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ENVIRONMENTAL FACTORS AFFECTING MECHANICAL PROPERTIES OF FACIAL PROSTHETIC ELASTOMERS

BY

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A THESIS SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL OF
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Every project has it's share of tribulations and this was no exception. However, there have been several people who have helped me along this "journey" and I will be remiss if I did not acknowledge them, for they made this all become possible.

First and foremost, I am indebted to my parents, Dada and Jiji, who over the years have encouraged and supported me in all my endeavors. They have always been my role models, whom I constantly strive to emulate. To them I dedicate this work.

My thesis director, Dr. James L. Sandrik, his patience and guidance throughout this project has been stellar. His encouragement when this project was in it's infancy and his enthusiasm throughout, has really seen this project to completion.

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To my friend Gayatri, my deep felt appreciation for fostering hope and motivating me at times when I was crestfallen, for goading me on towards excellence when I was complacent, and for just being there when I needed her most.

I also want to take this opportunity to acknowledge and thank everyone who provided me with background information and product specifications. For the sake of brevity I will limit myself to Mr. Ray W. Winter from the University of Wales, U.K. and Mr. Thomas W. Brodhagen from Dow Corning Corporation, MI for their support and interest in this project.

PREFACE

It was at the Veterans Administration Hospital, Oakland, Pittsburgh, that I came in extensive contact with oncology patients that needed maxillofacial rehabilitation and the realization that facial prosthetic materials were far from perfect.

The problem of material degradation is not a new one, but there is a certain paucity of information in the maxillofacial literature. There are very few textbooks in Dental Materials or Maxillofacial Prosthodontics for that matter, dealing at length with facial materials.

This "cookbook" approach is aimed at minimizing the uncertainty and confusion a neophyte is faced with upon first coming across facial prosthetic materials. Facial materials albeit similar to conventional dental materials, are significantly different to warrant some background information. This thesis is conceptualized in a logical sequence, starting with a short section on the history of facial materials, and later "walking" you through the basics of modern facial materials, including its applications, chemistry, advantages and shortcomings.

The materials tested in this project are the ones I have used previously and a cross-section of the materials used by others in contemporary maxillofacial rehabilitation. Obviously, a more extensive testing protocol would be ideal, but due to limitations in time, is beyond the realm of this project.

Finally, my thoughts go out to all the patients, who continually serve as an inspiration through their faith, courage and grit, and whose treatment continues to challenge our capabilities.

VITA

The author, Uday H. Mohite, is the son of Hambirrao 'Dada' Mohite and Indumati 'Jiji' Mohite (née Kate). He was born April 18, 1964, in Poona, India.

He received his primary school education at Loyola Primary School, Poona, India. His high school education was completed in 1979, at Loyola High School, Poona, India and he graduated with Distinction at the S.S.C. level. He then joined Loyola Junior College, Poona, India and graduated in 1981.

In August 1981, Uday entered the Government Dental College, Bombay, India, and received the degree of Bachelor in Dental Surgery from the University of Bombay in 1985. Dr. Mohite then did his General Practice Residency training, at the Government Dental Hospital, Bombay, India.

In July 1987, he joined the post-graduate specialty program in Combined Prosthodontics at Loyola University School of Dentistry, Chicago, IL. In 1988, Dr. Mohite joined the Dept. of Oral Biology, Loyola University Graduate School, Chicago, IL.

On graduating from the Combined Prosthodontics specialty program in 1989, Dr. Mohite joined a post-specialty program in Maxillofacial Prosthodontics at the Eye and Ear Hospital, University of Pittsburgh, Pittsburgh, PA and graduated from that program in June 1990.

In August, 1990, Dr. Mohite was granted an assistantship / fellowship by the Dept. of Oral Biology, Loyola University of Chicago, enabling him to complete the Master of Science in 1991.

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INTRODUCTION

Maxillofacial prosthetics is defined as the art and science of anatomical, functional, or cosmetic reconstruction by means of artificial substitutes of those regions in the maxilla, mandible and face that are missing or defective because of surgical intervention, trauma, pathology, and developmental or congenital malformation. The purpose of maxillofacial prosthetics is to restore both form and function to a missing or defective part of the face, thereby relieving the patient's psychological trauma and enabling the person to be reinstated in society. These goals albeit lofty, have been hampered for a plethora of reasons.

Jani and Schaaf[1] reported the results of a survey conducted with 143 subjects to evaluate patient's reactions to facial prostheses. Of the 76 patients who responded, 38 were wearing their prostheses and 38 were not. Reasons cited by the patients for not using their prostheses included lack of retention, additional surgery, discomfort and irritation. Most of the prostheses studied were fabricated from silicone rubber, and more than 69% of them were remade within one year because of rapid changes in the defect, the material, or prosthesis color. Of the 69% patients who had their prostheses remade within a year, 29% had returned for a new prostheses because of color change and 26% returned because the margins of the prosthesis had broken down or the material itself showed deterioration.

Jebreil[2] conducted a study to determine if those patients apparently dissatisfied with an orbital prosthesis might accept an eye patch more readily. The study was conducted with 27 patients seen over an 8 year period. Of the patients who responded, 12 were wearing their prostheses and 5 were not. Reasons given by the patients for not using their prostheses were discomfort, material deterioration, lack of retention, skin irritation caused by daily application and removal of adhesive, change in defect and ill-fitting prostheses.

Chen[3] evaluated 138 patients fitted with facial prostheses and reported that current materials have severe limitations, including poor durability and loss of esthetics. The survey revealed that the average wearing time for the prostheses was 10 months. The rapid deterioration was theorized to be due to exposure to ultraviolet light, air pollution and harsh cleansing agents like alcohol and gasoline.[3]

This study intends to evaluate the serious problem of environmental factors affecting mechanical properties of facial prosthetic elastomers. The resulting database is hoped to give us insights and a better understanding, while selecting from the myriad of facial prosthetic materials available today.

IN PURSUIT OF AN IDEAL FACIAL MATERIAL

The maxillofacial prosthodontist must eventually assume the burden of restoration following the earlier efforts of other specialists. This work is hampered by inadequate materials for prostheses. Like others in the dental profession and in the medical sciences, the maxillofacial prosthodontist has borrowed from industry a few materials originally designed for other applications, and has tried to adapt to them. Manufacturers and suppliers have offered little assistance since neither can justify the major investments in research and development required to design a material to fulfill exacting demands in a relatively small market.

In the 1970's vinyls such as Cordo (Ferro Corp.), Prototype III (Sartomer Industries) and Realistic (Realistic Industries) were very popular. They offered a fairly good combination of properties, but the prostheses lacked durability and were costly to fabricate as they required metal molds.

During the past ten years, the preferred materials for facial prostheses have been silicones, polyurethanes and acrylics. The principal commercial silicones have included Silastic (Dow Corning), Cosmesil (Cosmedica), heat-vulcanizing silicones (General Electric), and Dermasil (Artskin). Epithane-3 (Daro) a polyurethane is also used extensively for facial prostheses.

The three most serious problems associated with the facial prostheses currently available for rehabilitation of patients suffering from facial disfigurement are:

- the discoloration of the prostheses in a service environment
- the degradation of static and dynamic physical properties of the elastomer

- the difficulty of repairing the available materials, since the service lifetime of a facial prosthesis is usually less than one year depending on personal habits, climate and environment

The development of new and improved materials for facial prostheses has been the research goal of a limited number of investigators during the past two decades. The desperate need for better materials for facial prostheses was made clear in 1973 in a symposium on Dental Biomaterials Research Priorities organized by the National Institute of Dental Research. Subsequent efforts by the National Institute of Dental Research, the Veterans Administration, the U.S. Department of Defense, and other organizations have afforded significant research gains in the field. These intense research programs, albeit few, have enabled a variety of commercial and experimental materials to be clinically tested.

Researchers striving to provide an ideal facial prosthesis for clinical use have generally fallen into two categories: those seeking to develop or identify a better primary material or base polymer, and those attempting to improve clinical techniques, auxiliary materials or armamentarium that might result in an improved prosthesis. Research programs intended to provide a new base material, specifically an elastomeric polymer, have taken three well-defined routes:

- design and development of a completely new polymer system
- improvement or modification of an existing prosthetic material
- clinical or laboratory evaluation of a new commercial polymer, often aimed at an unrelated end use from a market standpoint

As yet no material is available that simulates all of the changing qualities and details of human skin. As a result the search for the ideal material continues. Its properties may be listed as follows:[4]

- **Nonirritant** The material must not irritate the tissues with which it comes in contact
- **Pliability** The material must be soft, pliable, and capable of adapting to facial movement
- **Weight** The material must be light in weight so that it may be supported without fear of detachment during wearing
- **Color** The material must be of a basic skin color, blending as much as possible
- **Hygiene** The material must be hygienic, nonporous, and capable of being washed and disinfected in approved solutions
- **Durability** The material must have an indefinite life and keep its texture when being washed and disinfected in approved solutions
- **Thermal Conductivity** The material must be a poor conductor of heat
- **Manipulation** The material must be easy to manipulate and require no complicated or extensive equipment
- **Texture** The surface of the material must be able to retain cosmetics and adhesives applied for characterization and retention
- **Availability** The material must be easy to obtain and inexpensive

HISTORICAL NOTES

At what point in history man first attempted to disguise the presence of congenital or a acquired facial deformity by artificial means cannot be ascertained. The material that perhaps could have been used would in all probability have been limited, possibly animal skins, clay and wood being the only substances available at that time that might have lent themselves for this purpose.[5]

EGYPTIAN PERIOD 2613-2494 B.C.

Excavation of tombs from the fourth Egyptian Dynasty have provided evidence of nasal, orbital and auricular prostheses. Egyptologists, however, are of the opinion that such prosthetic devices were in all probability inserted after death in order to meet the religious beliefs of the time.

GREEK-ROMAN PERIOD 1000 B.C.

The Greek word “prosthesis” means to add to or to replace. Many facial masks were fabricated in gold and silver during this period. Whether such masks were intended primarily for protection of the facial structures or whether they were intended to camouflage facial deformity (possibly acquired in battle) is an area for speculation.

200 A.D.

The first report of prosthetic rehabilitation in this millennium was that of *Popp*[6] who stated that prostheses were fashioned in China around the year 200. These prostheses were fabricated in lacquer supported by an unspecified type of metallic substructure. From around the same period, archaeologists in Greece have also found terra-cotta moldings of the ear, nose and orbit.

1000 A.D.

Paschke[7] reported a case of prosthetic rehabilitation for Kaiser Otto III (983-1002), a German Emperor, who is said to have worn a golden nasal prosthesis in order to disguise a nasal defect. Later, *Conroy*[5] claimed that the story was no more than a legend and the report to be erroneous.

1500 A.D.

The first well-documented account of facial prosthetics is provided by Ambroise Paré (1509-1590). Paré's famous book "The Opera" published in 1579, shows the basic design features of nasal, auricular and orbital prostheses. Ambroise Paré has, in many textbooks been given the title of "Father of Facial Prosthetics".[5]

Paré suggested that auricular prosthesis be constructed in papier maché or leather and be retained by means of a metal band passing over the patients head. He indicated that a nasal prosthesis could be supported by means of tapes that should pass over and around the patient's head and that the line of juncture at the lip be camouflaged by an artificial mustache.

1800 A.D.

'The Gunner with the Silver Mask' is perhaps one of the best-known instances of facial prosthetic rehabilitation reported in the literature.[8] The patient, Private Alphonse Louis, received an injury during the siege of Antwerp in 1832 involving most of the lower third of his face. Dr. Forget, a surgeon-dentist, designed a half-facial mask and M. Verschuylen, a master craftsman, fabricated the sectional facial mask in silver. The mask was supported on the patient's face by means of leather straps that fitted around the neck and the back of the head. Within the mask itself, a hinged mandibular section with gold teeth was sited under which a drainage chamber was provided. The external aspect of the mask was painted with oils to resemble the patient's facial coloring. This, together with false mustache and side whiskers, completed the disguise.

1900 A.D.

Tetamore was one of the first to report the advantage of spectacles to retain and disguise the margins of facial prostheses.[5]

Toward the end of the nineteenth century, vulcanite already having proved its value in conventional prosthodontics, found additional use in maxillofacial prosthetics. It replaced most earlier materials such as cellulose acetates, ceramics and metals.

Upham a dentist from Boston, reported that he had made dental plates, noses and ear prostheses using vulcanite.[5] A report by *Bruck*[9] stated that skin, wood, celluloid and rubber (thought to be vulcanite) could be used as means of artificial substitution of the face.

Vulcanite was used extensively for maxillofacial injuries sustained during World War I.[5] It was during this period that Kazanjian, using mostly vulcanite in combination with various metals, revived and revitalized the concept of maxillofacial prosthetics.[5] His pioneering work did much to improve the design and construction of many types of orofacial prostheses that were made from vulcanite as early as 1914. In time, however, some workers showed dissatisfaction with vulcanite and began to look for a more lifelike material that possessed translucence and pliability, physical properties that were totally lacking in vulcanite.[5]

In Germany, *Heenning*[10] developed a new facial material called Elastin. This was a combination of gelatin, glycerin and coloring. This formulation produced a very flexible, translucent and lightweight restorative material which permitted the fabrication of prostheses that had an esthetic quality hitherto not realized. The basic drawback of this material was its rapid deterioration resulting from absorption of its high water content into the atmosphere and its extremely short life of approximately 7 to 8 days. Elastin use was largely discontinued in the late 1920's.

At about the same time, other investigators in various parts of the world were extending the boundaries of facial prosthetics. One of the most outstanding contributors at that time was Dr. Arthur Bulbulian based at the Mayo Clinic. Bulbulian is credited with identifying and developing the use of latex rubber as a facial prosthetic material.[5] This material was particularly useful when hollow and hence lightweight prostheses were required for conditions presenting retention problems.[11] Perhaps the most significant contribution of the pre-vulcanized latex era was that it provided the impetus in the early 1930's to further research directed towards finding a material which combined the desirable qualities of latex, such as durability and strength.

