempted to exclude water in the bonding and bond testing process. Manufacturer's recommendations stated that trichloroethylene and acetone be employed as desiccants in preparing the PMMA surface for the application of the bonding agents (see **2.2.4 Selecting the wash methods**). These organic solvents are effective in removing water and organic contaminants from the surface of the PMMA but they can affect the surface character of the substrate. AcryliteFF, the PMMA polymer selected for this study, is described by its manufacturer as not resistant to either trichloroethylene or to acetone. Non-resistance is defined as causing to become swelled, dissolved or damaged in some manner (Physical properties of Acrylite®FF PMMA sheet).

Silicone manufacturers supply or recommend a primer for their product. Pretesting, however, indicated that primers from manufacturers unrelated to the silicone may provide stronger bonds[27] (see **2.2.5 Selecting the primers**).

1.2.9 The rationale and mechanics of peeling

The loads applied to a bond which lead to bond failure may be measured by mechanical means and estimated by mathematical means. A joint can be loaded by tensile, compressive, flexure or shear forces. Peeling may be considered a combination of these loads and resembles the load responsible for bond failure in anchored craniofacial and maxillofacial prostheses. Two characteristics of peeling are necessary in evaluating a peel test:

1. The peel test can control the rate of failure.
2. The peel force and time relationship is a direct measure of the work of detachment (Gent and Schultz, 1972).

The mechanism of peeling requires that at least one substrate be extremely flexible. Geometric and loading forces are incurred when flexibility is represented as elasticity. These forces are difficult to evaluate and theoretical analysis does not readily apply. Such testing is complicated by rheological energy losses in the adhesive and substrate. From the strict mathematical perspective,

$$\theta = P$$

where θ represents a characteristic amount of energy per unit area of separation and where P is the peel force per unit width of the test sheet (Veysey and French). This simplistic formula does not, however, effectively consider the complexities of peeling elastomeric adhesive materials. Gent and Hamed (1978) in studying adhesion of elastomers using peel testing concluded that

$$P = E_a + E_s + E_d$$

where

- P = the surface energy required for detachment
- E_a = energy dissipated within the adhesive
- E_s = energy dissipated with the stripping member
- E_d = energy of the newly detached strip (normally considered of little consequence).

This interpretation suggests that the work required to cause adhesive failure is the sum of:

1. thermodynamic surface energies arising from dispersion or chemical bonds acting across the interface;
2. mechanical energy dissipated by irreversible deformation processes within the adhesive;
3. energy dissipated within the adherend during detachment.

It is apparent from 2 and 3 (above) that if the thickness of layers of adherend and adhesive were infinitesimal, then the total energy expended may approach that of θ where $\theta = P$. However, as the thickness of the elastomer increases, there may be a proportionate increase in deformation energies stored within the elastomer. An accumulation of these energies occurs at or near the peel line. Eventually, this accumulation will cause the bond to fail. In a theoretical model the load at this point would constitute a mathematical constant since the bond strength would equal the accumulated energies stored within the elastomer stressing the bond (**Fig. 4**).

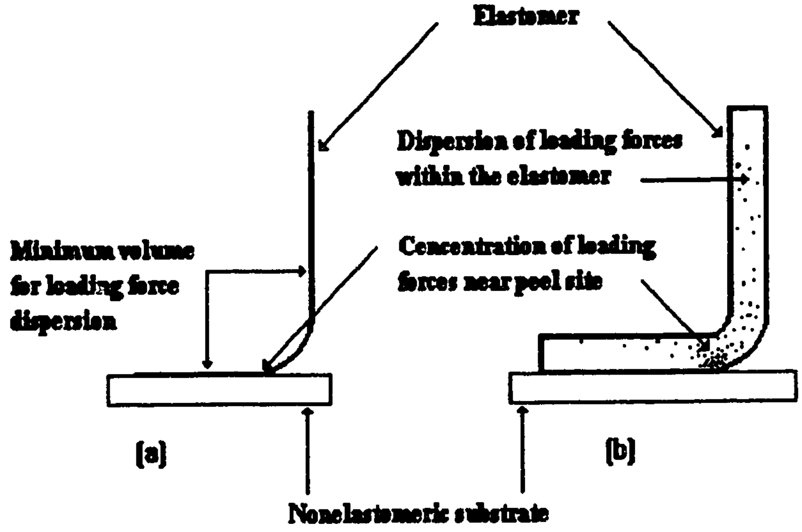


Figure 1.3: Schematic diagram comparing (a) an ultra-thin and (b) a thick elastomer bonded to a nonelastomer. The possible distribution of peel energy is indicated by stippling. The minimal volume of elastomer may prevent the dispersion that is apparent in (b).

Thermodynamics dictates that both temperature and rate of peel are factors associated with peel energies. Gent and Hammed (1978) reported that the peel characteristics of simple elastomers adhered to a solid substrate varied with the speed of detachment and temperature. They stated that this observation was in general agreement with the Williams, Landel and Ferry (WLF) rate-temperature equivalence theory governing the motion of molecules. The experimental results may closely parallel a mathematical model under conditions where temperature is stabilized and rate of peel approaches zero. In the current research, stable temperature was possible, but the extremely low peel rate was not practical.

A recent study on peel strength of resilient denture liners was published by Kutey (1994). This work measured the peel and tensile bond strengths of four different resilient liners bonded to Lucitone 199 (Dentsply International, York, Pa.) denture base PMMA resin. The peel rate was reduced to 5 mm/min to ensure measurement of adhesive bond strength rather than cohesive failure. A 180° peel angle was selected as suggested by a study reported by Fowler (1968). This study suggested that a more specific line was present demarcating the site of separation when this angle was used.

Andrews and Kinloch (1973) stated that two energy components are possible in creating a condition leading to adhesive failure:

1. The energy dissipated viscoelastically (θ), within the elastomer at the point where peeling occurs.

2. The intrinsic adhesive failure energy (θ_0). The intrinsic adhesive failure energy is related to the surface properties and composition of the materials forming the joint.

Their observations have shown that the energy dissipated in the elastomer deformation at the point of the crack θ is the dominant cause of thermodynamic adhesive failure. θ_0 tends to be independent of the rate of peel or the temperature. Its value depends on the type and strength of the bonding forces at the interface.

1.3.0 Rationale of the peel angle

ASTM [2] selected the angle of 90° when peeling a silicone from a nonelastic substrate. Lake and Stevenson[35] described testing angles from 10° to 180°. Their findings indicated that higher degrees of consistency occurred using angles between 40° to 130° The current research selected an angle of 90° as a midpoint between the range suggested above and used in ASTM testing.

CHAPTER 2

MATERIALS AND METHODS

2.1.0 PRETESTING

2.1.1 Test leading to final experimental design

Twelve flat wafers measuring 2.5 cm^2 were prepared from Flexacryl (Lang Dental Manufacturing Company Inc., Chicago Ill., U.S.A.) self curing denture PMMA. Each was treated by either sanding, sand blasting or polishing and primed with different primers. A2186 silicone was bonded to the treated surfaces and allowed to vulcanize at room temperature. The silicone from each of the strips was peeled by hand and a comparison of the force necessary to bring about peeling was subjectively noted. This pretest suggested that significant differences in bond strengths occur by using various combinations of surface character and primers.

A curing flask was designed following consultation with the Faculty of Mechanical Engineering University of Alberta, Edmonton, Alberta Canada, and members of the Craniofacial Osseointegrated Maxillofacial Prosthetic Rehabilitation Unit (COMPRU), Misericordia Hospital, Caritas Health Group, Edmonton, Alberta Canada. The flask supported six strips of PMMA AcryliteFF, (Johnson Plastics, Edmonton, Alberta Canada) to which 50 gm. of

A2186 silicone dough could be applied (for details, see **2.1.2 The curing flask**).

A jig was designed to support the test samples during the peeling process. The design was based on ASTM standard #D3167-76, Reapproved 1986 (for details see **2.1.3 The testing jig**).

Acrylite®FF, [illegible]cially available bulk cured PMMA was selected to [illegible] consistant high degree of physical and chemical properties. This material is available with a highly polished glass-like surface covered by a protective synthetic film.

The remaining equipment consisting of a curing oven (Secatherm 100, Bego, Bremen, Germany) and vacuum system (Nalgene™ Vacuum Chamber, Nalge Company, Sybron Corp., Rochester, New York, U.S.A.) was available in the laboratory of COMPRU.

2.1.2 The curing flask

A curing flask (**Figure 2.1**) was constructed (Maverick Surgical, Misericordia Hospital, 16940 - 87 Ave. Edmonton Alberta Canada). The flask consisted of 3 sections, made from stainless steel: a flat top, a milled center section which supported the PMMA strips and a base milled to contain the silicone. The milling was designed to support a PMMA substrate blank 214.20 mm X 19.05 mm X 6.00 mm. The base was milled to contain a channel for a quantity of silicone that when vulcanized would measure 201.60 mm in length and 6 mm thickness and 12.7 mm. in width. The silicone channels were designed to align with the PMMA strips.

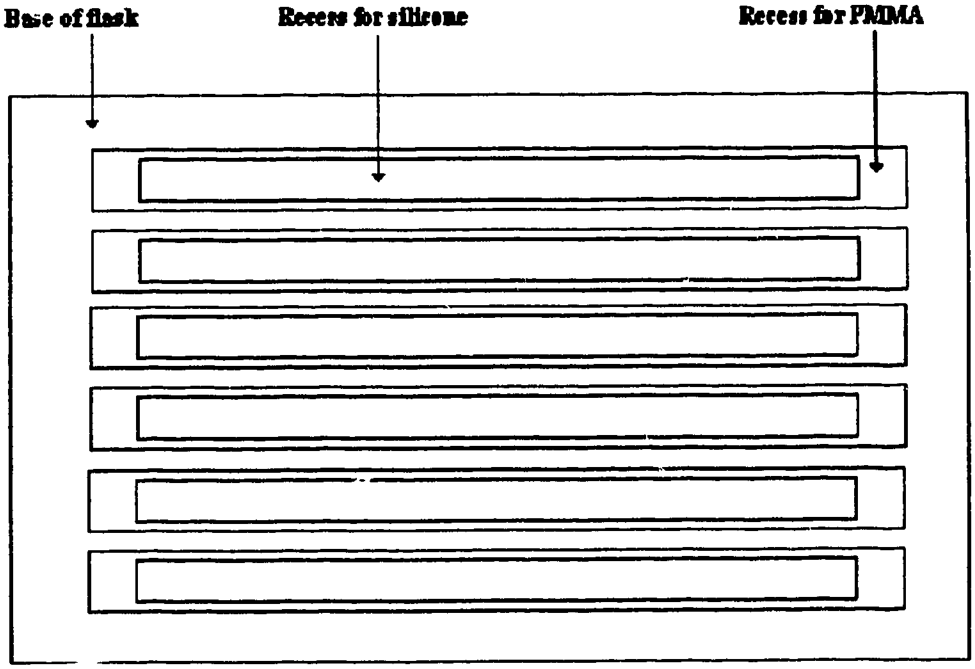


Figure 2.1

Schematic of curing flask base and center insert showing the recesses for the PMMA strips. The base represents the portion beneath and shows the recess for the silicone dough

The flat 6.0 mm stainless steel top covered the center section and provided a bearing surface for the flask press.

2.1.3 The peeling test jig

The jig consisted of two independent rollers and a rounded mounting post bolted together in a triangular pattern (**Figure 2.2**). These were spaced apart to allow a test strip to pass between one roller and the PMMA glide while permitting the debonded silicone to pass between the upper pair of rollers. The rollers were equipped with stainless steel ball bearings in order to reduce friction during the peeling process.

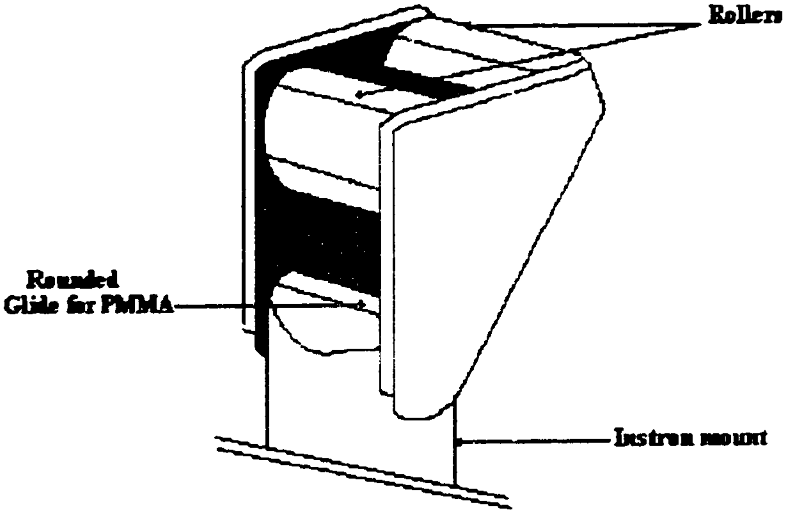


Figure 2.2 Schematic showing the peeling test jig based on design from ASTM standard.

The roller design aided in controlling the release of the energies stored in the elastomer during the elongation process prior to and during peeling and maintaining a consistant angle at the point of peel. The design assisted in limiting the amount of peeling that would occur through sudden energy releases within the stretched silicone when the adhesion limit was reached. The diameter of the pulley against which the silicone bears assisted in maintaining a fairly constant peel angle (**Figure 2.3**).

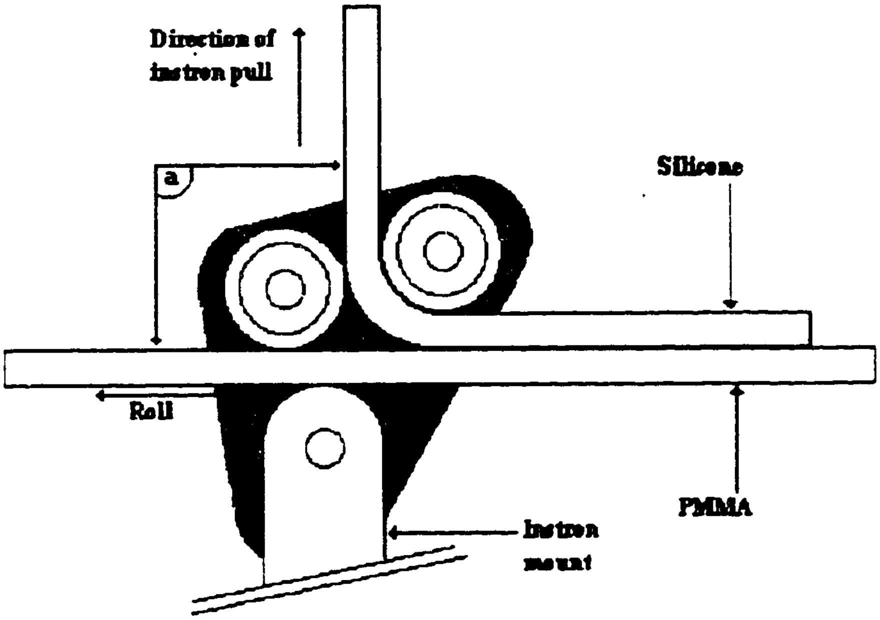


Figure 2.3: Cut-away schematic view of the testing jig showing the process of peeling. The Instron vise is attached to the detached silicone wafer placing a peeling force against the PMMA-silicone junction at a peel angle (a) of 90°.

2.2.0 EXPERIMENTAL DESIGN

2.2.1 Sample size

The sample size was determined on the basis of 4 repetitions of each of the prepared samples to provide a base for statistical analysis and to remain within budget.

The sample size considered the analysis of all variables within the scope of the current research. The end point of the research required the analysis of the effect of time (T) that the primer (P) remained in contact with the PMMA prior to silicone application. The following distribution allowed testing each event 4 times.

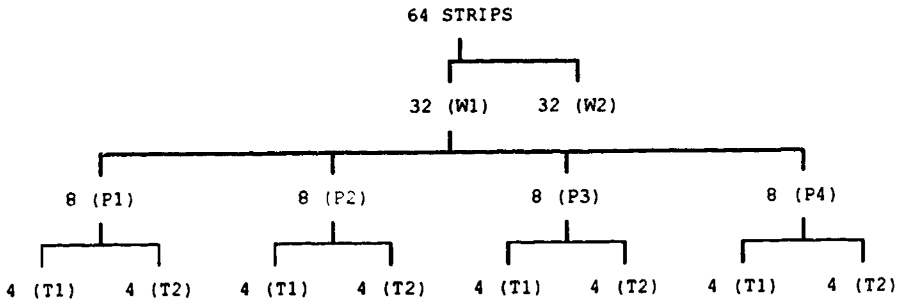


Figure 2.4: Chart showing the sample distribution of one half of the 64 strips used in the current research. W1 = wash method one; W2 = wash method 2; P1,2,3,4 represent the 3 primers and the no primer control; T1,2 represents the two time periods. The remaining 32 strips represented as 32 (W2) were treated identically and are not shown beyond the wash stage.

The total sample size was determined by the following distribution:

1. The first variable considered was the surface character of the PMMA. Two roughened experimental surfaces were chosen and the control selected was AcryliteFF in its manufactured form characterized by its smooth surface. Surface characteristic (SC) = 3
2. Two wash methods for cleansing the PMMA surface prior to priming were used:. Wash methods (W) = 2
3. Four primer types were tested; commercially available primers (3) and a control of no primer. Primer (P) = 4
4. Two time periods tested the effect of primer in contact with the PMMA substrate. Primer time (T) = 2)
5. Each sample was tested 4 times: N = 4

Total tests for each strip = SC * W * P * T = 3*2*4*2 = **48**

Total tests of all samples = 48*64 = <u>3072</u>

2.2.2 Selecting the poly(methylmethacrylate): PMMA

Consideration was given to PMMA that was unvarying in its chemical composition. Commercial grade bulk cured PMMA in the form of Acrylite®FF was thought to provide more consistency of the chemical and physical properties based on batch processing. The material selected measured 6.00 mm in thickness and was transparent and colorless. A band saw equipped with a standard 0.25 inch blade was used to saw the PMMA into strips 19.05 mm (0.75 inches) wide and 214.20 mm (8.50 inches) long. The cut edges were manually smoothed with a flat metal file.

2.2.3 Selecting the silicone

A2186 elastomer base and catalyst (Factor II, Lakeside, Arizona U.S.A.) was selected. This silicone was, at this time, in routine clinical use and appeared to possess desirable physical properties for human facial prostheses. It appeared to be biologically compatible with skin and produced no known byproducts during vulcanization that were irritating to human tissues.

This silicone is a room temperature vulcanizing (RTV) silicone and is catalyzed by platinum salts. Cross-linking is made possible by the inclusion of specific silanes which promote cross-linking during vulcanization (Raymond, 1977).

When vulcanized, A2186 silicone is typical of most dual mix RTV silicones displaying low surface energies causing resistance to bonding to other materials (see **1.2.6**).

2.2.4 Selecting the wash methods

Cleansing the surface of the PMMA prior to prebond treatment or bonding was considered necessary to leave the surface free of debris and water or oil contaminants. Trichloroethylene, acetone and other organic solvents were recommended by silicone manufacturers. Trichloroethylene was selected as the test material because it is recommended in several silicone instructions sheets. Methanol followed by a distilled water rinse was selected as a control because methanol contains the methyl groups that constitute the major radicals in PMMA. The immediate water rinse was selected to dilute the methanol and reduce its action upon the PMMA surface.

2.2.5 Selecting the primers

Three primers were selected for enhancing the bond strength. These primers were chosen from 2 different manufacturers that provide silicones suitable for facial prostheses. They were:

1. A4040 (Dow Corning, Midland, MI, U.S.A.)
2. 92-023 (Dow Corning, Midland, MI, U.S.A.)
3. A304 (Factor II, Lakeside, AZ, U.S.A.)

The New Product Information bulletin (1989) issued by Dow Corning Corp. relative to silicone primers refers to its products as silane couplers which may contain a flammable solvent that may be naphtha. Factor II provides information in their Safety Data Sheet (02/23/93) that their silicone primer belongs to the Silane - Titanate family. Its composition is 85% naphtha, 5% each of tetrapropylorthosilicate, tetrabutyl-titanate and tetra(2-methoxyethoxy) silane.

Naphtha is a volatile chemical that slowly evaporates at room temperature. Dow Corning advises that its primers reach a nonvolatile level of 10.6% after 6 hours at 46° C. This information would suggest a lengthy primer reaction time to allow for complete elimination of the naphtha prior to applying the silicone. The instructions with their product, however, suggest a period of 90 minutes.

2.3.0 THE EXPERIMENTAL MODEL

2.3.1 Preparation of the substrate (PMMA)

Precut Acrylite FF sheets measuring 214.20 mm X 151 mm covered with a protective self-adhering synthetic wrapping were obtained. Each sheet was measured and marked across its width according to the measurements illustrated below (**Figure 2.5**).