In the 1930's Axt, a French facial prosthetist, constructed prostheses using a gold base plate over which he electroplated the periphery and pigmented with celluloid Zapon paint.[5] He also fabricated a lip prosthesis in swaged aluminum which was colored in a similar manner. With the advent of acrylic resin in the early 1940's several investigators practicing in different parts of the world immediately saw the great potential of this material for application in facial restorative procedures.

In the mid-1940's, polyvinylchloride (PVC) came into vogue as there was a move toward the use of flexible materials in contrast to the hard and unyielding acrylics. The major innovators and developers of PVC in facial prosthetics were Dr. Cleaver (developed Cordo a PVC derivative) and Andy Anderson. Both PVC and Cordo, while popular for sometime, have now become obsolete, superseded by more suitable and dependable materials.[5] While the main reason for going out of vogue was their propensity to undergo degradation when exposed to the body environment, they also have been found to have toxic sequelae in those who were involved in material manipulation.

In 1950 the chemical firm Nelson-Kramer Corporation in Michigan developed a facial material called Flexiderm.[5] In 1961 the German chemical firm Kulzer introduced another new type of soft material called Palamed. This material, when processed, consisted of a foamed inner core covered by a thin homogeneous layer of Palamed. A nonfoamed variety called Palamed B was developed later. Unfortunately, the foamed variety did not prove to be completely satisfactory in clinical use because of the absorption of body debris that tended to be retained within the porous inner core. This resulted in both materials being removed from the market by the manufacturer.[5]

Kipping is considered by many, to be the founding father of silicone chemistry in the early 1900's.[12] Later, around the time of World War II, two chemists working independently investigated silicone as a possible tissue substitute for material development in the plastic industry. De Niola is credited with the first implantation in 1959; when he used silicone rubber tubing to replace the urethra.[12] In 1955, Holter developed the first shunt made of silicone for drainage of excess fluids in hydrocephalic children.[13] Marzoni and his group studied the biologic reaction of tissues to silicone fluid injections.[12] A major advance was made in 1961, when Cronin and Gerow developed a mammary prosthesis, now one of the most frequent and popular uses of silicone in clinical medicine.[12-14]

In 1960 a new silicone rubber, was developed by the Dow Corning Corporation. This material possessed flexibility, durability and an impervious structure. The early development of silicone was carried out by George Barnhart, a maxillofacial technician at the Zoller Dental Clinic, University of Chicago. Barnhart was, until his death in 1975, carrying out further research into the application of silicone materials, especially in relation to improved coloration and durability. In recent years, great progress has been made in the art and science of facial prosthetics, particularly in the development of better materials, such as MDX 4-4210* and improvement of clinical and laboratory techniques.

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* Dow Corning Corporation, Midland, MI.

MODERN FACIAL MATERIALS

POLYMETHYLMETHACRYLATE

Acrylic is available as heat cure, self cure, light cure and recently microwave cureable resin. It has been used extensively in the past for facial prostheses, and is still in occasional use today. Polymethylmethacrylate is described extensively in the conventional dental materials literature and will not be further elaborated here.

SILICONES

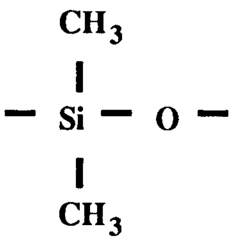
Silicones range in properties from rigid plastics through elastomers to fluids. As materials for maxillofacial prostheses, silicone exhibits good weathering properties and maintains good physical properties over a wide temperature range. Silicones used for maxillofacial prostheses can be cured either at room temperature or by applying heat. In either case, synthetic rubber results, which has wide applications in medicine and more recently in maxillofacial prosthetics.

Chemistry of Silicone Polymers

Silicone rubber polymers are classified as:[15]

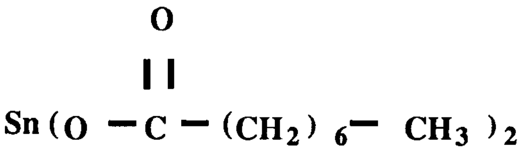
- polydimethylsiloxanes
- methylvinyl / dimethylsiloxanes
- phenyldimethylsiloxanes
- fluorodimethylsiloxanes

Polydimethylsiloxanes and methylvinyl / dimethylsiloxanes are manufactured as medical-grade polymers. Medical-grade silicones are those that have a long history of successful implantation in animals / humans and are manufactured under pharmaceutically clean conditions qualifying them for medical applications. Phenyldimethylsiloxanes and fluorodimethylsiloxanes are used in industrial applications. Medical-grade silicones are composed primarily of dimethyl siloxane units:



$$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-O-$$

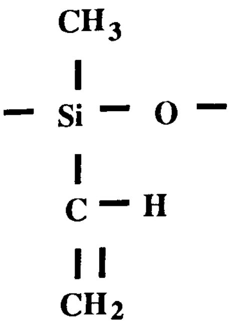
Room temperature vulcanizing (RTV) polydimethylsiloxane which is an implantable medical-grade silicone rubber, is a two component system. In this system, liquid stannous octoate catalyzes the liquid prepolymer component:



$$Sn(O-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_6-CH_3)_2$$

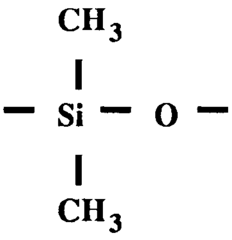
A heat temperature vulcanizing (HTV) medical grade polymer is also available as a one component system. The material is of semisolid or doughlike consistency impregnated with a peroxide catalyst. The second category of medical-grade silicone rubber, methylvinyl / dimethyl silicone copolymer, is a two-component liquid system. The primary component consists of dimethyl siloxane units with small quantities of methylvinyl siloxane units. The methylvinyl unit encourages a more complete vulcanization and yields a material with better rubber properties. Methylvinyl / dimethylsiloxanes commonly use a platinum catalyst.

Methylvinyl siloxane unit:



$$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH=CH_2}{Si}}-O-$$

Dimethyl siloxane unit:



$$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-$$

RTV Silicones

According to *Braley*[12] the room temperature (RTV) silicone rubbers are composed of comparatively short-chain silicone polymers which are partially end blocked with hydroxyl groups. Fillers are added to strengthen the final rubber. With the addition of a catalyst such as stannous octoate, condensation takes place between the hydroxyl of the polymer and the alkyl group of the cross-linking agent, yielding an alcohol and a network forms as a result of the cross-linking. The advantages of RTV silicone are:

- the material has a wide latitude in proportioning of the catalyst, so that proportioning errors primarily change vulcanization time.
- the material can be used in stone molds thus eliminating the need for metal molds
- the prosthesis can be fabricated in a regular dental laboratory
- speed and processing ease

The main disadvantages of RTV silicones are:

- the material is weaker than the vinyl plastisols
- the material exhibit's "the zipper effect", i.e. although the material can withstand considerable stress, a small tear, once initiated, will continue throughout the entire length of the material under a much reduced load

- the material is stiffer or less flexible than flesh, such as the human cheek
- the material has a high specific gravity and thus is heavy
- color is incorporated intrinsically resulting in a monotone prosthesis
- chloroform used to remove the adhesive, degrades the silicone

HTV Silicones

The mechanism for the formation of a heat-vulcanizing silicone rubber involves the use of a polydimethyl siloxane.[16] When this liquid material is heated with benzoyl peroxide a reaction occurs between one of the methyl radicals in the chain and a similar methyl group in the adjacent chain. The two polymers are thus crosslinked with benzoic acid as a by-product. A synthetic rubber results which has found increasing use in maxillofacial prosthetics in recent years. *Chalian*[17] evaluated physical properties of polyvinyl chloride (Realistic), RTV silicone (Silastic 382) and HTV silicone (MDX 4-4514), and found HTV silicone the material of choice. *Jones*[18] evaluated the physical properties of silicone (MDX 4-4210) and HTV silicone (MDX 4-4514), finding the latter to be a superior material for maxillofacial prosthetics.

HTV silicone contains dimethyl and methylvinyl siloxane polymer, a filler, usually silica and vulcanizing agent 0.54%-0.71% 2,4-dichlorobenzoyl peroxide. The polymer molecules interact with the silica particles in a manner that reinforces the rubber. Without this filler the rubber has little strength. In general, the more filler used, the harder the resultant rubber. The polymer-filler mixtures have a consistency of putty. Dichlorobenzoyl peroxide is the vulcanizing agent used in all HTV silicones. This peroxide is unstable. When heated it decomposes to initiate free radical reactions that form cross-linkages between adjacent polymer chains. These cross-linkages change the mixture from a putty like mass to rubber like with a permanent shape.

Low Temperature Vulcanizing Silicone

MDX 4-4210 is a low temperature vulcanizing polymer. The elastomer is based primarily on a modified polydimethylsiloxane structure and the vulcanization mechanism involves the addition of silicone-vinyl units. A platinum catalyst initiates the cross-linking reaction. The curing reaction is sensitive to any contaminant which chemically inhibits the platinum catalyst. Due to changes in the nature of the filler the elastomer is not opaque as are most of the Silastics and other highly filled silicones. This improvement allows fabrication of a prosthesis of exceptional appearance. The elastomer is a pourable two-component product which cures to a translucent silicone rubber at room temperature or slightly elevated temperatures. The elastomer component consists of a dimethyl siloxane polymer, a reinforcing silica and a platinum catalyst. The curing agent component consists of a dimethylsiloxane polymer, an inhibitor and a siloxane crosslinker.

Advantages of MDX 4-4210 are :

- room temperature and heat accelerable cure
- good thick section cure
- essentially no shrinkage when cured at room temperature
- superior appearance due to nature of filler

Medical Adhesive Type A

This material is a one component, low slump, translucent silicone material for bonding silicone elastomers to each other and to some synthetics. This methyltriacetoxy silane is a translucent non-flowing paste containing no solvents or plasticizers. No catalyst or curing agents are required. It is cured by absorbing water vapor from the atmosphere at room temperature. During the curing process silicone adhesive releases acetic acid vapor as a by-product. The final cure generally requires about 24 hours. The material can be processed at low temperatures in a stone mold and its colorability is good. After the final cure the resulting silicone elastomer possesses the appearance, texture and general composition of many conventional silicone elastomers.

Advantages of Medical Adhesive Type A are:

- cures at room temperature at moderate relative humidity
- can be shaped by spatula or other hand-held tools
- appearance and texture comparable to conventional elastomers
- provided in ready-to-use tubes

VINYL PLASTISOL

Polyvinylchloride (PVC) has been widely used for maxillofacial applications, but newer materials have been developed with properties superior to PVC. PVC is a rigid plastic with a glass transition temperature higher than room temperature. For maxillofacial applications, plasticizers are added to produce an elastomer at room temperature. Vinyl resins are relatively rigid in their pure state but are made flexible by the addition of the plasticizers. The degree of flexibility depends on the amount of plasticizer used. Color pigments are incorporated to match the individual skin. Other ingredients added to PVC include cross-linking agents for added strength and ultraviolet stabilizers for color stability.

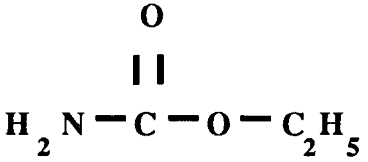
There is no chemical reaction involved when the material is processed. The product is supplied as finely divided PVC particles suspended in a solvent. When the fluid is heated above a critical temperature, PVC dissolves in the solvent. When the mix is cooled, an elastomeric solid is formed. Processing times and temperature are very important. If the material is heated for too high a temperature or too for long the physical properties are altered and the material will eventually discolor. PVC is processed at 150^{o} C, and metal molds are generally used. The procedure is very time consuming and technique sensitive. A prosthesis made from PVC loses its flexibility with age. Plasticizers migrate from the surface of the prosthesis as aging occurs, and this makes the prosthesis hard. Another disadvantage is the degradation or destruction by ultraviolet light. PVC prostheses are made in Linotype metal molds.

CHLORINATED POLYETHYLENE (CPE)

Chlorinated polyethylenes are thermoplastic elastomers. This type of material is available in the form of thin sheets in a variety of shades. The sheet is heated at 190° C for 10 minutes and placed between heated linotype mold halves and the prosthesis is formed in a hand press. Sometimes heating and pressing are repeated. The prosthesis is recovered from the mold after cooling under running water. Chemically, CPE closely resembles PVC though the material is resistant to environmental degradation and can be developed into a soft, tough elastomer without the need for plasticizer. CPE is compatible with many polymeric materials and is readily mixed with them to further increase its range of available properties. CPE is a stable thermoplastic and can be molded to complex shapes at low temperatures.

POLYURETHANES

Polyurethane , urethane, or "isocyanate" polymers are the polymers that have been more recently used in the field of maxillofacial prosthetics. The polyurethane polymers are characterized by the linkage or presence of urethane:[19]



$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5$$

However, other groups such as esters, ethers, and biuret may be present in the molecule. These elastomers are synthetic preparations of long-chain linear polyesters or polyethers reacted with diisocyanates. They can be thermoplastic or thermosetting polymer systems. When properly processed these elastomers are chemically inert, resistant to solvents and ozone, odorless, abrasion resistant, have high tear and tensile strength, do not require the use of plasticizers to attain or control their flexibility and have a wide range of flexibility and softness.[18] Thus a prosthesis with softness and elasticity similar to the tissues that are being replaced or a prosthesis with different degrees of flexibility, eg. in the nose, can be prepared. The bridge of the nose is hard and rigid, whereas the tip of the nose and alae are soft and flexible. It is possible to reproduce closely the modulus of elasticity of living tissues. The materials do not harden with wear and are dimensionally stable when processed. They can be colored easily, intrinsically and extrinsically, and are easily processed. However, they require great precision and care in processing because otherwise poor elastomers may result that are readily degraded.