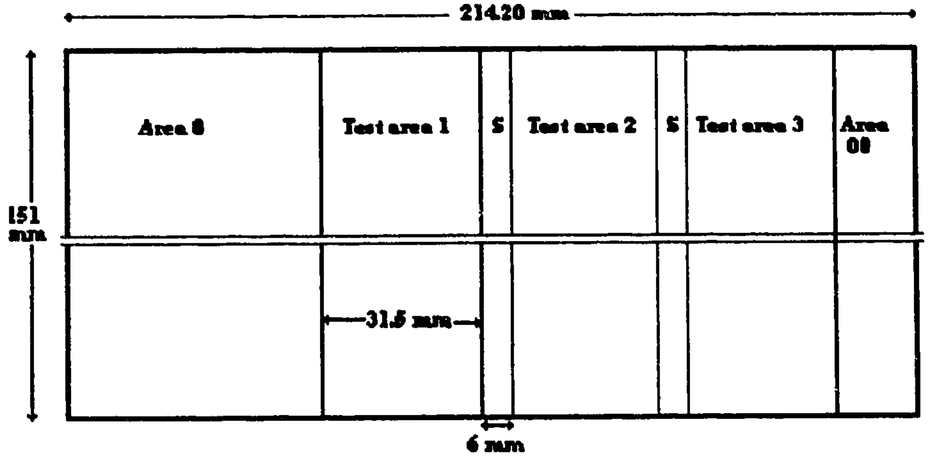


Figure 2.5. Schematic of PMMA sheet showing test areas corresponding to the surface treatment characteristics. Area 0 = unbonded for Instron grip to grasp the silicone; Test area 1, 2, and 3 = surface treatment; S = unbonded to separate each test area; Area 00 = glide area for Instron jig balancing pulley.

The AcryliteFF sheets were available in several thicknesses. A 6 mm thick product was selected to fit into the curing flask. This thickness seemed appropriately rigid for the purposes intended.

Rigidity was considered essential to withstand the expected peel forces with minimal distortion to the PMMA substrate.

2.3.2 Rationale for the random surface sequence

Pretesting different surface characteristics for protocol design indicated that bond failure occurred from significant variations in the amount of applied load. The load measurements varied from 2.1N to 10.0N. This variance suggested that problems may occur when transferring the load from one surface characteristic to another during peeling. The problem was anticipated when the peel load was high and moved to a surface where the peel load was low. The energy transfer stored in the elastomer and applied to the adjacent surface could cause data inaccuracies.

Two approaches were used to adjust for this potential problem:

1. Each test area was separated from the adjacent by 6 mm of unbonded space. This space was intended to release the applied load before testing began on the next test area. It provided the time to decrease the applied load manually by adjusting the Instron testing machine.
2. Randomizing the order of the surface preparation on each strip allowed unbiased statistical management of problems associated with energy transfer.

Sheets of AcryliteFF that were visibly free of surface defect were selected. Each sheet would produce 6 strips after cutting to size. The protective covering was removed from alternate 31.5 mm spaces and the exposed PMMA was sandblasted using a Campbell Hausfeldt sandblaster Model 1851 (Campbell Hausfeldt Manufacturing Co., Harrison, Ohio, U.S.A.). High quality silica sand triple screened to 75 mesh was blasted at 550 Pa (80 lbs.in^{-2}) air pressure. The nozzle used was a size 3 (0.5 mm) hand held at an approximate distance of 250 mm with the sheet of PMMA at an angle of approximately 120°. This process required approximately 5 seconds of time.

A second 31.5 mm section was then exposed and hand sanded with 120 grit aluminum oxide commercial sand paper. Care was taken to sand up to the protective cover separating one test area from another. This procedure required approximately 20 seconds to complete.

The third 31.5 mm section was left protected since it would constitute the smooth control area for the comparative study.

All sheets were prepared by this method. The order of the surface treatment was randomized which produced all possible combinations of location of the treated surface. Each sheet was sawed into 6 identical strips for repetitive testing. The cut borders of each sheet were debrided manually using a fine file confined to the sawed surface. The dimensions of each strip were 214.20 mm X 19.05 mm. This size was appropriate for the curing flask.

Each strip was marked on the side opposite its prepared surface according to the nature of the surface treatment. Sandblasted was marked with a "B", sanded with an "S" and the clear area marked with a "C".

Six combinations were designed for testing:

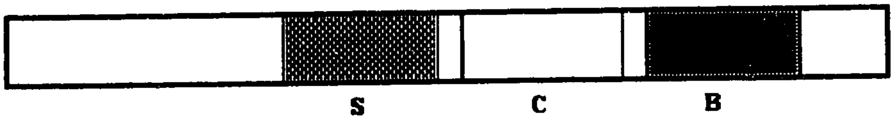


Figure 2.6. Schematic of a PMMA strip showing a distribution of SCB indicating S = sanded; C = clear; B = sandblasted.

CBS BSC SBC

CSB BCS SCB

The 6 mm space separating the treatment surfaces was left protected. Each strip was cleansed by a compressed air jet to remove loose particles from the sandblasting and sanding.

The six strips for each <u>set</u> were selected representing one strip from each of the 6 possible combinations and these placed in the flask in random order.

2.3.3 Preparation of the control and experimental group

A soft nylon bristle brush was used to scrub the test areas of the control set with methanol to remove soluble surface contaminants followed immediately by a distilled water rinse. The strips were allowed to air dry before inserting into the appropriate slots in the curing flask. To compare each of the 3 surface characteristics against each primer required 8 sets each containing 6 strips.

The effect of trichloroethylene as a wash agent was compared with a control of methanol/water. Trichloroethylene was allowed to air dry in the same manner used for the control.

Primer time was defined as the time the primer is allowed to react with the surface of the PMMA prior to the application of silicone. Primer time was tested by comparing 0 time the control (as brief as possible), to 3 hours, the experimental time. Half of the sets were treated as controls and the other half as experimental models.

2.3.4 Preparation of the silicone

1. 150 grams of silicone was weighed and placed into a 500 cc beaker.
2. The manufacturer's recommended amount of catalyst was added and the mixture thoroughly mixed using a plastic blade spatula.
3. The beaker was placed under a vacuum jar for degassing at a pressure of -55 mm (-22 in) Hg. The silicone effervesced rapidly under vacuum. When the beaker became filled, the vacuum was disconnected allowing a sudden compression which tended to fracture many air bubbles. This procedure was repeated 3 times.

2.3.5 Silicone application to primed PMMA

The highly viscous silicone was spatulated into the appropriate channels designed within the flask assembly. Care was taken to flow the silicone with a minimum of interruption in order to minimize air entrapment. Once the channels were filled, the PMMA strips were applied by introducing the test side surface to the silicone at one end and gradually lowering the other end allowing an avenue for air escape. All 6 strips were applied as rapidly as practical.

The cover plate was positioned and the prepared flask was placed in a manual press and tightened until no further silicone excess was being expressed. The flask was allowed to remain in the press for 90 minutes.

The flask was clamped using "C" clamps and transferred to the preheated oven (Secatherm ICO, Bego, Bremen, Germany) at 49° ± 3° C for 2 hours as per instructions with A2186 silicone.

Upon removal from the oven, the flask was allowed to cool to room temperature, the clamps removed and the AcryliteFF strips with the bonded A2186 silicone recovered. A sharp trimming knife was used to cut away any silicone flash. The test strips were later transferred to the testing laboratory where they were stored in a controlled environment (see **2.4.1**).

2.4.0 MEASURING THE BOND STRENGTH

2.4.1 Pretesting bonded samples

Pretesting was conducted on several samples of bonded silicone to AcryliteFF to determine problems that may occur during the experimental run. Two problems were identified:

1. Silicone elastomer volume tended to escape from the gripping mechanism of the Instron with the increase in the applied load.

The result was equivalent to a reduced volume of silicone within the grip space leading to the sudden release of the silicone wafer. Periodic retightening of the grip mechanism was necessary to prevent the silicone from slipping. This manipulation produced large fluctuations in the data due to the loads applied manually and was identified as null data during that time interval.

2. The elastomeric nature of the silicone caused energy to be stored within the elastomer and influenced the measurement of direct force to the peel surface. This effect was represented by indefinite starting points of the peel since the load energy was being stored within the stretching silicone.

To overcome these problems, consideration was given to including an inflexible screen embedded into the exposed surface of the silicone wafer (**Figure 2.7**). The presence of this screen was intended to allow very limited elasticity during the loading process and largely exclude volume flow from the grip mechanism and the effect of energy build-up in the elastomer. Conventional screen-door nylon or wire mesh was adapted to the base of the flask over which the silicone dough was applied. Vulcanizing procedures remained the same as previously described (see **2.3.4**). Neither the metal nor the nylon screen adhered to the silicone during the peeling test. This modality was abandoned.

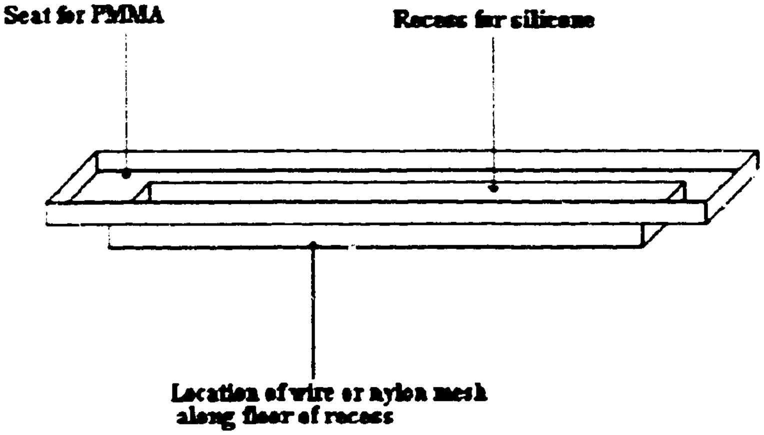


Figure 2.7: Schematic showing the relationship between mesh, silicone and PMMA

2.4.2 Preparing the bonded strips for peel testing

Following removal from the flask, the bonded test strips were allowed to rest for approximately 24 hours prior to transferring to the controlled environment in the peel testing laboratory. This time period was selected to allow further polymerization to occur and simulated a clinical time between prosthesis construction and its eventual placement.

Testing was carried out at the Alberta Research Council laboratories, 250 Karl Clark Road, Edmonton, Alberta. Test strips were stored for a minimum of 3 hours in a controlled environment maintained at an ambient temperature of 22° ± 1° C and a relative humidity of 58% ± 4%. The controlled environment was maintained throughout the peel test.

2.4.3 Setting crosshead speed and computer readings

The crosshead speed of the Instron testing machine was set at 50.8 mm (2 in) per minute. This speed was selected based on ASTM testing. The computer was configured to make readings at a rate of 10 data points per second and this data was stored in Microsoft Excel version 5.0 software (Microsoft Canada, Mississauga, Ontario Canada). Each recording was identified on the computer according to the code of the strip being tested.

Each bonded test strip was inserted into the Instron jig and the unbonded silicone tag was attached to the Instron grip. The hydraulic ram was calibrated to rise at the selected rate of 50.8 mm per minute. The computer was configured to begin readings as the slack within the silicone disappeared. Readings continued until the silicone wafer was peeled from the substrate PMMA throughout the full length of the strip (**Figure 2.8**). This method was used to peel all test strips. When tightening the grip mechanism was necessary, the data during that time period was marked for exclusion from the results.

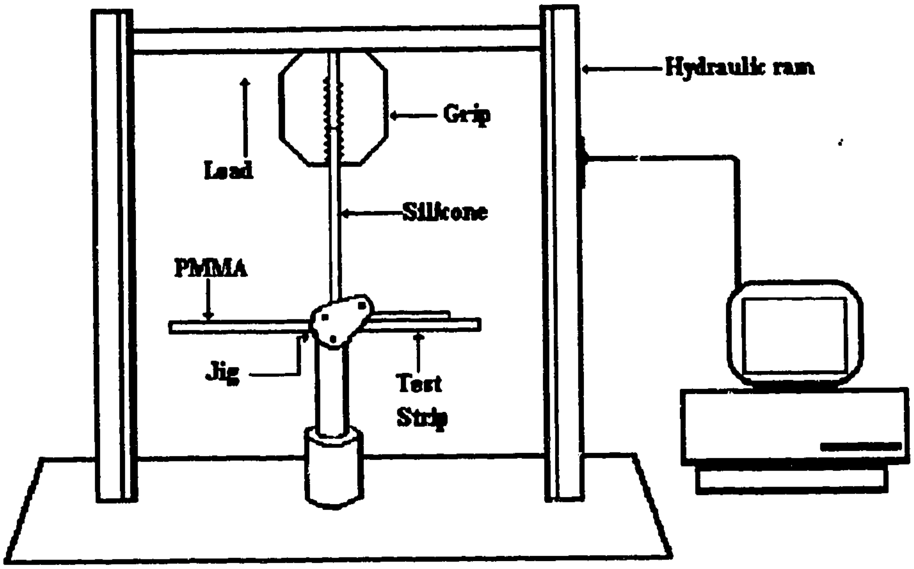


Figure 2.8. Schematic of Instron Testing Machine showing mechanics of peeling and recording of data.

Instances of cohesive failures occurred in which the silicone fractured between the grip and the peel line. When this occurred, data collection was terminated. The data were accepted only when fracture occurred in the last of three treatment surfaces and sufficient data were collected prior to fracture (>100) to permit analysis; otherwise all the data from the peel test on that specific strip were rejected.

In some tests, the force required to initiate peel on one surface treatment was several times the value necessary for the remaining surface treatments. In these cases, the 6 mm space separating the test areas was insufficient. This condition caused unzipping to occur in the low bond strength areas (see **1.2.7 for definition of unzipping**). Where this problem occurred, the data from the strip was not factored into the statistical analysis unless the peel rate was stabilized for a sufficient period of time for the data collected to be statistically valid. Validity was determined by the recording of a minimum of 100 data points Graphically, the time along the X-axis indicated data collected over 10 seconds. This represented a space of not less than 1.5 cm of test area of the surface treatment.

CHAPTER 3

STATISTICAL METHODS AND RESULTS

3.1.0 Statistical methods

3.1.1 Sample size and distribution of variables

Data was collected from peeling 64 strips each of which represented 3 surface characteristics. The treatment of these strips through the bonding process is represented by Figure 2.4, repeated below as Figure 3.1 for the convenience of the reader.

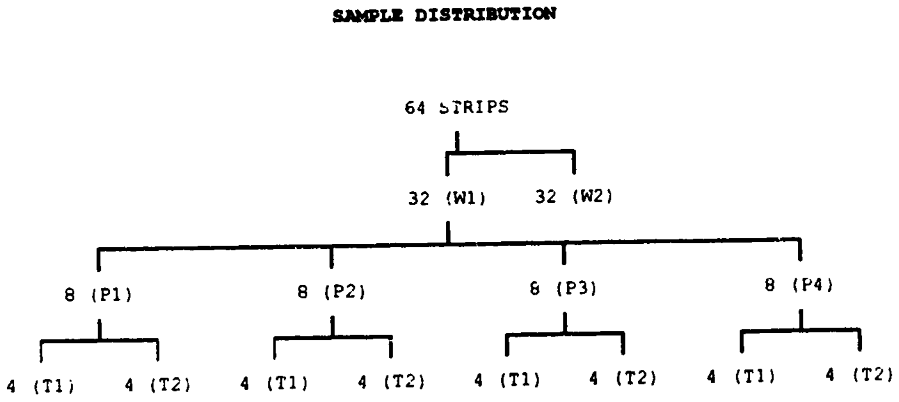


Figure 3.1: Chart showing the sample distribution of one half of the 64 strips used in the current research. W1 = wash method one; W2 = wash method 2; P1,2,3,4 represent the 3 primers and the no primer control; T1,2 represents the two time periods. The remaining 32 strips represented as 32 (W2) were treated identically and are not shown beyond the wash stage.

3.1.2 Organizing the data for analysis

The data collected from the Instron/computer recordings represented approximately 1,800 ,000 data points. These were plotted to designate silicone stretch as a function of time along the X-axis and force applied on the Y-axis. All measurements were collected in U. S. Customary System of Units (English) measurements and were converted to metric; the X-axis from inches to centimeters by the function X′ = X * 2.54 and the Y-axis from pounds per square inch to Newtons of force by the function Y′ = Y * 4.45. Each segment of all PMMA strips was plotted with beginning and end points of each plot identified. Within each segment the following data were computed:

a. the slope of the debonding force curve

b. the maximum debonding force attained

c. the minimum debonding force measured

d. the range of the debonding forces (maximum-minimum)

e. the average of the debonding force data

f. the standard deviation of the debonding force data

g. the standard error of the debonding force data

3.1.3 Identifying the debonding force variables

The maximum, minimum and the average constituted estimates of the amount of force required to create the initiation and continued debonding of the test space. The range, standard deviation and standard error estimated the degree of distribution of the data. The above data were defined as the debonding force set of variables.

3.1.4 Identifying the initial debonding force variables

The specific point at which debonding commenced was identified by analyzing the debonding force curve. The commencement of peel was concurrent with an initial interruption in the generated curve as it reached the point of debonding (see **Figure 3.2 at Time = 3.4**). Data was considered valid for peeling force in this example through the range of **Time 3.4** to **Time = 18**. At **Time 18** the entire portion of the PMMA selected for analysis was peeled and the peel force dropped to zero representing the unbonded 6 mm section reached the peel line. The slope of the range was computed. The continuation of the debonding (X-axis) and the amount of force to cause this effect (Y-axis) were recorded. These data comprised the initial debonding force variables.

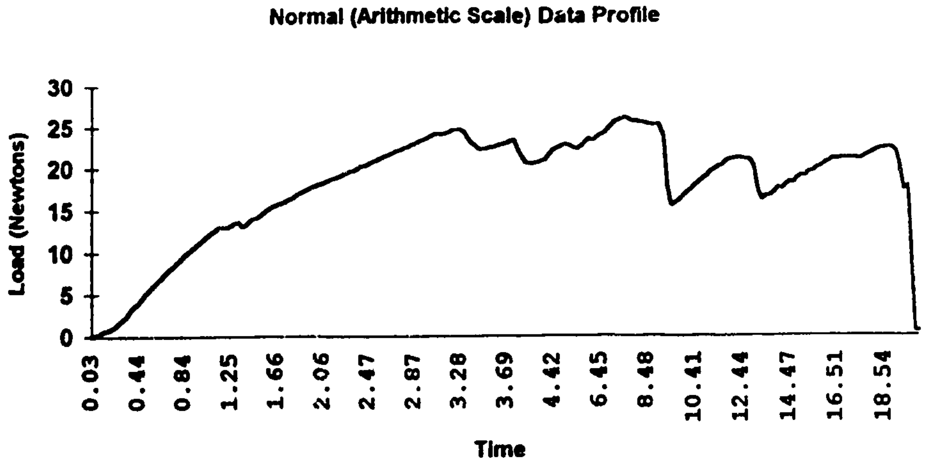


Figure 3.2: Sample peeling force curve to illustrate the location of the initial peeling at Time = 3.4 and the end point of the peel range at Time = 18

3.1.5 Statistical Analysis

The debonding force data (Y-axis) were transformed to the $\log_{10}(Y+1)$ in order to compute the geometric rather than the arithmetic averages for the two data sets (Steel and Torrie, 2nd Edition).[*] Each data set was analyzed applying the factorial analysis of variance (ANOVA) (Snedecor and Cochran, 6th Edition) where the variables were the PMMA surface treatments (3 treatments); types of wash (2 washes); type of primer (3 primers);

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[*] $\text{Log}_{10}(Y+1)$ is an accepted statistical computation when logarithmic computations are necssary for equalizing data variances over a large range. $\text{Log}_{10}(Y+1)$ behaves like the square root transformation for numbers up to 10 and differs little from log Y thereafter.

time between priming and application of silicone (2 time periods); and for the first data set, the location on the PMMA strip of the of the three treatments (3 locations). The slope and the spread of the initial debonding force data set were treated as covariates in a factorial analysis of covariance (ANCOVA). Least square means were computed for each level of factor and Student-Newman-Keul's Range Test[27] was applied to determine significant differences among the means for factors with more than two levels. For clarity and identification, the least mean squares were reconverted to the original scale of Newtons.

3.1.6 Preparation of data for analysis

The data collected from the Instron was the amount of time over which force was applied (X) and the amount of force necessary to

peel the silicone from the PMMA (Y). The X data remained the undefined time but related to the Instron measuring instrument set at 5.08 cm per minute while the Y data were transformed to Newtons with $Y' = Y * 4.45$. Both X and Y data were adjusted to a base reading of 0 by subtracting the first reading of X and Y from all data of X and Y, respectively. The adjusted X-Y data for each PMMA strip were plotted and the beginning and end points of each treatment segment was identified. The Y data was recorded as normal data (Y), and also transformed to the $\log_{10}(Y+1)$ scale.

Within each treatment segment the following data were computed for both scales:

a. the maximum peeling force,

b. the minimum peeling force,

c. the mean of the peeling force,

d. the standard deviation of the mean peeling force,

e. the standard error of the mean peeling force

The maximum, minimum and mean were estimates of the amount of peeling force required to separate the silicone form the PMMA; whereas, the standard deviation and standard error estimated the amount of distribution of the data around the mean peeling force. The above data were defined as the peeling force variables.