The polyurethane described here is a four-component system known as Epithane-3.* The polyol (Part A) is a combinations of polyesters; the isocyanate (Part B) is mixture of non-yellowing aliphatic diisocyanates; a catalyst (Part C) is a stannous octoate or dibutyltin dilaurate, plus a thermosetting deglossing emulsion of a polyurethane elastomer with a silica powder. The latter serves as a barrier coat to protect and seal the surface colorants. The colorants (pigments and inks) used are inorganic colorants specially designed for this system and are claimed to be harmless to humans and resistant to ultraviolet light.

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* Daro Products, Inc. (Dermathane), Butler, WI.

TABLE I gives an accurate guideline as to the amount of Part A and Part B to be mixed, to get the softness of the prosthesis to simulate pre-existing tissue.

TABLE I

HARDNESS OF POLYURETHANE ELASTOMERS

PART A (gm)	PART B (gm)	SHORE-A HARDNESS†
30	4.0	7.0 ± 1
30	4.2	15.0 ± 2
30	4.3	22.0 ± 2
30	4.4	30.0 ± 2
30	4.5	35.0 ± 2

† Softness of final prostheses is determined by ratio of Part A and Part B

REVIEW OF RELATED LITERATURE

EVALUATION OF FACIAL PROSTHETIC MATERIAL

In 1966, a Workshop of the American Academy of Maxillofacial Prosthetics was held in Washington D.C.. One of the primary recommendations made at that time was to establish objective criteria for the evaluation of facial prosthetic materials. No objective criteria for the evaluation of facial prosthetic material existed and there was no published evidence to indicate that clinical success could be correlated with measurable material properties.

In 1969, *Cantor and Ryge* [20] reported their progress in developing objective means for evaluating esthetics, durability, processing accuracy of existing facial prosthetic materials and an objective analysis in the development of new materials. They stated that reflectance spectrophotometry or color analysis which measures and records the amount of light reflected for each wavelength in the visible spectrum represented the most accurate method of skin color characterization. They proposed that this well documented method be applied to the evaluation and development of facial prosthetic materials. By analyzing the color of selected materials as well as human skin through spectrophotometry, it was hoped that a means of characterization could be developed.

Furthermore, the authors felt that the most distressing aspect of facial prosthetic treatment, was the fact that an attractive appliance often became unsightly after a few months due to color changes and distorted margins. They elucidated that the durability and the stability of "feather" edges was likely to be reflected in the tearing behavior of thin sheets of the test material, and a test which was relatively independent of specimen geometry would be advantageous because of the variations in size and shape of facial appliances. They felt that tearing of standardized trouser-shaped specimens under controlled conditions provided a convenient basis for determining the energy required to create a unit area of torn surface. The dimensions of the specimens was not critical since tear energy is characteristic of the material. Testing was done with specimens of three types of materials with dimensions defined by the ASTM Test # D1938-62T (referred to as the "pants test" because of the specimen shape) and torn in a tensile testing machine at a fixed rate of grip separation of 2 cm per minute. The tear energy per unit area was computed for each material under those conditions with the stretch-compensated method developed by *Webber and Ryge.*[21]

The American Society of Testing and Materials (ASTM) has issued several standards for testing the tear resistance of plastics and elastomers, including tests to measure the forces needed to initiate and propagate tearing.[22] However, these methods are sensitive to specimen geometry since they measure force and neglect contributions caused by stretching.

To make a meaningful comparison of the tear resistance of various types of facial prosthetic materials it is desirable to measure the energy per unit area required to generate a newly torn surface. *Greensmith*[23] has shown that during tearing of a thin trouser-shaped specimen the energy put into the system must equal the energy of deformation plus the energy necessary to propagate the tear. This can be expressed as :

$$F2\lambda dc = W_0 ahdc + Thdc$$

dc is the differential of the tear length

F is the applied force

a is the width of the leg of the specimen

h is the thickness

λ is the extension ratio of the legs of the specimen

W_o is the work per unit volume done during extension

T is the tear energy in erg / cm^2

After integration and rearrangement :

$$T = 2F\lambda / h - 2W_o a \qquad (1)$$

Webber and Ryge[21] extended this treatment by assuming that Hooke's law is obeyed:

$$W_o = (F / 2ah) . (\Delta x / x_o)$$

$$= F\Delta x / 2ahx_o$$

λ is defined as $(x_o + \Delta x) / x_o$, and can be substituted in the W_o term yield

$$W_o = (F / 2ah) . (\lambda + 1)$$

Substituting this term into equation (1) results in

$$T = 2F\lambda / h - 2 (F / 2ah) . (\lambda + 1) a$$

$$= F / h (2\lambda - \lambda + 1)$$

$$= F / h (\lambda + 1) \qquad (2)$$

This can be used to calculate tear energy from force-displacement data. The advantage of the Webber and Ryge analysis is that the resulting value is an inherent property of the material and should therefore :[24]

- be independent of specimen geometry
- correlate with clinical experience
- allow comparisons between different types of materials
- allow establishment of criteria for tear resistance

When using this technique the energy per unit area should be calculated from data obtained during quasistatic propagation of the tear. Experimentally however, it is often difficult to maintain a stable crack. *Gurney*[25] has defined the criteria for crack stability. Experimentally, modification of the rate of displacement during the test, specimen geometry, and sample thickness may aid in obtaining a quasistatic mode of tearing. *Gurney*[26] has noted that the tear energy of a given material depends on several factors including temperature, specimen thickness, cycling of load or displacement, environmental factors such as the presence of water, air or an organic liquid and speed of the crack front.

In 1972, *Sweeney and Castleberry*[27] reported the results of research and testing of vinyl plastisol type formulations for use as facial material. Vinyl plastisol is a fluid dispersion of polyvinyl chloride (PVC) resin of high molecular weight in a liquid plasticizer. The PVC is soluble in the plasticizer at elevated temperatures. Upon heating of the material, gelation and fusion occurs. The viscosity of the mix is lowered by the temperature increase and raised by the swelling and gelation of the PVC particles. The development of a material that contained usable working properties required the testing of a large series of compositions. They proposed specifications for maxillofacial materials and recommended testing methods to determine the physical properties of the vinyl plastisol material **(TABLE II)**. The following methods were used in determining the physical properties reported:

- Tensile properties were made on standard specimens with a reduced section of width (ASTM), using 0.25 inch width and gauge length of one inch cut from sheets of material of various thicknesses from 10 to 100 mils. The elongation was measured and automatically recorded as the specimen were stressed. A 10% pip was used to show the elongation as the specimens were loaded. The specimens were loaded at one inch per minute in an Instron testing machine from start to the breaking point, and strength was calculated on the basis of original cross section in pounds per square inch (p.s.i.)
- Hardness was measured on a Durometer using a Shore A scale at room temperature
- The modulus of elasticity was determined from the stress strain curves in tension. The values were computed at a strain of 100%
- The stiffness was measured on a Tinius-Olsen torsion stiffness tester as described in ASTM D1043-61T which measured the apparent shear modulus of rigidity (G),

using a specimen 0.25 inch wide and various thicknesses from 0.010 to 0.10 inch and a 2 inch effective length. The specimen was tested from -70° C to -10° C or higher. The G was computed by the following:

$G = 917TL / ab^2\mu\phi$

G is torsion modulus in p.s.i.

T is applied torque (in./lb)

L is the specimen length (in.)

a is the width

b is the specimen thickness (in.)

ϕ is the angle of deflection of torque in degrees

μ is the ratio of a to b

Elastic Modulus E = 3G (assuming 0.5 Poisson's ratio)

- The tear resistance was measured by methods outlined in ASTM D1938-62T, referred to as the "pants test". The load in pounds per inch (p.p.i.) was used to record the results. The load application was applied at 2 inches per minute
- The stability was evaluated on a Weatherometer machine which exposed the specimens to radiations from an arc, which approximates sunlight under various humidity and temperature controls. Specimens were observed for long periods up to 2000 hours or more. The radiation contained ultraviolet (uv), which is effective in deteriorating many polymer materials. This test also evaluated the "tackiness" or "spew" of the specimens caused by plasticizers leaching at the elevated temperatures
- The viscosity was determined on a Brookfield Viscometer and reported in centipois (cps)

TABLE II

PROPOSED SPECIFICATIONS FOR FACIAL MATERIALS

Viscosity		6000 - 8000 cps
Gelation		75 - 80° C
Fusion		150 - 175° C
Hardness		48 - 52 Shore A
Modulus of Elasticity		600 p.s.i.
Torsion	- 70° C	700 x 10^3
	- 10° C	60 x 10^3
Tear Resistance		33 p.p.i.
Tensile Strength		1800 p.s.i.
Tear ("pants test")		30 - 35 p.p.i.
Weathering (Weatherometer)		2000 hours
		No Color Change

In 1978, *Chu and Fischer*[28] examined the stability of polyurethane for maxillofacial applications using an Atlas twin-lamp carbon arc Weatherometer (Model HVDL-X with a globe #9200-PX; #70 uncored and #20 cored carbons). The rationale for using the Weatherometer as a UV source was, that the instrument was readily available and its spectral distribution had a general similarity to that of solar radiation (**TABLE III**).

TABLE III

COMPARISON OF THE SPECTRAL DISTRIBUTIONS OF SOLAR AND WEATHEROMETER RADIATION

SPECTRAL RANGE (nm)	PERCENT TOTAL RADIATION †	
	ARC ENCLOSED (9200-PX GLOBE)	NOON JUNE SUNLIGHT
279-290	00.05	00.00
290-320	04.60	02.00
320-360	06.20	02.80
360-480	15.00	12.60
480-600	08.30	21.90
600-1400	14.90	38.90
1400-4200	21.30	21.40
4200-12,000	29.65	00.40

† **To limit of fluorite transmission to the infrared**

In 1977, *Moore*[29] criticized earlier studies done for evaluating facial prosthetic material using specimens that had been die-cut from sheets of polymer. The use of die-cut specimens for tensile stress-strain testing introduced small nicks and flaws that have been implicated in the growth of cracks and thus in the ultimate failure of the specimens. Die-cut samples also required clamps or end-bonded grips that introduced unwanted artifacts, thus the use of O-ring samples was recommended.

Moore[29] evaluated three materials and tested them for their ultimate tensile stress, ultimate elongation, tensile stress at 100% elongation, resistance to tear propagation and indentation hardness. Tensile stress and elongation were evaluated by the standard method using an Instron tensile tester and molded O-rings (ASTM designation D412-68 “Standard Method of Tension Testing of Vulcanized Rubber”). The O-ring tensile stress-strain samples were stretched on pegs clamped in the tensile tester. The pegs served as axles for freely rotating Teflon wheels that had been machined to act as self-lubricating bearings; while being stretched the rubber O-rings slipped freely around the wheels. The peg axles were cast in chrome-cobalt alloy chosen for its strength and resistance to bending. Colinear alignment and absence of torsional forces on the test specimen during stretching were necessary. The C cell for load measurement was installed in the tensile tester, and crosshead and recorder chart movement was established at 5.1 cm per minute. Full-scale load was 10 kg in all measurements. Resistance to tear propagation was evaluated by the standard method with thin molded rectangular strips (75 x 25 x 0.5 mm) clamped in the Instron tester. Indentation hardness (a compressive test) was measured with a Shore A Durometer using molded disks of polymer 30 mm in diameter and 10 mm thick (ASTM designation D1938-67 “Standard Method of Test for Resistance to tear Propagation in Plastic Film and Thin Sheeting by a Single Tear Method” also referred to as the “pants test” and D2240-68 “Standard Method of Test for Indentation Hardness of Rubber and Plastics by Means of a Durometer”).

Gonzalez[30] studied the physical and mechanical properties of polyurethanes, using specimens molded in a five-piece, stainless steel dumbbell shaped mold according to ASTM D412. Each specimen was 4.50 inches long and 1.00 inch wide, with a neck 1.31 inches long and 0.48 inches wide. The thickness of the mold was modified to 0.25 inch to enable the surface hardness of the specimen to be recorded according to ASTM 2240.

- A Shore-A-2 durometer, mounted on a Shore Conveloader that operated the durometer at a constant load and velocity, was used to measure surface hardness of the elastomers at room temperature (22 ± 2^{o} C)
- A power driven MTS machine which had a fixed and a movable member with a specimen grip-holder, was used for the tensile testing. The grip to prevent slippage of the specimen was provided by a rubber coat. The grip was self-aligning so that the long axis of the test specimen coincided with the direction of the applied load through the center line of the grip assembly. An MTS load cell with a sensitivity of 0.01 lb was attached to the lower member of the MTS machine to record the force applied to the specimen. The force was read directly from a digital voltmeter attached to the load cell.
- The deformation of the specimen was recorded by using the LVDT (linear vertical displacement transducer), and using a motion picture camera. The LVDT method recorded the deformation that occured between the grips, whereas the photographic method recorded the deformation of the specimen at predetermined reference points. A micrometer with an accuracy to 0.001 inch was used to measure the width and thickness of the specimen prior to testing. A Vanguard analyzer modified with a Sonic Graf-Pen-Digitizer GP-3 was used to obtain the data from the movie film. The data was stored on magnetic tape and processed in a CDC 3500 computer.

In 1975, *Koran*[31] studied the dynamic mechanical properties namely dynamic modulus, internal friction and dynamic resilience of maxillofacial materials using a Goodyear Vibrotester. The Vibrotester consisted of an electrical coil energized by alternating current that creates a magnetic field. The coil surrounds a yoke of suitable mass and it was possible to vibrate the yoke longitudinally at specific frequencies. The samples were used in pairs and they were made in a steel mold. The samples were right cylinders one half inch in diameter and one half inch in length. The samples dampen the amplitude of the vibration of the yoke and they function as springs. The system was tuned to resonate at 60 hertz (or other convenient frequencies) by changing the mass of the yoke. The amplitude at resonance and the phase shift between the applied force and the resulting motion were measured optically by the motion of a light attached to the end of the yoke. The amplitude of the vibration was measured by the width of the light beam on a ground-glass optical assembly. The data collected consisted of the mass of the yoke which can easily be measured and changed, the frequency of the system at resonance, and the current required to resonate the system at a specific magnitude. This information was used to calculate the dynamic modulus, internal friction and dynamic resilience.

Dynamic modulus = $E = mqp^2$ (1)

m is the mass of yoke in grams

q is the height / 2 x cross-sectional area of specimen

p is the angular frequency at resonance in radians per second

Internal Friction = $N = Fq / p X_{res}$ (2)

F is the driving force in dynes

q is the height / 2 x area of specimen

p is the angular frequency in radians per second

X_{res} is the amplitude at resonance

Dynamic resilience = $R = 100e^{-2pN / E}$ (3)

p is the angular frequency in radians per second

N / E is the ratio of the internal friction to the dynamic modulus

The rationale for studying the dynamic properties was " .... if the premise is accepted that maxillofacial materials should simulate the oral tissues, then the dynamic nature of these tissues must be considered. The oral tissues are constantly moving and are subjected to a multitude of forces in many directions in both tension and compression.

These oral tissues are soft, tough and quite resilient. Unfortunately, the dynamic properties of the oral tissues have not been determined, although estimates can be made. It is quite possible, however, to measure the dynamic properties of the elastomers as a function of the temperature range over which they are called upon to function."

The obvious weakness in this line of reasoning is that the materials studied, polyurethane, PVC and silicones are never used intraorally. Although the need to measure dynamic properties of facial material is valid, the materials tested are used extraorally and the attempt to correlate dynamic properties of intraoral tissues to facial elastomers is misplaced.

STATIC AND DYNAMIC MECHANICAL PROPERTIES

Moore[29] evaluated Silastic 382, MDX 4-4210 and MDX 4-4210 with thinner (10% 360 silicone fluid by weight), using the O-ring tensile test for tensile modulus at break, elongation percentage and tensile modulus at 100% elongation. Resistance to tear propagation test and Shore A durometer test were also done.

Comparison of values obtained from these tests showed that the yield stress values (tensile modulus at break) of the Silastic 382 samples and the MDX 4-4210 unmodified samples were the same. The elongation at break (yield) of the MDX samples was almost three times that of the Silastic 382 samples. The modulus of elasticity of the Silastic 382 samples was nearly constant over the entire stretch of the sample almost up to the breaking point. The MDX modulus of elasticity was approximately one fourth that of Silastic 382 at low elongations and instead of remaining constant the elasticity increased very slowly. However, it never approached the high values of the Silastic 382. The addition of thinner to MDX reduced the material's tensile modulus by approximately 50% and did not appreciably change its elongation at break. MDX demonstrated a threefold reduction in tensile modulus at 100% elongation. No permanent deformation in the samples was noted following loading up to the breaking point followed by a return to zero load.

The MDX samples fared much better than the Silastic 382 samples in the resistance to tear propagation test. Elongation and maximum load were found to be significantly greater for the MDX samples than for the Silastic 382 samples. Even at the large values of load and elongation, the MDX did not appear to fail completely. This contrasts to the "zipper effect" demonstrated in the Silastic 382 samples. The MDX samples initially developed a small failure "blip" and then continued to support an increased load. The addition of 10% thinner to samples of MDX increased the elongation factor and surprisingly these thin samples were able to support a slightly greater load than that was tolerated by either the Silastic 382 or the unmodified MDX material. Comparison values obtained in the Shore A durometer test showed that the MDX material is significantly softer than the Silastic 382 material (41.4 ± 1.3 and 26.8 ± 1.2 respectively). The silicone fluid thinner further reduces the surface hardness of MDX 4-4210 (18.4 ± 1.2).

Bell[32] evaluated and compared the physical properties of HTV silicones including MDX 4-4515, Q 7-4635, Q 7-4650 and SE-4524U which are condensation reaction, one component putty silicones. Q 7-4735 an addition reaction, two component putty silicone was also tested using the same parameters.

Tensile strength, a general measure of the overall strength of facial prosthetic material was tested using the ASTM D412 test, and an arbitrary range of 1000 to 2000 psi was considered acceptable for these materials. The tensile strength of the five materials tested in the study fell well within the proposed range. Three of the materials, SE-4524U, Q 7-4650 and Q 7-4635, demonstrated significantly greater tensile strength than the other two materials, MDX 4-4515 and Q 7-4635.

Elongation, a measure consistent with flexibility, an indicator of the overall flexibility of a prosthetic material with facial motion was tested using the ASTM D412 test. *Sweeney and Castleberry*[27] considered a range of 400% to 800% to be acceptable. *Conroy*[33] disagreed, and stated that elongation at failure should have an optimum value of 500% to 1000%. It must be noted, however, that the values determined, depend on the formula used in the calculations. The literature does not relate the desired limits of elongation to a method of calculation, so that the relationship between the determined elongation percent units in the different studies reviewed remain uncertain. It is not possible to relate the tensile modulus at 100% elongation and at failure, because the means of calculation is not described. *Conroy*[33] made no reference to the use of moduli. *Moore*[29] described tensile moduli at 100% elongation and at break. *Sweeney and Castleberry*[27] stated that although the modulus at 100% extension is commonly measured, values of initial modulus are probably more meaningful because facial movement rarely exceeds 10%. The elongation of the materials tested in this study fell within the proposed range with the exception of Q 7-4735, which exhibited 1135% elongation.

Tear strength is indicative of marginal integrity and durability of a material in clinical service. A range of 30 to 100 ppi was proposed to be acceptable using the ASTM D624 test. All materials tested, exhibited tear strength significantly greater than the proposed range.

Durometer hardness, another measure of flexibility and indicative of lifelike feel was tested using the Shore A durometer as per ASTM D2240 test. *Sweeney and Castleberry*[27] considered a range of 25 to 35 Shore A units to be acceptable. *Conroy*[33] indicated that optimum hardness should be 25 to 55 Shore A indentation units. The results ranged from 50.8 ± 0.6 to 39.6 ± 1.1 Shore A units, and the results were believed to be "clinically acceptable".

Wolfaardt[34] examined the mechanical properties of two relatively new products Cosmesil-H and Cosmesil-S, and compared it to Silastic 382, MDX 4-4210 and Silskin. Cosmesil-H had no "flexibilizer" and an increased "crosslinker" content compared to Cosmesil-S.

Tests for tensile strength at failure revealed that Cosmesil-H and Cosmesil-S could tolerate higher loads than other silicone elastomers tested. The coefficient of variation revealed that Cosmesil-S behaved more predictably than Cosmesil-H under load at failure. Silastic 382 showed low elongation at failure, while all materials were found to approach the lower end of the limits of *Conroy*.[33]

Investigation of the resistance to tear propagation, revealed that Cosmesil-S was the most resistant, followed by Cosmesil-H, Silskin and MDX 4-4210. Silskin exhibited the highest degree of predictability for tear strength, with a coefficient of variation of 8.9% and MDX 4-4210 had the least predictability of behavior, with a coefficient of variation of 30.8%. It should be noted, that only the tear strength at failure was considered and the force that initiates tear propagation which is equally important to the behavior during was not tested. Shore A hardness testing revealed that with the exception of Silskin, the values fell within the limits proposed by *Conroy*.[33]

Gonzalez[35] tested the physical and mechanical properties of Epithane-3 after varying time and temperature of the curing process. The surface hardness measured with a Shore A durometer revealed that the hardness of elastomer polymerized at different temperatures or for different lengths of time had no statistical difference. The stress-strain curve revealed that the curve starts with a large initial modulus and then rapidly changes to a lower tensile modulus at 100% elongation. The ultimate tensile strength and elongation varied with different polymerization temperatures and times. However, no definite trend was indicated. The results of resistance to tear propagation test revealed no statistical difference between the different groups though initial tear strength seemed to increase slightly for the materials with a longer polymerization time or higher polymerization temperature. One can conclude that the curing time and temperature seem to have a very limited influence on the material properties, possibly due to the low exothermic reaction conditions in which the hydroxyl components reacts at the same rate.

ELASTOMERS IN A SERVICE ENVIRONMENT

Color Stability

In 1978, *Koran*[36] studied the color stability of elastomers for maxillofacial applications under conditions of accelerated aging, in an effort to simulate a service environment. A polyurethane (Epithane), three RTV silicones (Silastic 382, 399, 4-4210) and HTV silicone (Silastic 4-4515) were evaluated by reflectance spectrophotometry with a double-beam, ultraviolet visible spectrophotometer and integrating sphere. In this method of color analysis, the amount of light reflected at each wavelength in the visible spectrum (400-700 nm) was measured and recorded. The luminous reflectance (a measure of the total amount of light reflected by the specimen) is a measure of lightness or darkness. It is similar to value in other color systems. Dominant wavelength (the actual color of the specimen when compared to a standard observer and is similar to hue), and excitation purity (a measure of the amount of color present in the sample and is similar to chroma) were calculated for each test specimen by using a computer program based on the C.I.E. chromaticity diagram 1931 and Source A. Samples 3.5 x 4 x 6 cm were placed in a weathering chamber for accelerated aging. A 2500 watt xenon light source with borosilicate glass filters were used to simulate natural sunlight. Water was sprayed for 18 minutes every 102 minutes and relative humidity maintained at 90% RH. Spectral reflectance was evaluated after 100, 300, 600 and 900 hours in the weathering chamber. Polyurethane exhibited severe degradation and poor color stability. In general, the silicones all showed good color stability and Silastic 4-4210 appeared to have the best overall properties.

In 1979, *Koran*[37] examined the color stability of a pigmented elastomer using the same method described earlier. Eleven dry mineral earth pigments were incorporated into silicone base (RTV Silastic 4-4210) at a concentration of 0.2% by weight and processed. Very small changes in color could be detected after removal from the accelerated aging chamber.

In 1979, *Koran*[38] studied the resistance of Silastic 4-4210, Silastic 382, Silastic 4-4515, and PVC Prototype III to staining with tea, lipstick and disclosing solution. The method used, to evaluate the stain resistance, was with reflectance spectrophotometry before and after staining. Silastic 4-4210 had the least changes after staining, although many factors such as type and percentage of fillers, presence of plasticizers and the wettability of the material by the stain play an important role and were not taken into consideration.

In 1981, a study by *Koran*[39] examined the effects of stain removal on Silastic 4-4210, a silicone proven to be superior as regards color stability. Lipstick, methylene blue and disclosing solution were applied to the silicone specimens and then removed with toluene, benzene, 1,1,1-trichloroethane and n-hexane. Results obtained from spectrophotometric measurements before and after solvent extraction demonstrated the effectiveness of solvent extraction in removing stains, while there was little or no change in the color of the base elastomer.

In 1982, *Koran*[40] studied the effects of environmental stains on pigmented Silastic 4-4210. Eleven dry earth pigments were used for the study and the base elastomer was stained with lipstick, methylene blue and disclosing solution. These stains were then removed using 1,1,1-trichloroethane. Color parameter measurements both before and after staining and after solvent extraction with 1,1,1-trichloroethane, demonstrated the effectiveness of removing these stains by solvent extraction while causing little or no change in the color of the pigmented samples.

A similar study was done by *Koran*[41] in 1983 to study the effect of cigarette smoke stain on Silastic 4-4210 and the effect of stain removal using 1,1,1-trichloroethane. The smoke produced large color changes in the elastomer as measured from spectrophotometric reflectance curves. The solvent was totally effective in removing the cigarette stain without changing the color of the silicone base.

In 1987, *Koran*[42] examined samples made from pigmented porcelain and Silastic 4-4210, for color stability after accelerated aging; similar to previous studies, in order to determine the potential of colored ceramic powders as maxillofacial pigments. These pigments demonstrated good clear color stability compared with the same pigments which were not incorporated into a porcelain matrix.

In 1984, *Turner*[43] tested isophorone polyurethane with 7.4% plasticizer. Four color systems were tested: artist's oil paints, dry earth pigments, kaolin modified with dry earth pigments and Daro skin pigments. In addition to these four systems, isophorone polyurethane with no color additives was tested as a control. Specimens were prepared with a spin-casting technique to form a uniform layer of material on the inner wall of a hollow cup spinning on a lathe. A major advantage of spin casting was claimed to be the consistent uniform thickness of the specimens which reduced the amount of material needed. Aging of the samples was accomplished using a Weatherometer. Color stability evaluation was done by visual comparisons and reflectance spectrophotometer. The results using visual comparisons revealed "slight color changes". The Daro system was graded the best, followed by dry earth pigments, artist's oil paints and the kaolin system.

Reflectance spectrophotometer and a computer program was used to calculate dominant wavelength, excitation purity, luminous reflectance and contrast ratio. For each of the five color systems there was no statistically significant difference in color from before aging to after aging of the specimens.