3.1.7 Statistical methods described

Both data sets were analyzed with a factorial analysis of variance (ANOVA) where the factors (main effects) were PMMA surface treatment (3 treatments); type of wash (2 washes), primer (3 primers); time between priming and application of silicone (2 times); and the location on the PMMA strip of the treatment (3 locations). The ANOVA model included the main and two-way interaction effects while the higher order interactions were pooled with the Error term. Least square means were computed for each level of the factors and Student-Newman-Keul's Range Test was applied to determine significant differences among the least squares means for factors with more than two levels. Least square means were also computed for each cell of the two-way interactions. For presentation, the least squares means for the $\log_{10}$ analyses were converted to the antilog(Y)-1 (i.e., geometric rather than arithmetic means).

3.2.0 Results of Statistical Analysis

3.2.1 Effects on bond strength by interaction of variables

Bonding silicone to clear PMMA appeared to require more peeling force than either the sandblasted or the sanded treatments of the PMMA strip (**Table 3.1**). Primer 92-023 appeared to be the superior primer while the methanol/water was found to be the better cleaning agent. The time following priming of application of the silicone and the location of the treatment on the PMMA strip were not significant factors by this analysis.

Table 3.1: Least squares means for the mean, maximum and minimum peeling force variables from the normal and $\log_{10}$ analysis of variance.

Main Effect	**N**	**Normal Analysis** **Mean**	 **Maximum**	 **Minimum**	**Log_{10} Analysis** **Mean**	 **Maximum**	 **Minimum**
Treatment							
B	57	27.6b*	34.2b	21.1b	16.4b	20.2b	13.0b
C	59	45.7a	58.9a	32.1a	38.4a	52.3a	27.0a
S	56	23.0b	28.9b	17.4b	18.2b	22.9b	14.5b
Primer							
1	69	23.6b	30.2b	17.7b	21.2b	22.3b	11.5b
2	38	51.2a	67.5a	35.5a	39.4a	63.3a	36.0a
3	65	21.0b	24.3b	17.4b	19.2b	21.1b	15.2b
Wash							
W	88	41.1a	52.1a	30.3a	35.9a	44.4a	28.8a
T	84	22.8b	29.2b	16.9b	16.2b	21.8b	11.9b
Time							
0 Hrs	104	30.0a	38.8a	21.6a	21.6a	28.8a	15.6a
3 Hrs	68	33.9a	42.5a	25.5a	27.1a	33.8a	22.1a
Location							
1	60	30.2a	34.2a	21.1a	25.2a	33.0a	18.4a
2	59	30.4a	58.9a	32.1a	21.3a	27.2a	17.4a
3	53	35.2a	28.9a	17.4a	26.4a	33.7a	21.2a

@ least square means for this analysis are expressed as antilogs (geometric means)

* means within each main effect and column which are followed by the same letter are not significantly different

Legend: (Treatment) B = sandblasted, C = clear; S = sanded; (Primer) 1 = A304, 2 = 93-023, 3 = A2020; (Wash) W = methanol and water, T = trichloroethylene.

3.2.2 **Measures of Peeling Force**

The ANOVA tables for the measures of peeling force (mean, maximum and minimum) indicated that there were highly significant differences for the PMMA surface treatment, primer and wash main effects (**Table 3.2**). These differences among the treatment, primer and wash main effects were found in both the arithmetic and geometric scales. The time main the location main and interaction effects were generally found to be non-significant (**Table 3.2**).

Table 3.2: Mean square for the mean, maximum and minimum peeling force variables from the normal and log$_{10}$ analysis of variance

		Normal analysis			**Log$_{10}$ analysis**		
Source	df	mean	maximum	minimum	mean	maximum	minimum
T	2	6,671***	12,445***	5,687***	1.395***	1.782***	0.901***
P	2	4,319***	8,667***	1,631***	0.999***	1.051***	1.110***
W	1	10,844***	16,952***	5,654***	3.560***	4.277***	2.912***
H	1	279	268	298	0.165	0.087	0.390*
L	2	357	384	338	0.107	0.115	0.124
Interactions							
TxP	4	576*	914*	358*	0.043	0.056	0.059
TxW	2	344	539	164	0.212*	0.201***	0.185
TxH	2	427	1,017*	121	0.004	0.025	0.007
TxL	4	122	160	147	0.008	0.016	0.011
PxW	2	7,904***	12,582***	4,088***	2.723***	2.371***	3.060***
PxH	2	991**	1,798**	496*	0.702***	0.638***	0.871***
PxL	4	120	138	43	0.035	0.013	0.039
WxH	1	1,797**	2,160*	1,657***	1.073***	0.893***	1.645***
WxL	2	86	188	12	0.018	0.021	0.035
HxL	2	42	63	102	0.006	0.021	0.002
Error	138	182	320	130	0.050	0.035	0.092

***,**,* significant at $P<0.001$, 0.01 and 0.05, respectively

Legend: T = Surface treatment; W = wash; P = Primer; H = time, L = Location.

3.2.3 Analysis of interaction effects using normal data

The analyses of variance of the peeling force variables indicated that there were significant interaction effects between some of the main effects (**Table 3.2**). An exploration of these interactions would be in order to identify interaction combinations of factor levels. The least squares means for the significant interactions from the analysis of the mean peeling force variable is graphically presented in figures 3.3 to 3.5.

Figure 3.3. Interaction effects of <u>Treatment X Primer</u>: Least squares means for mean peeling force from the normal data analysis of variance.

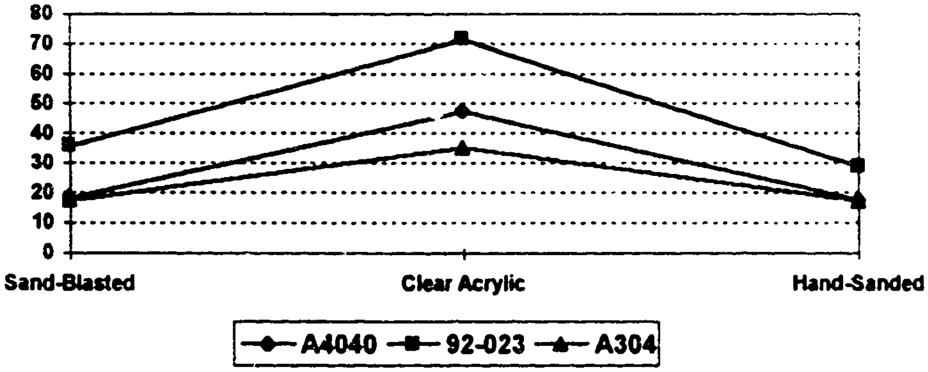


Figure 3.4. Interaction effects of PrimerX Wash: Least squares means for mean tearing force from the normal data analysis of variance.

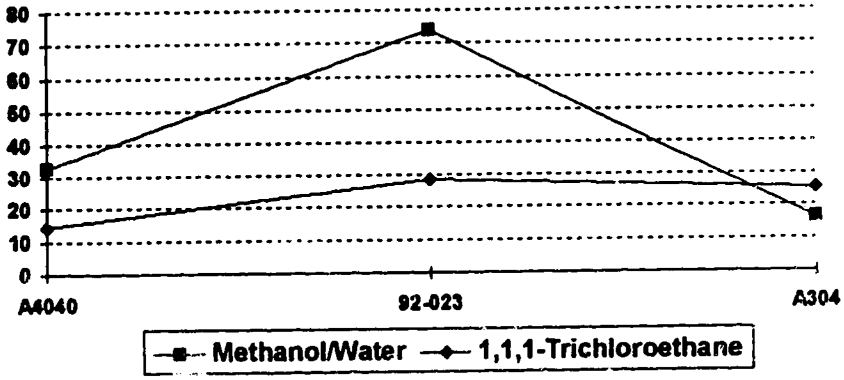


Figure 3. 5. Interaction effects of PrimerX Time: Least squares means for mean tearing force from the normal data analysis of variance.

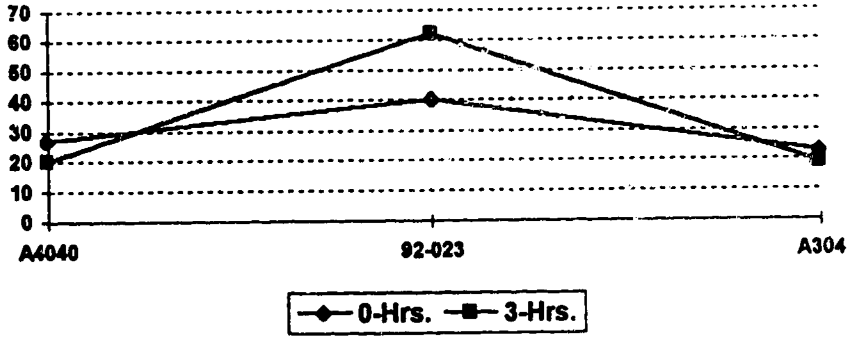
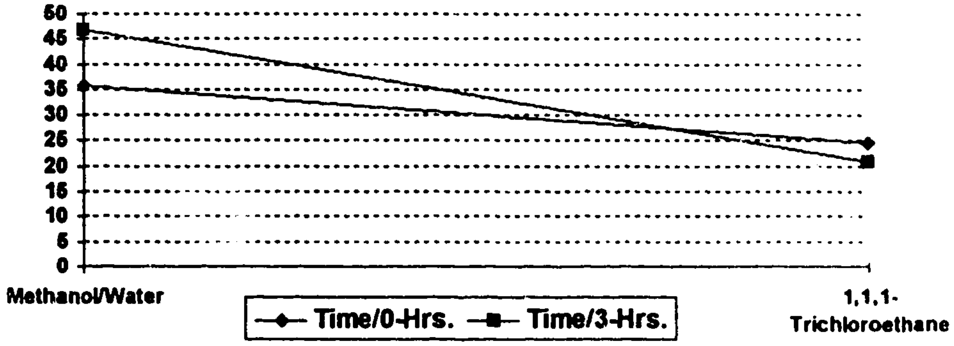


Figure 3.6. Interaction effects of WashX Time: Least squares means for mean tearing force from the normal data analysis of variance.



3.2.4 Analysis of interaction effects using $\log_{10}$ data

$\log_{10}$ data analysis were plotted to determine the stability of logarithmic data when compared to the results of normal data. Figures 3.6 - 3.9 show the least squares geometric means for mean peeling force for the $\log_{10}$ analysis of variance for each of the interaction combinations plotted in Figures 3.2 - 3.5.

Figure 3.7. Treatment X Primer: Least squares geometric means for mean peeling force from the log data analysis of variance.