Physical Properties

Determination of the amount of permanent deformation for maxillofacial elastomers is essential in evaluating the potential for permanent dimensional change as a result of stress on the peripheries of maxillofacial prostheses. *Koran*[44] investigated the permanent deformation and volume change of elastomers under conditions of accelerated aging using a Weatherometer. Silastic 382, Silastic 399, Silastic 4-4210, Silastic 4-4515, Prototype III and Epithane were evaluated in the aging chamber. The new values of permanent deformation were determined by elongating a tensile sample to the point of rupture, measuring the increase in length after 24 hours of recovery and representing this value as percentage of the original length. Each elastomer was taken to the ultimate elongation and then allowed to recover with no stress. This was claimed to be relevant to the mode of failure around the thin edges of a prosthesis under service conditions. This test was obviously more challenging to those materials having a higher ultimate elongation. The volume measurement of each sample before and after accelerated aging was determined by buoyancy technique in distilled water. The results of this study, complemented the results of earlier studies. Silicones, in general under conditions of accelerated aging were more stable than other elastomers like polyurethane.

In 1980, *Koran*[45] evaluated the physical properties of maxillofacial elastomers as a function of accelerated aging. Later, the same year *Koran*[46] examined the physical properties of pigmented silicone as a function of accelerated aging. In both these studies, protocols identical to the ones described earlier, including the sample type and size were followed. The physical properties, characterized by the tensile strength, tear energy, and Shore A hardness were determined before and after 600 and 900 hours of exposure in a Weatherometer. The results were supposed to establish the relative stability of each material under conditions of accelerated aging.

The overall physical properties of various silicone elastomers demonstrated no change on accelerated aging. This stability was postulated to be due to the unique characteristics of the inert inorganic backbone of the molecular chains. The wide range of ultimate tensile strength, shear strength, and Shore A hardness of different types of silicones, along with the tear resistance and high percent elongation for Silastic 4-4210 and Silastic 4-4515 was thought to be due to the chemical nature of the fillers and the configurations of crosslinkage in the materials.

The PVC material was observed to be less stable than the silicones. Prior to accelerated aging, syneresis of the plasticizer on the surface of processed PVC was noticed. Slight alterations in ultimate tensile strength and Shore A hardness were seen after 900 hours of aging. The largest change was a decrease in shear strength by 17%. These changes were thought to be a direct result of leaching out of plasticizer from the elastomer. The degree of this exudation is believed to be controlled by the efficiency, compatibility and miscibility of plasticizer from the elastomer. The degree of this exudation is controlled by the efficiency, compatibility and miscibility of plasticizer and PVC in their molecular interactions. Since PVC is readily susceptible to decomposition under the influence of UV light and the presence of an oxidant, the observed changes were also thought to be due to ultraviolet irradiation.

The least stable material studied were the polyurethanes. The material suffered serious physical deterioration on aging, and it proceeded further to total disintegration after 600 hours of aging. This failure was hypothesized to be due to the hydrolytic degradation at the ester linkages of the polyurethane molecules when reacted with water under the influence of ultraviolet irradiation.

The effects of accelerated aging on Silastic 4-4210 with eleven dry earth pigments were studied by *Koran*[46]. The values of ultimate tensile strength, maximum percent elongation, shear strength, Shore A hardness and permanent deformation were determined for the pigmented elastomer before and after accelerated aging for 900 hours. Results obtained indicated that the incorporation of 0.2% by weight of pigments altered the physical and mechanical properties of the base elastomer, even before the samples were placed in the aging chamber. The largest change observed was a decrease in the ultimate tensile strength of the elastomer by 20.7% and a 4.4% decrease in percent elongation. There was also a decrease in Shore A hardness by 30.9%. Accelerated aging had no effect on the physical properties of the pigment / elastomer combinations except for a decrease in Shore A hardness units after 900 hours. Although the changes observed were statistically significant, they were insignificant in clinical applications. When the pigments were incorporated into the polymer matrix, the results obtained for physical and mechanical properties were largely contributed by physical interactions and were not of a chemical origin. If there were a chemical reaction between the pigment and the elastomer, the result of chemical bonding between polymer and pigments would be reinforcement, whereas in physical interactions, pigment particles can be treated as inert media, in that their presence has been accounted for by simple geometric modification of the elastic chains in a polymer network and a reduction in the numbers of chains passing through a unit cross-sectional area of the sample. No reinforcement can be expected, but a reduction in physical and mechanical strength of the elastomer results.

Turner[47] evaluated the effects of aging on an aliphatic polyurethane prepolymer, isophorone, using a Weatherometer. The average value for ultimate tensile strength of isophorone with 7.4% plasticizer was 696 psi. While this value is lower than the desirable range, it is considerably greater than the ultimate tensile strength of MDX 4-4210 with 10% plasticizer, which has been reported to be 469 psi.[28] In addition, the percent elongation of MDX with 10% plasticizer was reported to be 410% and is comparable to isophorone's 595%. Isophorone has lower tear strength and hardness values than that of MDX, nevertheless these values are much higher when compared to the commercially available polyurethane Epithane-3.

MATERIALS AND METHODS

MATERIALS

The facial prosthetic materials tested in this study were silicone and polyurethane type material. The silicones tested were room temperature vulcanizing (RTV) or low temperature vulcanizing materials. These materials were provided by the manufacturer and manipulated as per their instructions. **TABLE IV** lists the facial prosthetic materials tested in this study.

TABLE IV

FACIAL PROSTHETIC MATERIALS TESTED IN THE STUDY

FACIAL MATERIALS	BATCH #	MANUFACTURER
Silastic MDX 4-4210 (Silicone)	HH070897	Dow Corning Corporation Midland, MI
Cosmesil Maxillofacial Prosthetic System (Silicone)	10 / A / 90	Cosmedica Limited University of Wales College of Cardiff Cardiff, U.K.
Epithane-3 (Polyurethane)	591845	Daro Products, Inc. Butler, WI

Silastic MDX 4-4210

This elastomer is a pourable two-component product which, when combined, cures to a translucent silicone rubber, at room temperature **(FIGURE I)**. One part of the curing agent was throughly mixed with ten parts of the base elastomer. The base elastomer and the curing agent were carefully weighed on a balance to an accuracy of 0.1 gram. During mixing, care was taken to minimize entrapment of air. The viscosity of the mix was about one-half of the original base viscosity.

The mix was exposed to house vacuum for thirty minutes, in a container that was at least four times the volume of the mixture, to allow for expansion. The vacuum was released several times during the early phase, which helped break the bubbles that formed.

The material was then packed into the specimen mold, taking care to minimize the entrapment of air. A cure time of 24 hours at 23^{o} C was allowed prior to handling the specimen and exposing it to the environmental factors.

Cosmesil Maxillofacial Prosthetic System

This maxillofacial prosthetic system, a room temperature vulcanizing (RTV) silicone, consists of a semi-transparent silicone elastomer base and curing additives, a catalyst and a crosslinker **(FIGURE II)**.

The elastomer base was carefully weighed, on a balance to an accuracy of 0.1 gram, in batches of ten grams. The base was spatulated on a clean, dry, flat working surface in order to freshen the consistency. The elastomer base was spread uniformly on the working surface and a pattern of intersecting cuts made in the material, with the spatula.

Drops of catalyst were dispensed with a pipette at the intersections and mixed thoroughly. The amount of catalyst dispensed was as per the proportion recommended by

Dow Corning MDX 4-4210

FIGURE I

Cosmesil Prosthetic System

FIGURE II

the manufacturer (**TABLE V**). In this study, the proportions used, were for the firm consistency.

Using a different pipette, the exact proportion of crosslinker was dispensed and mixed. An uniform mix was achieved and packed into the specimen mold, taking care to minimize the entrapment of air. A cure time of 24 hours at 23^{o} C was allowed prior to handling the specimen and exposing it to the environmental factors.

TABLE V

PROPORTIONS FOR COSMESIL CURING ADDITIVES

FORMULATION	FIRM	MEDIUM	SOFT
Cosmesil Base S (grams)	10	10	10
Catalyst 4D (drops)	12	10	10
Crosslinker M (drops)	18	15	12
Worktime (minutes)	20-40	50-60	70-80

Epithane-3

This polyurethane material consists of a polyol Part A, the isocyanate Part B and a catalyst Part C (**FIGURE III**).

Part A was preheated to 90^{o} C in an oven for one hour, thus reducing its viscosity and making it easier to handle. Part A and Part B were weighed on a balance to an

Daro Epithane-3

FIGURE III

accuracy of 0.1 gram, using the ratios as recommended by the manufacturer **(TABLE I)**. In this study, the proportions used, were for a Shore-A hardness of 22.0 ± 2.

Part A and Part B was mixed slowly by hand for five minutes, and the mixture was returned to the preheated oven for five minutes to allow the temperature to return to 90^{o} C. The mixture was removed from the oven and three drops of catalyst C was added and mixed slowly but thoroughly for two minutes. The mixture was placed under vacuum for three minutes, making sure that the container was large enough to allow for the expansion of the mixture while degassing.

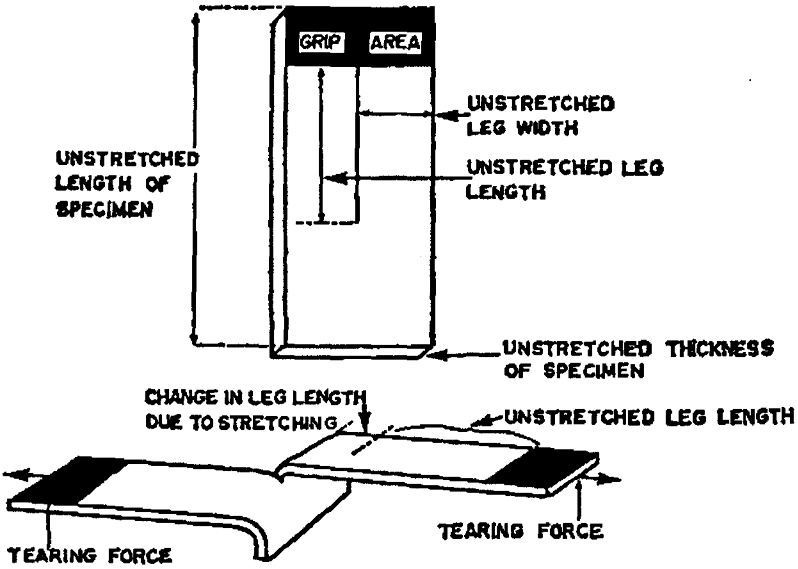
The material was then packed into the specimen mold, taking care to minimize the entrapment of air and placed in the oven at 127^{o} C for thirty minutes. A cure time of 24 hours at 23^{o} C was allowed prior to handling the specimen and exposing it to the environmental factors.

SPECIMEN PREPARATION

Specimens were fabricated using precisely machined aluminum molds. The dimensions of the specimen mold were as per ASTM specification D 1938 “pants tear test” **(FIGURE IV, V & VI)**.

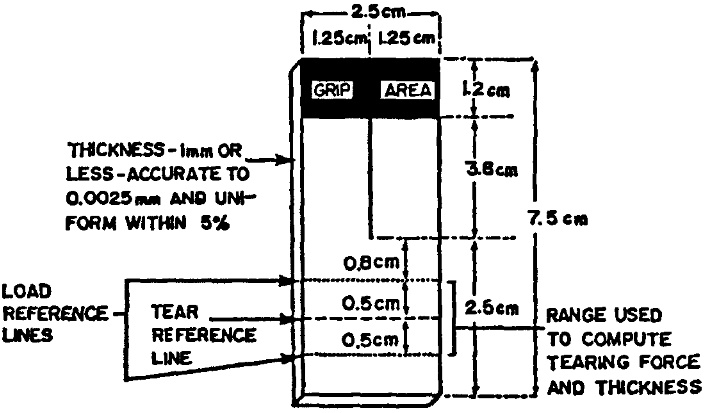
A Mylar sheet was placed on a glass slab and the specimen mold placed on it. The material was then packed into the specimen mold, taking care to minimize the entrapment of air. Another Mylar sheet was then placed on the packed material and a glass slab placed on the sheet and material. Using a C clamp, external pressure was applied to the mold, to disperse the pockets of air, inadvertently trapped in the mold. A cure time of 24 hours at 23^{o} C was allowed prior to handling the specimen and exposing it to the environmental factors. The excess flash was trimmed, using a sharp pair of scissors.

FIGURE IV

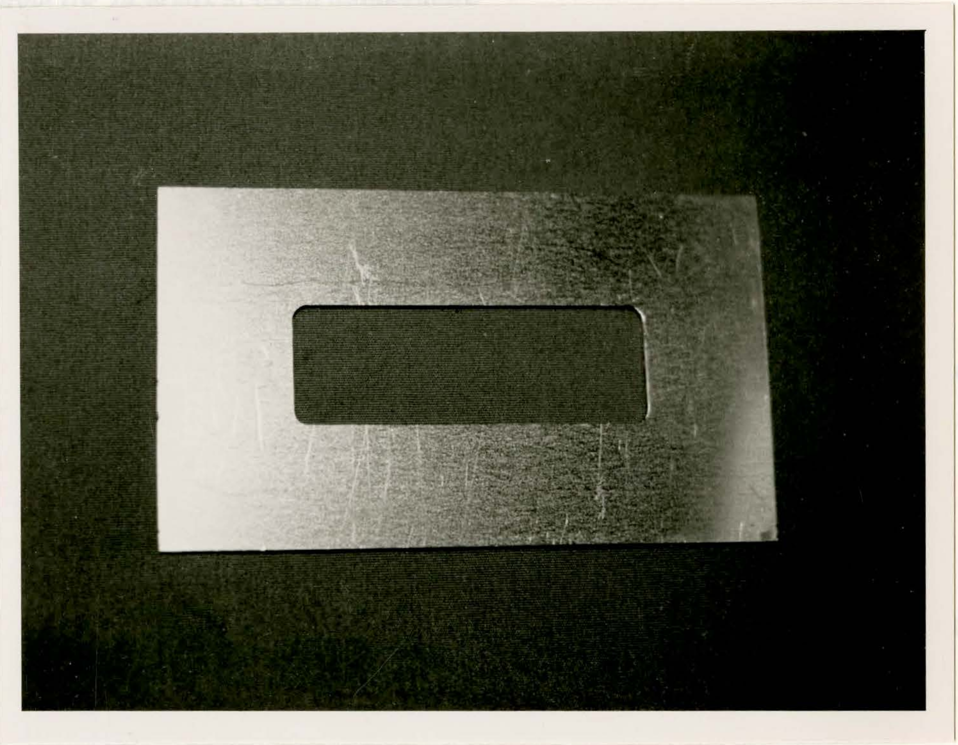


TROUSER-SHAPED TEAR SPECIMEN

FIGURE V



ASTM TEAR SPECIMEN DIMENSIONS



Specimen Mold

FIGURE VI

EXPERIMENTAL METHODS

Environmental Factors

Five specimens per material tested, were exposed to the following environment :

- control for 24 hours at room temperature
- control for 24 hours at 60^o C
- ultraviolet (uv) radiation for 500 hours
- ozone for 24 hours at room temperature
- simulated sebum for 24 hours at 60^o C
- chlorine for 24 hours at room temperature
- nitrogen dioxide for 24 hours at room temperature

Control for 24 hours at room temperature

The cured specimens were placed on tin foil and exposed to air, for 24 hours at room temperature. These were control samples to obtain baseline data.