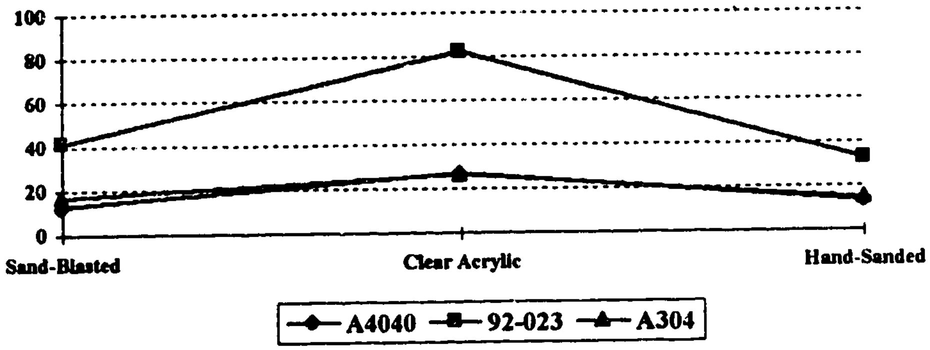


Figure 3.8. PrimerX Wash: Least squares geometric means for mean tearing force from the log data analysis of variance.

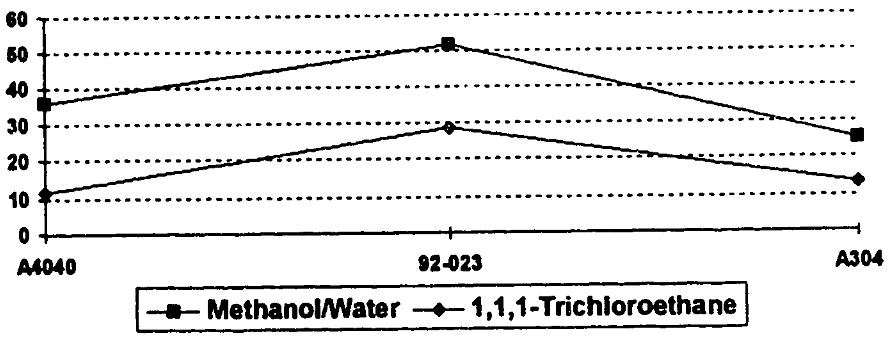


Figure 3.9.. Primer X Time: Least squares geometric means for mean tearing force from the log data analysis of variance.

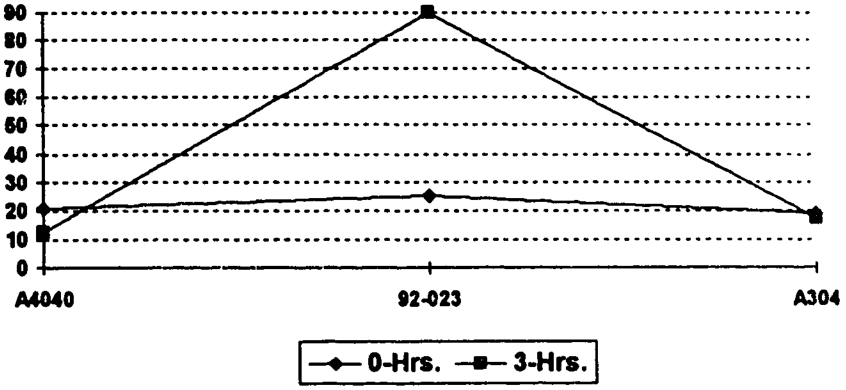
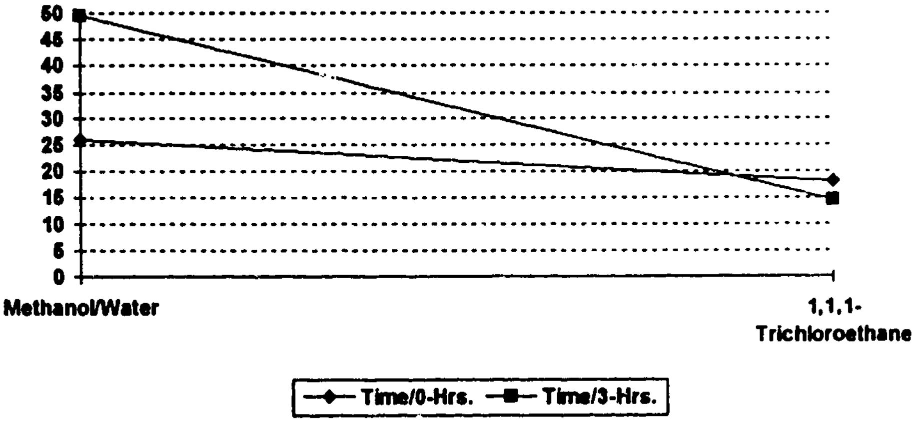


Figure 3.10. Wash X Time: Least squares geometric means for mean peeling force from the log data analysis of variance.



3.2.5 Deviation of Data along the Peeling Force Curve

Analysis of standard deviation and standard error are not usually carried out when data is compressed into mean, maximum and minimum data points. However, in order to insure that the first order of statistical analysis (compressed raw data) was representative of the original data, analysis of the standard deviation and standard error was carried out. This analysis compared the mathematical with the geometric computations (**Tables 3.3 and 3.4**).

The analyses of mean squares of the standard deviation and standard error data indicated that treatment, wash and primer main effects were again highly significant. The ANOVA data for both the normal and the $\log_{10}$ analysis were found to be identical. Standard deviation and standard error related to location of the treated surface on the PMMA substrate, was also found to have significance. Time main effects were not significant. Interaction effects were shown for primer x wash and primer x time (**Table 3.3**).

The least means squares for standard deviation and standard error peeling force variables suggest that the data for the clear PMMA segments were substantially more variable with respect to the peeling force required than the other treatments (**Table 3.4**). These data indicate that when the average bonding strength of the silicone to the PMMA is high for various preparations, the consistency of that strong bond is not necessarily repeatable over many preparations.

Table 3.3: Mean squares for the standard deviation and standard error peeling force variables from the normal and $\log_{10}$ analysis of variance

		Normal Analysis		$\log_{10}$ Analysis	
		Standard	Standard	Standard	Standard
Source	df	Deviation	Error	Deviation	Error
Main effects					
T	2	37.25***	0.520***	37.25***	0.520***
P	2	8.32***	0.119***	8.32***	0.119***
W	1	7,76**	0.179***	7.76**	0.179***
H	1	0.42	0.018	0.42	0.018
L	2	2.43***	0.259***	2.43***	0.259***
Interaction effects					
TxP	4	0.54	0.007	0.54	0.007
TxW	2	1.24	0.022	1.24	0.022
TxH	2	1.89	0.026	1.89	0.026
TxL	4	1.36	0.031*	1.36	0.031*
PxW	2	4.87**	0.105***	4.87**	0.105***
PxH	2	7.24***	0.174***	7.24***	0.174***
PxL	4	1.14	0.013	1.14	0.013
WxH	1	0.17	0.051*	0.17	0.051*
WxL	2	0.16	0.006	0.16	0.006
HxL	2	0.39	0.003	0.39	0.003
Error	138	0.81	0.010	0.81	0.010

***,**,* significant at $P<0.001$, 0.01 and 0.05 respectively

Legend: T = treatment; P = primer; W = wash; H = time; L = location. Note that the Figures for the normal are identical to the Figures for the $\log_{10}$ analysis, confirming that data compression had no significant effect.

Table 3.4: Least square means for the standard deviation and standard error from the normal and $\log_{10}$ analysis of variance.

		Normal Analysis		**Log_{10} Analysis**	
Source	**N**	**Standard Deviation**	**Standard Error**	**Standard Deviation**	**Standard Error**
Treatment					
B	57	1.565 b*	0.273 b	1.565 b*	0.273 b
C	59	3.038 a	0.437 a	3.038 a	0.437 a
S	56	1.484 b	0.246 b	1.484 b	0.246 b
Primer					
1	69	1.774 b	0.289 b	1.774 b	0.289 b
2	38	2.823 a	0.414 a	2.293 a	0.414 a
3	65	1.490 b	0.254 b	1.490 b	0.254 b
Wash					
W	88	2.274 a	0.356 a	3.374 a	0.356 a
T	84	1.784 b	0.282 b	1.784 b	0.282 b
Time					
0 Hrs	104	1.955 a	0.303 a	1.955 a	0.303 a
3 Hrs	68	2.103 b	0.334 b	2.103 b	0.334 b
Location					
1	60	1.565 b	.273 b	1.565 b	0.273 b
2	59	3.038 a	0.437 a	3.038 a	0.437 a
3	53	1.484 b	0.246 b	1.484 b	0.246 b

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* means within each main effect and column which are followed by the same letter are not significantly different

Legend: B = sand blasted; C = clear; S = sanded. Primers 1 = A304; 2 = 92-023; 3 = A4040. Locations 1,2,3 signify order of treatment on test strip.

3.2.6 Interaction between primer and other variables

Analysis of the effect of the surface characteristics (clear treatment) of the PMMA combined with primer (92-023) suggests that, on average, clear PMMA had more influence on the bond strength than primer 92-023 (**Table** 3.2). However, the particular combination of clear PMMA with primer 92-023 created a much stronger bond than any other Treatment X Primer combination (**Figure 3.1**). Similarly, the wash of Methanol/Water X Primer 92-023 was superior to the other wash x primer combinations (**Figure 3.3**). Primer 92-023 also was more effective if the application of the silicone was delayed for three hours while the other primers were more effective when the silicone application followed immediately (**Figure 3.4**). The data for the mean peeling force variable also suggested that PMMA strips which were washed with methanol/water bonded more strongly if the silicone application was delayed for three hours (**Figure 3.5**).

For the interactions of the $\log_{10}$ data analysis, Treatment X Primer interactions were not significant; however, Treatment X Wash were significant indicating that clear PMMA washed with methanol/water more regularly effected superior bonding (**Table 3.2**). Results for the other interactions between normal data analysis and the $\log_{10}$ data analysis, listed in Table 3.1, were found to be similar.

CHAPTER 4

DISCUSSION OF RESULTS

4.2.1 Surface characteristics and bond strength

Three surface characteristics of the PMMA were tested to determine the influence on bond strength of a smooth surface, a sanded surface and a sandblasted surface. The results showed that on average, the smooth surface was superior in bond strength production to either of the two roughened surfaces. The advantage of the smooth surface remained generally constant regardless of how the PMMA surface was cleansed or primed.

Superior bonding to a smooth surface can be explained by surface phenomena related to adhesives in general. Cohesive bonds (chemical bonding) occur only when surfaces are within 1 to 2 Ångstoms of each other allowing the possibility of electron sharing. Van der Waals molecules have large bond lengths (Truhlar, Resonances 1984) and can occur only if inter-surface space is within 0.1 to 1000 nanometers (Li, 1995). The difficulty of approximating a viscous silicone to roughened surfaces becomes apparent and may be considered as possible only in reaching the "hills" and not filling the "valleys". This condition would allow only periodic opportunity of bonding.

4.2.2 Wash methods and bond strength

Chemical solvents are capabgle of affecting the surface of PMMA. In this study trichloroethylene, used as a surface cleanser, was allowed to remain on the surface until it air-dried, a period of approximately 30 minutes. Methanol either rapidly evaporated or was diluted by a water rinse immediately after appropriate application. Both solvents are reported to have the capacity to affect the surface of PMMA (Physical properties of Acrylite®FF). The time that trichloroethylene was allowed to remain in contact with the substrate may have affected the smoothness of the surface more than the methanol. The surface effect may have been equivalent to the effects on bond strength of sandblasting or sanding.

Methanol contains methyl groups that constitute the major part of the PMMA radicals; whereas trichloroethylene radicals may be foreign to PMMA. Chemical reactions may have occurred on the surface changing the methyl to chloroethyl groups. The result may have caused an incompatibility with bond specific primers. The result of either or both of these two effects, may explain the stronger bonds from methanol/water cleansing.

4.2.3 Primer effect on bond strength

Three commercially available primers for bonding RTV silicones to PMMA were tested. The control consisted of an unprimed PMMA surface. The results showed that 92-023 primer, when allowed a prolonged period of surface contact, appeared to create a higher bond strength than the remaining primers or the control (refer to Figure 3.4). The control produced no measurable bond, while the other two primers were equal in most respects. Primer 92-023 produced bonds not significantly improved over the other primers tested when primer time was brief (refer to **3.2.4 and 3.2.6** for details).

Primers that are suitable for bonding PMMA with RTV silicones usually contain forms of reactive silanes. Their chemical formulations are are not published but their reaction with both substrates is understood. Primers must contain radicals capable of sharing electrons with either substrate in order to provide adhesion between two different materials. Primers usually contain some wetting agents like naphtha to carry the active silanes to the entire surface of the substrate. The ability of a primer to allow adequate cohesive bonding to occur may depend on the wetting agent and upon the nature of the reactive silane.

Primer 92-023 may have the formulation that allows a gradual bonding reaction to take place. The essential primer time may be related to either the nature of the silane and its reactivity or to the evaporation rate of the wetting agent. Allowing 3 hours for the reactivity to occur may explain the advantage of this primer over the other primers tested.

The current research did not test times other than the two time periods described. It is possible that shorter or longer primer time periods may have affected the bond strength produced by the primers used in the current research. Further research to establish the optimum primer time may provide more appropriate time periods.

4.3.1 Cohesive and adhesive failures

Cohesive failure was identified by observing silicone remnants still attached to the PMMA following the debonding process (Figure 4.1). Adhesive failure showed no remnants present following debonding (figure 4.2). Fractures of the silicone strip occurred when the bond strength exceeded the ultimate strength of the silicone (figure 4.3). Such limits were exceeded only in a few instances when the PMMA surface was left smooth, cleansed with methanol and water, primed with 92-023 primer, and a primer time of 3 hours.

Figure 4.1:. Cohesive failure of bond between PMMA and silicone. Remnants of the silicone remain on the surface of the PMMA.

The data showed that this treatment consistently demonstrated the highest bond strengths. The same data also showed the largest scatter of data when plotted on a graph. This caused a large standard deviation and standard error as the bonding force increased.

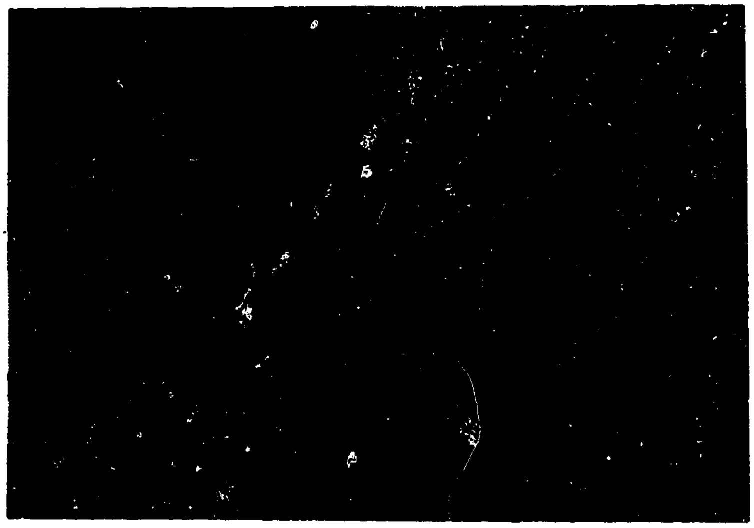

Figure 4.2:. **Adhesive failure of bond between PMMA and silicone. No remnants visible.**

Figure 4.3:. Total fracture of silicone during peeling process. Note the cohesive nature of the bond failure.

4.3.2 Air entrapment in the silicone

It may be postulated that the causes of high standard deviation and standard error are common to all test samples but their presence is observed only when the applied forces are sufficiently large to make them apparent. The degree of porosity of the silicone wafer may represent one cause of this occurrence. Air entrapment posed a problem during the mixing and application of the silicone dough. The silicone dough was highly viscous which induced the entrapment of air during the spatulation process.

Vacuuming after spatulation was partially limited by time since RTV silicones tend to rapidly initiate vulcanization.

Air entrapment occurred when the silicone dough was transferred into the flask recesses. The viscosity caused entrapment of air bubbles of random size and distribution. Examination of the bond area showed that these bubbles were present within the body of the silicone and could extend to the bonded junction with the PMMA. Twenty power magnification using a standard light microscope showed that the silicone wafer contained numerous bubbles ranging in size from 0.10 mm to 10 mm.

Mechanical load applied to the silicone wafer was transferred through the length of the free-end to the bond site. Silicone stored the load as energy within the free-end portion. The density of the silicone would relate directly to the amount of energy that could be stored. The volume of entrapped air may have inversely affected the density. In this study, the effect of varying densities within the silicone wafer during peeling would affect the applied peel force. Such fluctuations would be represented in the data as periodic peaks above and below the mean according to the following explanation:

> The assumption can be made that a mean peeling force has been established based on data close to the mean and represented by

a line of slope = 0. When a more dense portion of silicone enters the peel space, the adhesive properties may be considered to be higher requiring more peel force to be applied. Data collected during this stage of peeling will be represented by higher numbers and data will appear above the mean peel line. The reverse would be true as less dense silicone was being peeled.

The high standard deviation and standard error may have been caused in part by air entrapment at of very near the bonded surface. The energy required to cause peeling was reduced during the time when the peel line was affected by air bubbles. This event resulted in a lower reading showing as a dip in the peel force graph.

As the peel line progressed, this area became part of the debonded section of silicone. The presence of entrapped air within the wafer may have resulted in a weakened state of the silicone at that point. The consequence of this weakening allowed further stretching of the silicone without additional force applied to the peel line. During this time period, peeling may have ceased until the stretch in the silicone stored sufficient energy to overcome the peel strength. This event was recorded as a flat surface along the X axis graphically (time continued but no change in applied force) and no change in the data numerically. The event represented data below the mean.

The storage of energy in the elastomer would then continue with increasing graphic and numerical data until the applied load superseded the peel. The energy storage may have exceeded actual peel load causing a high spike (above the mean) to show in the data. This erratic nature is demonstrated by Figure 4.4.

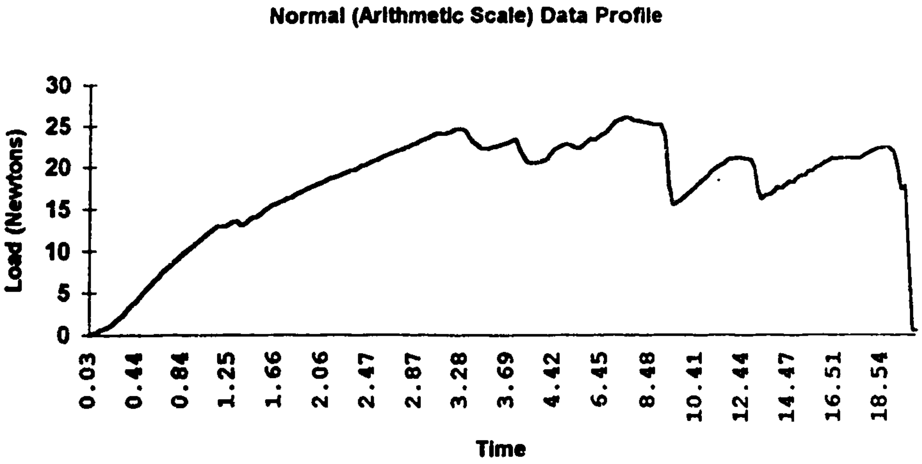

Figure 4.4: Graph showing the erratic nature of peeling forces. Possible causes are related to the nature of elastomers and defects in the elastomeric material. Note the recurrent flat areas at 3.4, 4.4 and 17 may represent entrapped air bubbles passing through the peel line.

4.3.3 Contamination of the bonded surface

High standard deviation and error may be related to contamination of the bond surface prior to silicone application. Possible causes of contamination may have been related to the physical handling of the PMMA strip. While efforts were constantly employed to maintain a protected PMMA surface, skin oils and water condensation may have contaminated the surface. These surface contaminants may have been responsible for the substantial areas of unzipping that occurred on occasion. Moisture from condensation may explain instances in which complete strips debonded from forces substantially less than expected (**Figure 4.5**).

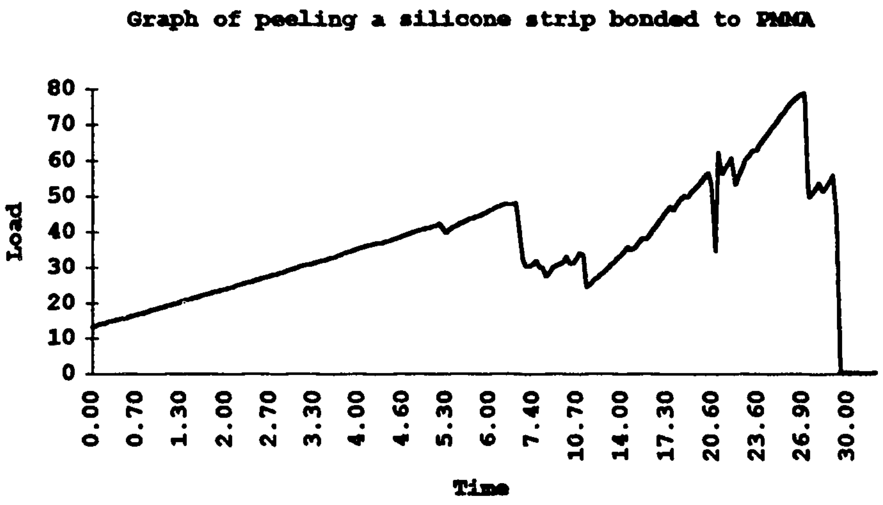

Figure 4.5 Showing the sudden drop in load at the 7.0 and 27.4 time intervals indicating an unzipping of the silicone from the PMMA.