Control for 24 hours at 60^o C

The cured specimens were placed on tin foil and exposed to air for 24 hours, at 60^o C in an oven. These were control samples to obtain baseline data.

Ultraviolet (uv) radiation for 500 hours

The specimens were exposed to ultraviolet (uv) radiation (1700 $\mu W / cm^2$) in a color stability test apparatus* for 500 hours (**FIGURE VII**). The ultraviolet radiation

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* S & W Precision Instruments, Chicago, IL

Color Stability Test Apparatus

FIGURE VII

was monitored using a long wave uv meter[*].

Ozone for 24 hours at room temperature

The specimens were exposed to 6-8% ozone and stored for 24 hours at room temperature. Ozone was manufactured using a high frequency generator. The ozone was collected and stored in airtight containers.**(FIGURE VIII)**.

The apparatus consisted of a glass chamber 32 mm in diameter with # 6 rubber stoppers on both ends. Two electrodes were passed through, one of which was electrically grounded and the other was connected to a high frequency generator. 5 psig pure oxygen was passed through one end of the chamber and a combination of 6-8% ozone and oxygen exited through the other end.

Simulated sebum for 24 hours at 60° C

Sebum was simulated using a combination of fatty acids, palmitic and linoleic acids and tripalmitin.

10% by weight of palmitic acid[**] ($CH_3 (CH_2)_{14} COOH$) and 2% by weight of tripalmitin[***] ($C_{51} H_{98} O_6$) was dissolved in 88% by weight of linoleic acid[****] ($C_{18} H_{32} O_2$). The specimens were submerged in "sebum" for 24 hours at 60° C. Prior to testing, the specimens were removed from the "sebum" and air dryed.

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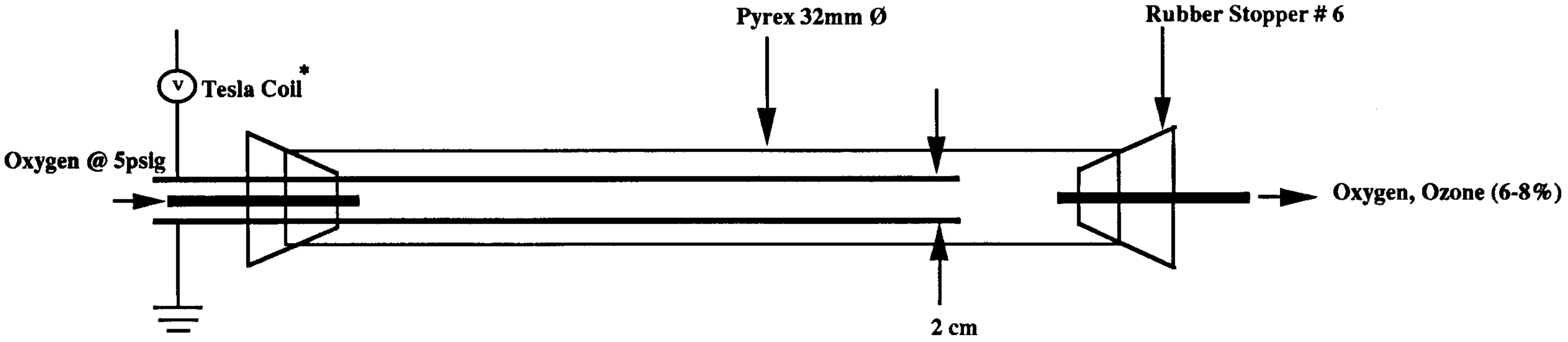
[*] Blak-Ray Ultra-Violet Products, San Gabriel, CA

[**] Eastman Kodak Co., Rochester, N.Y.

[***] Eastman Kodak Co., Rochester, N.Y.

[****] Sigma Chemical Co., St. Louis, MO



OZONE GENERATOR

FIGURE VIII

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[*] Model BD 10, Electro Technic Products, Chicago, IL

Chlorine for 24 hours at room temperature

The specimens were exposed to chlorine and stored for 24 hours at room temperature prior to testing. Chlorine gas was generated using manganese dioxide* and 37% hydrochloric acid**.

15 grams of manganese dioxide and hydrochloric acid was heated in a flask, chlorine was collected in a container and the specimens were exposed to the gas.

Nitrogen dioxide for 24 Hours at room temperature

The specimens were stored in an environment containing nitrogen dioxide, for 24 hours at room temperature. Nitrogen dioxide was generated using copper chips and 70.5% nitric acid ***.

Nitric acid was added to a flask containing copper chips. The nitrogen dioxide gas generated was collected in a container and the specimens were exposed to the gas.

Specimen Testing

The dimensions of the unstretched specimen leg was marked on graph paper. After the specimen was exposed to a specific environmental factor, it was placed on a glass slab and the graph paper. Using a sharp surgical blade, a nick was made along the length of the unstrectched specimen leg.

The specimen was tested for tear propagation resistance by a single-tear method as per ASTM specification D 1938. The specimen was aligned so that the major axis coincided with an imaginary line joining the center of the grips. Using a load cell of

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* Mallinckrodt Inc., Paris, KY

** Mallinckrodt Inc., Paris, KY

*** Mallinckrodt Inc., Paris, KY

ten pounds and a grip separation speed of 10 inches / minute, the specimen was tested on an Instron universal testing machine* **(FIGURE IX)**.

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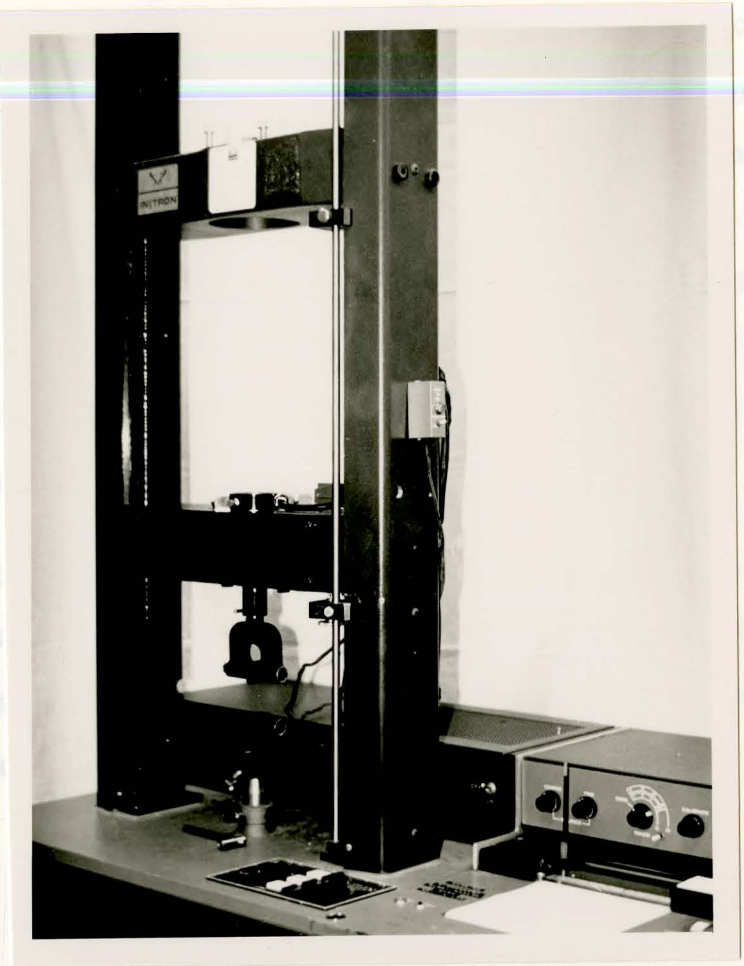
* Instron Corp., Canton, MA



INSTRON TESTING MACHINE

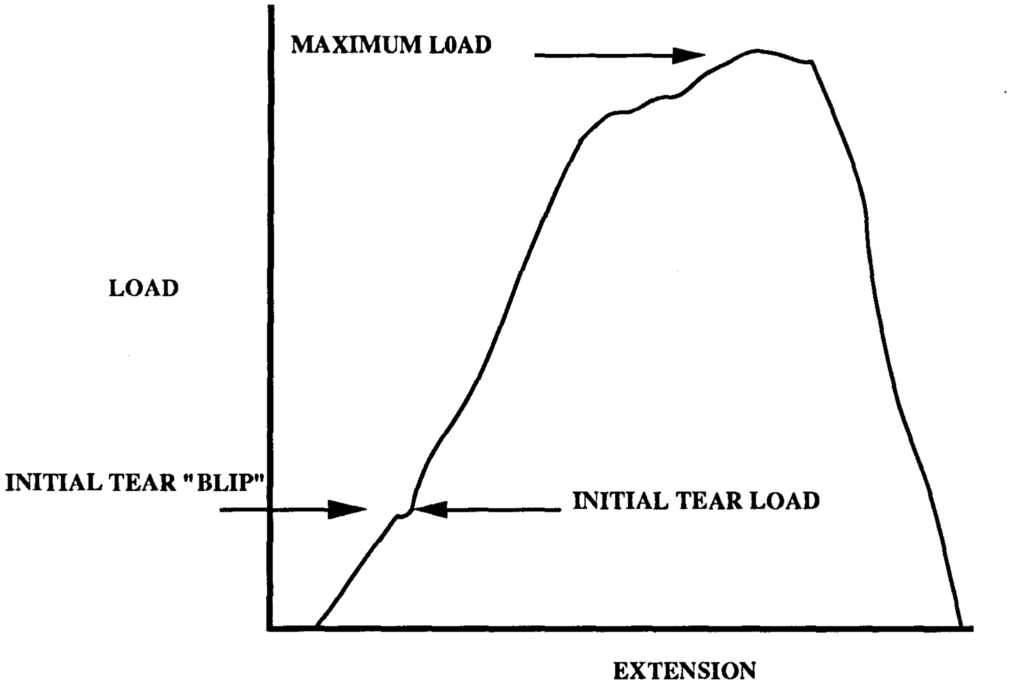
FIGURE IX

RESULTS

The load-extension chart generated, revealed distinct trends. Silicones (Cosmesil, MDX 4-4210) and polyurethane (Epithane-3) produced characteristic charts (**FIGURE X, XI**). The parameters studied were $F_{Critical}$, F_{Final} (load in grams) and $L_0L_{Critical}$, L_0L_{Final} (extension in centimeters). The mean and the standard deviation values of these parameters for MDX 4-4210, Cosmesil and Epithane-3, exposed to the different environments are shown in **TABLE VI-XII.** The mean values of these parameters are graphically illustrated in **FIGURE XII-XXV**. The † notation denotes that the material was depolymerized after exposure to a particular environment. Since the environment caused total destruction of the material, sample testing was not possible.

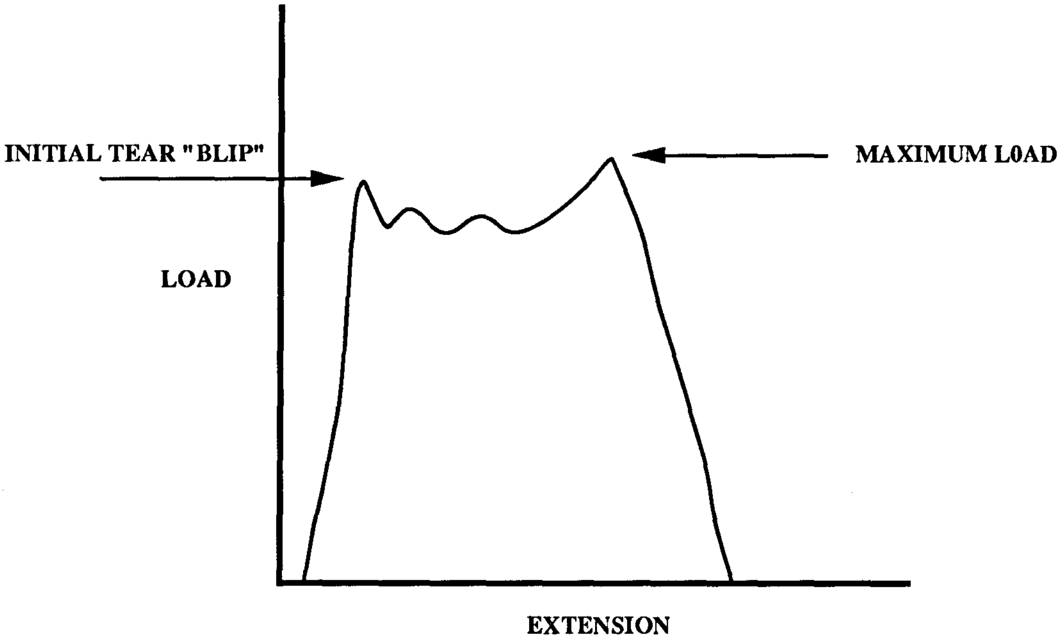
For all the parameters tested, data was statistically analyzed with a one-way analysis of variance and Student-Newman-Keuls (SNK) multiple comparison test ($\alpha = 0.01$). A statistically significant difference was evident between the control specimens and those that were exposed to some environments.