Occasionally, following unzipping, the load necessary to bring about continued debonding remained uncharacteristically low. This phenomenon was reported by Singer et al (1988) when measuring bond strength between silicones bonded to polyurethane. A similar characteristic occurred during the present study, although inconsistently. In some tests the load did reach and exceed the original load where unzipping occurred while in other instances, further debonding continued at a load scarcely above the minimum at which unzipping ceased.

Unzipping occurred in most experimental sets, indicating that this phenomenon seemed to be independent of the variables associated with the test. The problem appeared to be associated with areas of inadequate bonding extending from a few millimeters to the remaining length of the test strip. Two explanations may be considered:

1. Contamination of the area prior to applying the silicone dough.
2. Inappropriate proximity of the silicone dough to the PMMA substrate through:
    - a. Pooling of primer
    - b. Excessively thick and viscous silicone dough

A more thorough cleansing of the PMMA surface may have reduced the presence of surface contaminants. Storing the primed strips prior to the application of silicone in an dry atmosphere may have aided in reducing condensation. An alternate primer application method may have been helpful to prevent the accumulation of primer at hollowed sites.

SEM measurements were made of two samples of bonded silicone to PMMA. Visible spaces between the silicone and PMMA were shown reaching 20 microns (**Figure 4.6**). Cutting the silicone and the PMMA for SEM survey may have created distortions to the sample and appropriately, this evidence was not considered valid.

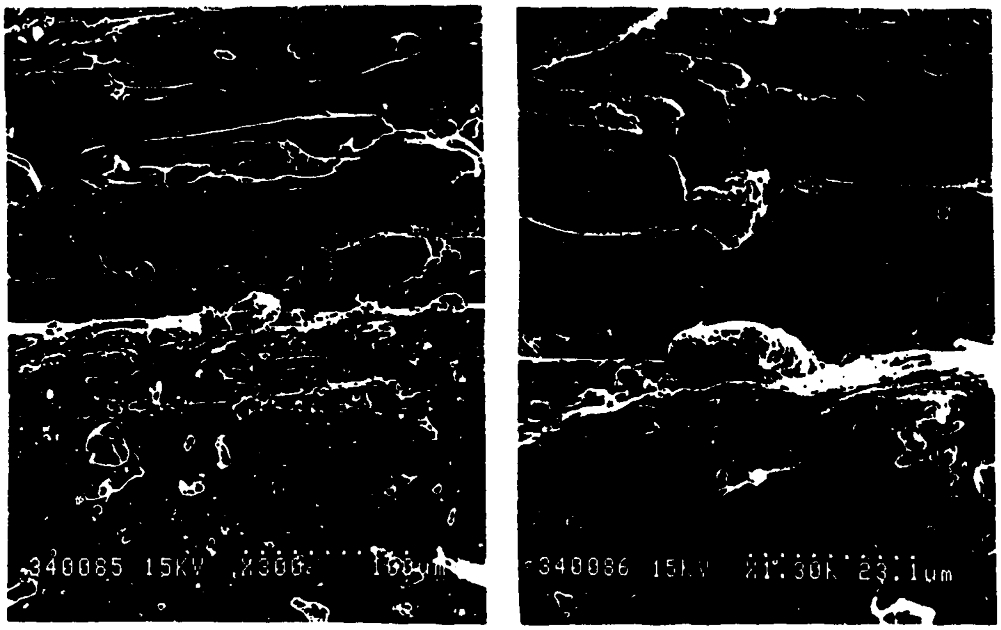

Figure 4.6 SEM showing debris and 20µ gap between silicone and PMMA

Difficulty placing the highly viscous silicone dough against the PMMA raises the possibility for substantial spaces to develop between the two substances.

4.4.0 CRITIQUE OF EXPERIMENTAL DESIGN

The present study was adequate to test the hypothesis as stated. It used conventional laboratory methods and materials of bonding silicone to PMMA in the construction of facial prostheses. Modifications to the original design were carried out before data was collected. These modifications involved only minimal alterations to conventional technical procedures.

4.4.1 Randomization of surface characteristics

The randomization of the surface treatment of the PMMA substrate was shown to be an unnecessary test. Peeling the clear surface of the PMMA before the roughened surfaces produced a large variation in the load level. The 6 mm space provided between these surfaces appeared to be insufficient. The length of the test strip was limited by the size of the flask which was designed to fit into the flask press. A better model would have been to begin each test with either the sanded or sandblasted surface treatment leaving the clear to the last test.

No significant difference in the data was recorded for sandblasted or sanded surfaces. The experimental design could have tested a roughened surface compared to a smooth surface. This model would have provided an increase in the free space between the two surface characteristics. The load release may have allowed sufficient reduction of the stored energy in the elastomer to prevent or reduce unzipping events. The resulting data may have remained more consistent throughout the peel test.

4.4.2 Critique of primer thickness

The present study did not attempt to control the thickness of the primer application beyond assurance of complete surface coverage. Primers are normally very low viscosity substances that flow readily over the surface being primed. In this application, they would usually be reactive silanes with appropriate groups to bond cohesively to the PMMA substrate and to the silicone. Theoretically, their surface thickness should be infinitely thin providing only a surface molecular effect to the PMMA. Insuring complete coverage may have resulted in uneven distribution on application. The influence of this variation was not established and may constitute the necessity for further research.

4.4.3 Critique of the peel test

The Instron measuring instrument was set at 5.04 cm per minute. This rate may have been too rapid for reducing the amount of stored energy within the elastomer. A slower rate may have reduced the degree of unzipping that frustrated data analysis and caused erratic peaks and valleys that appeared graphically. The results from a slower peel rate may have shown lower standard deviations and standard errors.

4.4.4 Critique of surface characteristic

Measurements to ascertain the degrees of smoothness or roughness that the three surface characteristics represented were not made. Such tests may have shown a relationship between the integrity of the PMMA surface and the results of strength measured. An analysis of the surface of each test type prior to the application of silicone may have provided information on the effect of surface treatment, wash effects and the primer effects on the PMMA surface.

Discussions were held with an expert in surface phenomena relative to the effects that surface characteristics of the substrate may have on bonding (Li, 1995). A mathematical model was suggested that may have the potential to predict the optimum primer and surface characteristic for bonding. Further research is being planned to investigate this hypothesis.

4.4.5 Analysis of the bond interface

Bond interface analysis using SEM was attempted. Samples could have been included in the curing process of a size suitable for SEM survey thereby eliminating the need to cut samples out of stock material. The heat and tearing effect in cutting through both the silicone and the PMMA may have affected the joint interface. Examination of samples under SEM suggest that the space between PMMA and silicone in this application may reach 20 microns (**Figure 4.6**). Comparisons could have been made between the proximity of the two bonded substrates based on the various surface characteristics that the test pieces represented. The results may have helped explain the reason for the superior results obtained from smooth PMMA

4.4.6 Critique of the silicone wafer

The silicone wafer that was produced by the conventional mixing and application method contained numerous air spaces. The full impact of air entrapment was not evaluated. The results from the present study seem to indicate that such air spaces may seriously affect some data

Further study is necessary to more clearly understand the effect of air entrapment in the silicone portion of a prosthesis. This study was carried out in a controlled environment where the impact of entrapped air may have been minimized. In the clinical application, the effect of the changing environment may place significant strains on the bond surface by creating a differential between the silicone and the air spaces within it.

4.5.0 CONCLUSIONS

4.5.1 Conclusions based on the revised hypothesis

The revised hypothesis suggests:

1. That there is an effect upon the bond strength associated with the physical surface treatment of the PMMA substrate. The results of the present study seemed to show that a smooth PMMA AcryliteFF substrate provided a better bond surface for A2186 silicone than it did when its surface was sanded or sandblasted.

2. That chemically treating the PMMA surface prior to priming had an effect on the quality of the ensuing bond. Treating the surface with trichloroethylene and allowing it to air dry negatively affected the bond strength. Removing oils and othe potential contaminants with methanol followed by an immediate wash with distilled water followed by allowing the surface to thoroughly dry prior to the application of primer provided a substantially better silicone to PMMA bond within the parameters of the present study.

3. That the choice of primers seemed to affect the quality of the bond. Of the three primer used in this study, there was a statistically significant difference in the bond strength dependent upon the primer. Primer 92-023 seemed to provide statistically better results than results from A4040 or A304.

4. That the length of time the primer was allowed to act upon the surface of the PMMA seemed to affect bond strength. The present study indicated that when a 3 hour priming time was compared to the shortest possible time the bond strength varied with the primer. 92-023 seemed to perform better when allowed the longer period whereas A304 and A4040 seemed to provide higher bond strengths with the shorter time. The results suggest that primer time was specific to the primer.

4.5.2 Relating the conclusions to the null hypotheses

The conclusions from the present study reject the original null hypotheses. The results of the present study indicate that the surface treatment of the PMMA substrate, the wash methods prior to priming, the specific primers used in the study and the priming time affect bond strength between AcryliteFF and A2186 silicone.

The data seems to support the use of primers to create any measurable bond between the substances tested. The no primer control did not yield any recordable data regardless of the influence of the remaining variables.

4.6.0 APPLICATION OF RESEARCH

4.6.1 In osseointegrated facial prostheses construction

An improved bond between A2186 silicone and a commercially available PMMA (AcyliteFF) by applying conventional laboratory procedures has been identified. The control of the surface of the PMMA has the potential to alter the convention by which the surface character is prepared prior to silicone bonding. The wash methods suggested by manufacturers of RTV silicones are not necessarily appropriate to improved bonding. It seems probable that primers react in different ways to improve or weaken bonds between the substrates in this application.

The present study provided evidence that the best bond using the materials selected for study was achievable by using a smooth surface PMMA, a wash method using methanol followed by an immediate rinse with distilled water, priming the PMMA surface with 92-024 primer and allowing the primer to remain in contact with the substrate surface for 3 hours.

4.6.2 The need for further research

More research is necessary to identify the optimum conditions for bonding silicones to PMMA within the laboratory setting. Better methods are needed to eliminate air from the silicone dough. [illegible] time may be more clearly identified specific to the primer. In the clinical application, the PMMA is not necessarily even, and methods of primer application may need careful consideration in order to maintain an optimum primer application. Methods of identifying and manufacturing primers specific to surface chemistry offer exciting possibilities for adhesives in medical and industrial application. These needs can be addressed by further research and may provide solutions to some of the frustrating problems that face patients, clinicians and technicians relative to bond failures.

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