FIGURE X



LOAD-EXTENSION CHART FOR MDX 4-4210 AND COSMESIL

FIGURE XI



LOAD-EXTENSION CHART FOR EPITHANE-3

TABLE VI

CONTROL FOR 24 HOURS AT ROOM TEMPERATURE

MATERIAL	L_0L_C (cms)		L_0L_F (cms)		F_C (gms)		F_F (gms)	
n = 5	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.
MDX 4-4210	2.79	0.36	14.27	0.92	84.37	8.24	701.25	51.17
COSMESIL	2.34	0.28	6.71	1.17	141.52	17.39	163.29	36.14
EPITHANE-3	2.54	0.31	9.14	2.29	109.77	26.91	142.42	20.44

TABLE VII

CONTROL FOR 24 HOURS AT 60^{0} C

MATERIAL	L_0L_C (cms)		L_0L_F (cms)		F_C (gms)		F_F (gms)	
n = 5	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.
MDX 4-4210	2.69	0.14	12.55	0.96	81.65	6.42	680.38	48.01
COSMESIL	2.79	0.00	7.98	0.53	195.95	14.84	210.47	25.37
EPITHANE-3	1.57	0.21	6.65	0.21	69.85	8.84	69.85	7.59

TABLE VIII

ULTRAVIOLET (UV) RADIATION FOR 500 HOURS

MATERIAL	L_0L_C (cms)		L_0L_F (cms)		F_C (gms)		F_F (gms)	
n = 5	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.
MDX 4-4210	2.34	0.11	11.48	2.37	40.82	3.21	366.50	72.53
COSMESIL	2.13	0.14	7.75	1.67	121.56	10.83	161.48	24.56
EPITHANE-3	†	†	†	†	†	†	†	†

† = Depolymerized

TABLE IX

OZONE FOR 24 HOURS AT ROOM TEMPERATURE

MATERIAL	L_0L_C (cms)		L_0L_F (cms)		F_C (gms)		F_F (gms)	
n = 5	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.
MDX 4-4210	2.54	0.25	12.59	0.96	80.74	20.39	653.17	54.15
COSMESIL	2.69	0.14	7.21	1.37	94.35	8.12	101.60	26.36
EPITHANE-3	2.59	0.46	8.74	0.53	66.23	19.41	91.63	19.15

TABLE X

SIMULATED SEBUM FOR 24 HOURS AT 60^o C

MATERIAL	L_0L_C (cms)		L_0L_F (cms)		F_C (gms)		F_F (gms)	
n = 5	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.
MDX 4-4210	2.85	0.49	14.03	5.87	87.99	17.45	633.21	97.16
COSMESIL	3.40	0.66	22.96	3.13	56.24	7.59	386.45	66.54
EPITHANE-3	2.24	0.28	8.07	0.75	55.79	9.16	76.20	27.71

TABLE XI

CHLORINE FOR 24 HOURS AT ROOM TEMPERATURE

MATERIAL	L_0L_C (cms)		L_0L_F (cms)		F_C (gms)		F_F (gms)	
n = 5	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.
MDX 4-4210	2.74	0.92	8.23	0.82	27.21	9.62	390.09	158.07
COSMESIL	†	†	†	†	†	†	†	†
EPITHANE-3	†	†	†	†	†	†	†	†

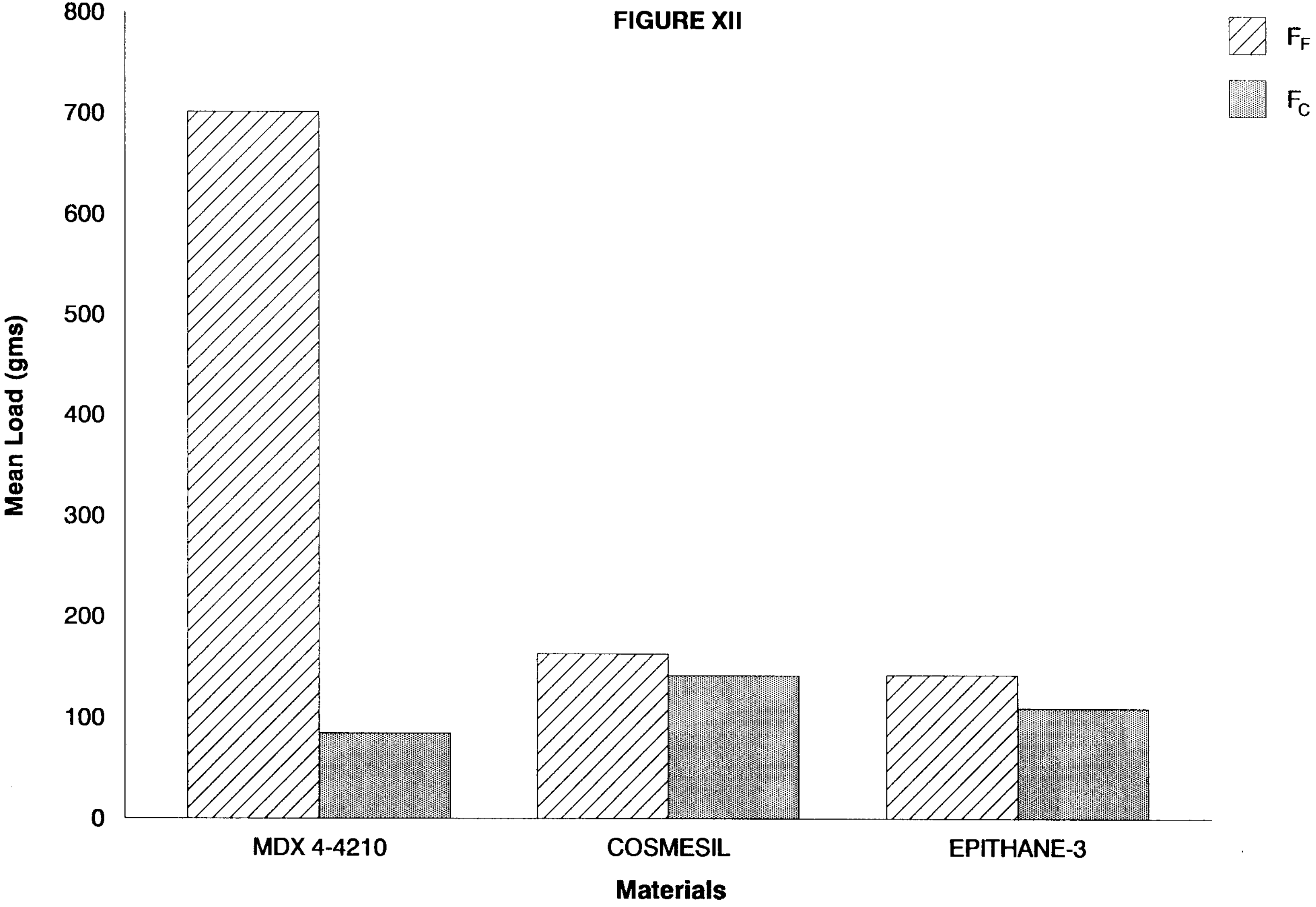
TABLE XII

NITROGEN DIOXIDE FOR 24 HOURS AT ROOM TEMPERATURE

MATERIAL	L_0L_C (cms)		L_0L_F (cms)		F_C (gms)		F_F (gms)	
n = 5	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.
MDX 4-4210	4.62	0.92	11.38	2.78	107.95	37.73	269.43	59.37
COSMESIL	†	†	†	†	†	†	†	†
EPITHANE-3	†	†	†	†	†	†	†	†

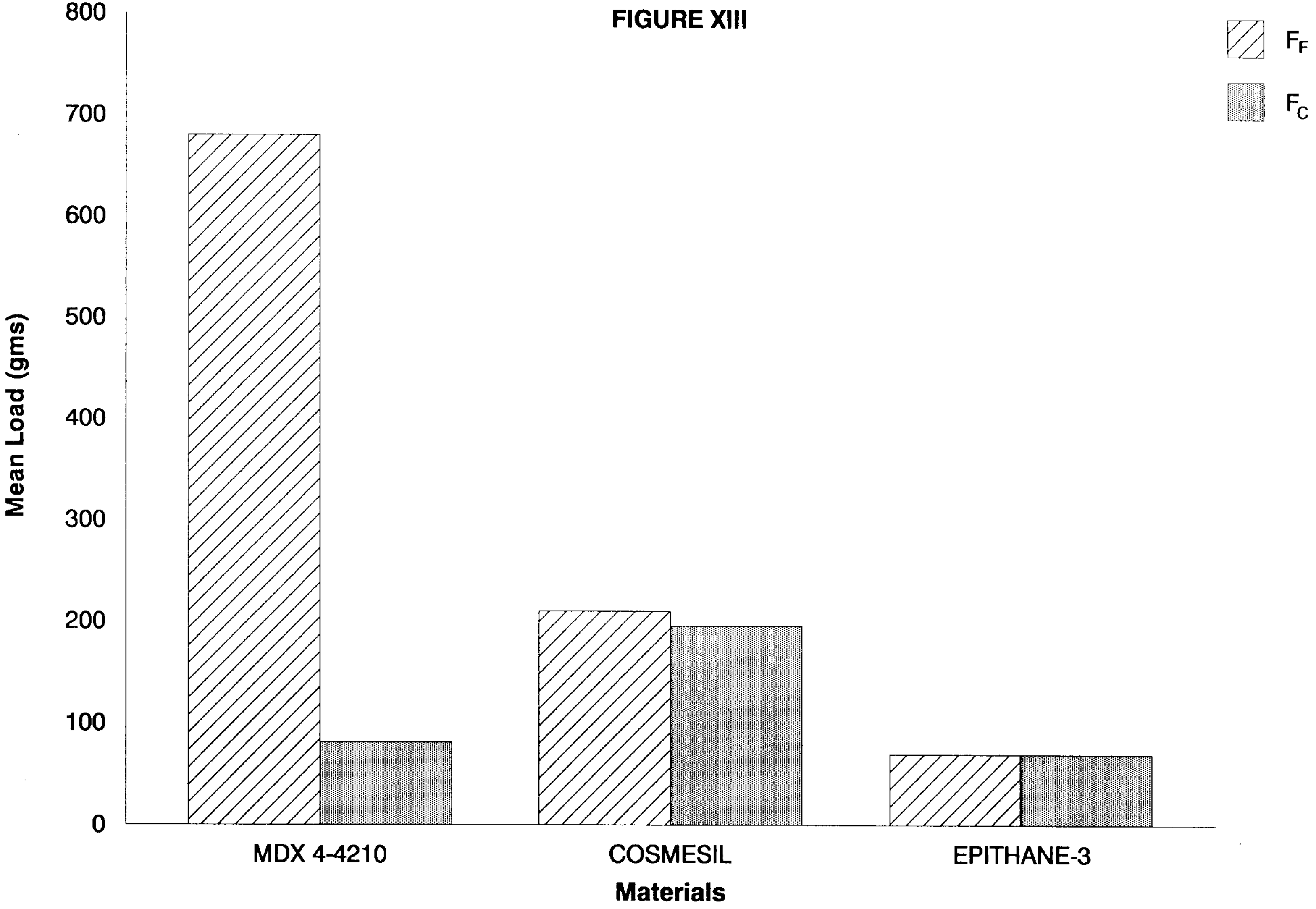
Control for 24 hours at R.T.

FIGURE XII



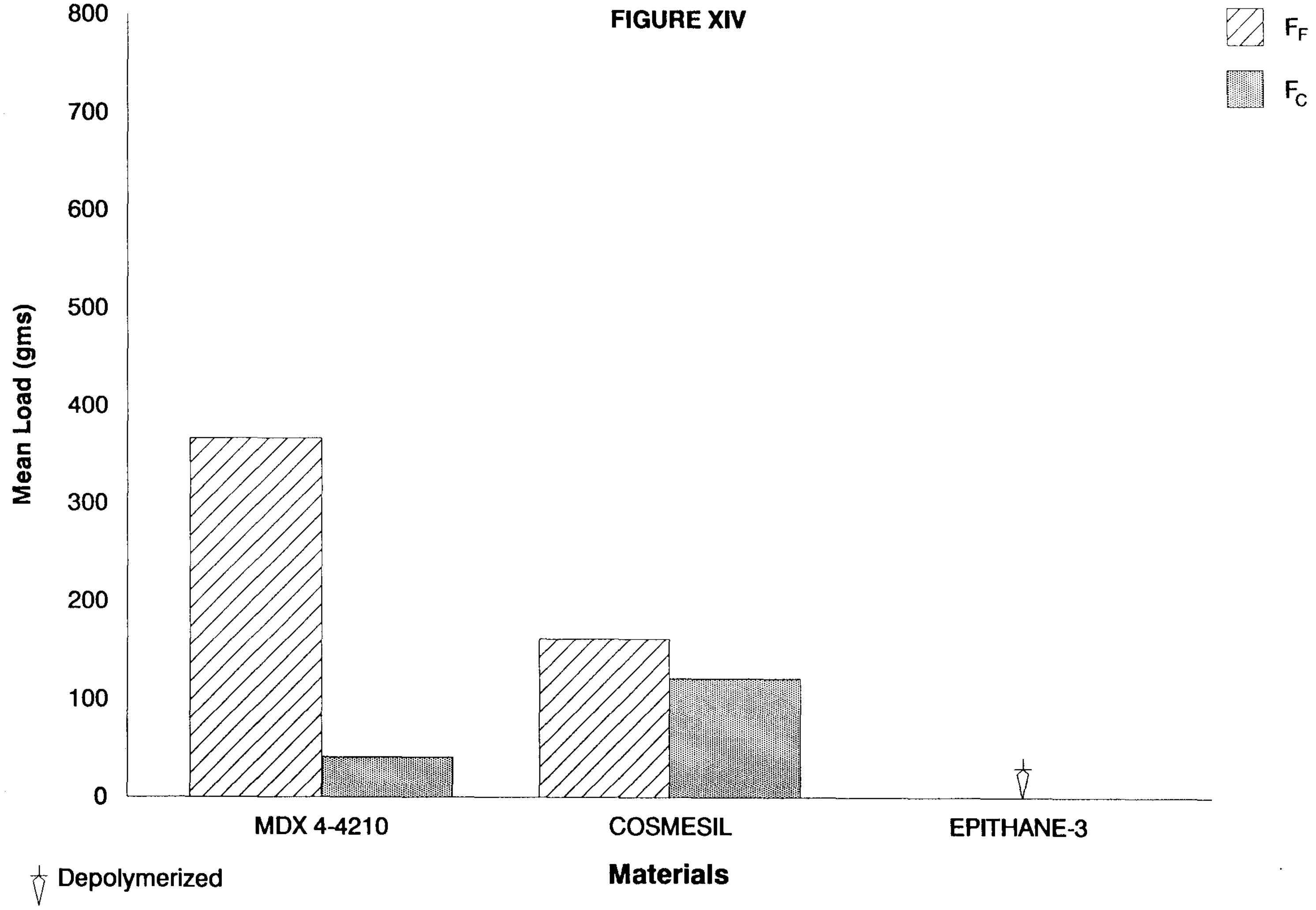
Control for 24 Hours at 60°C

FIGURE XIII



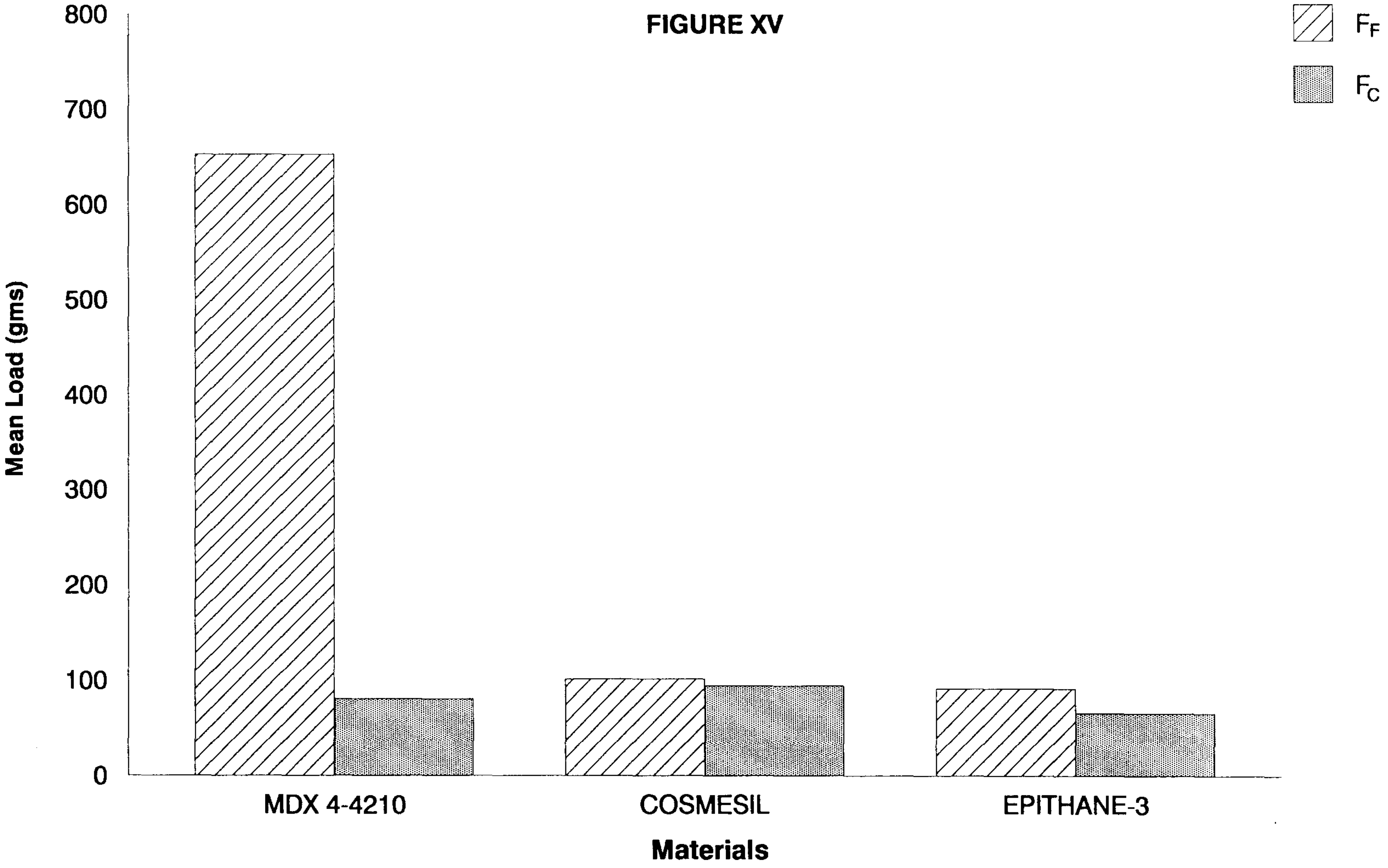
UV Radiation for 500 Hours

FIGURE XIV



Ozone for 24 Hours at R.T.

FIGURE XV



Simulated Sebum for 24 Hours at 60°C

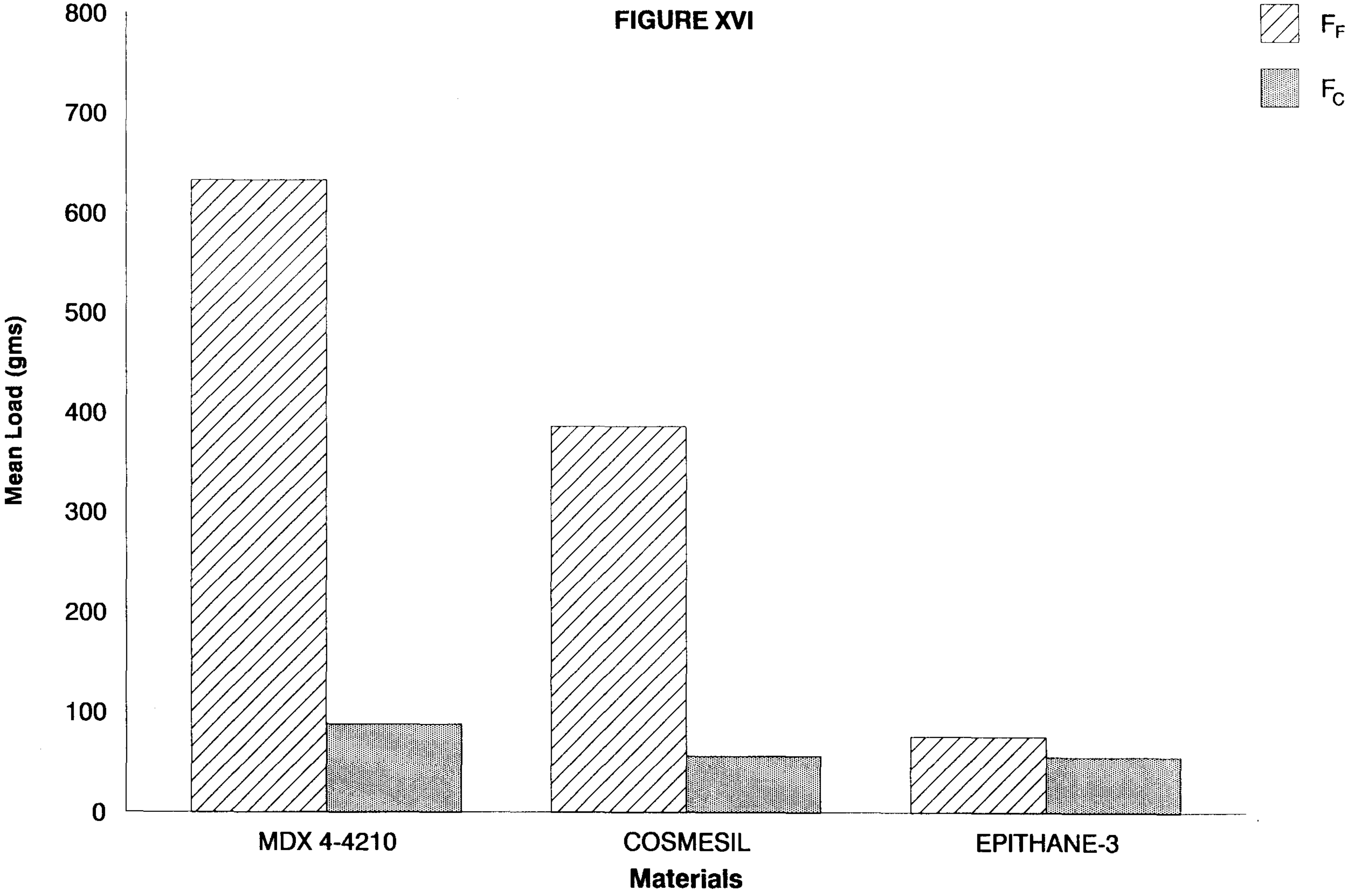
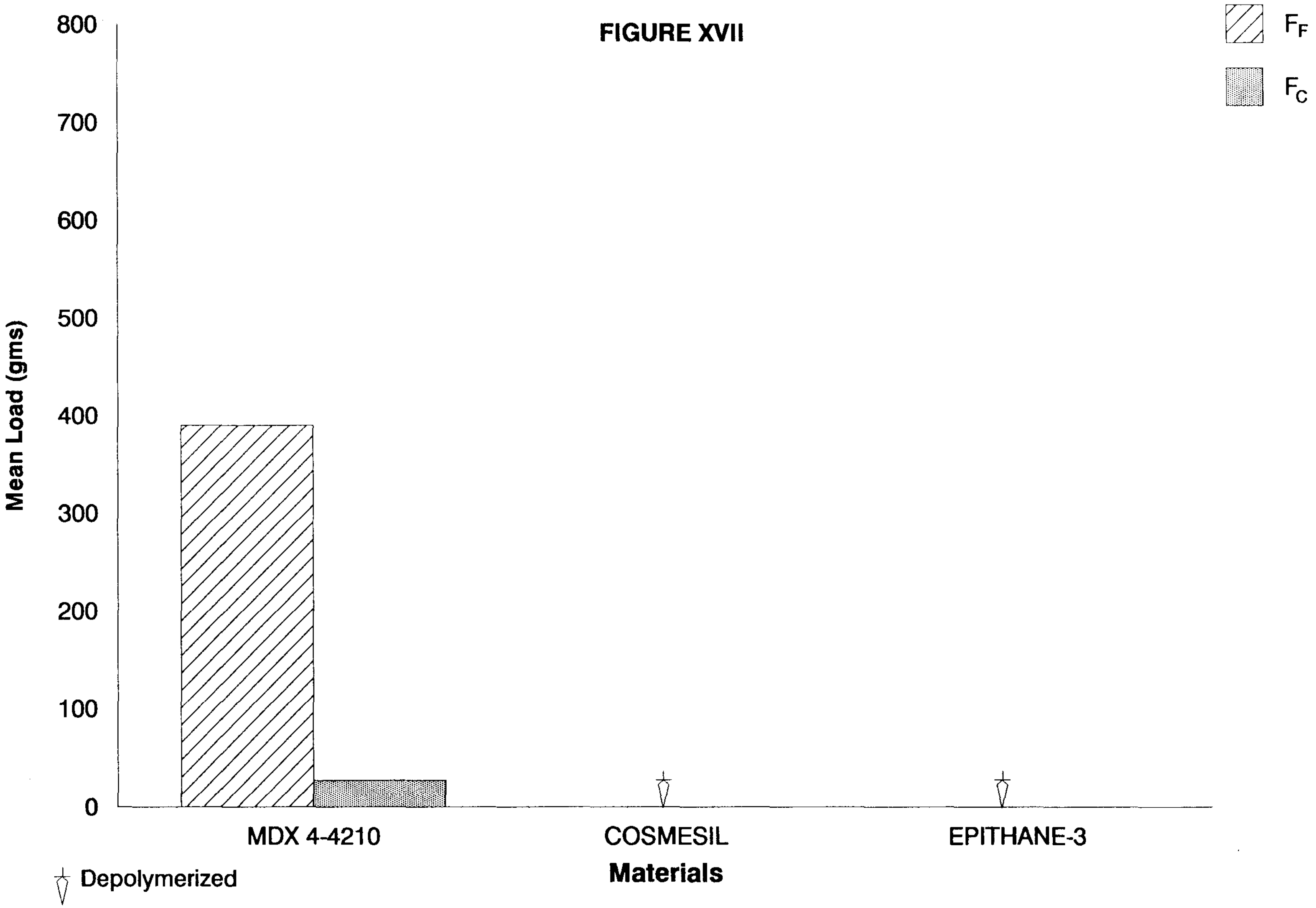


FIGURE XVI

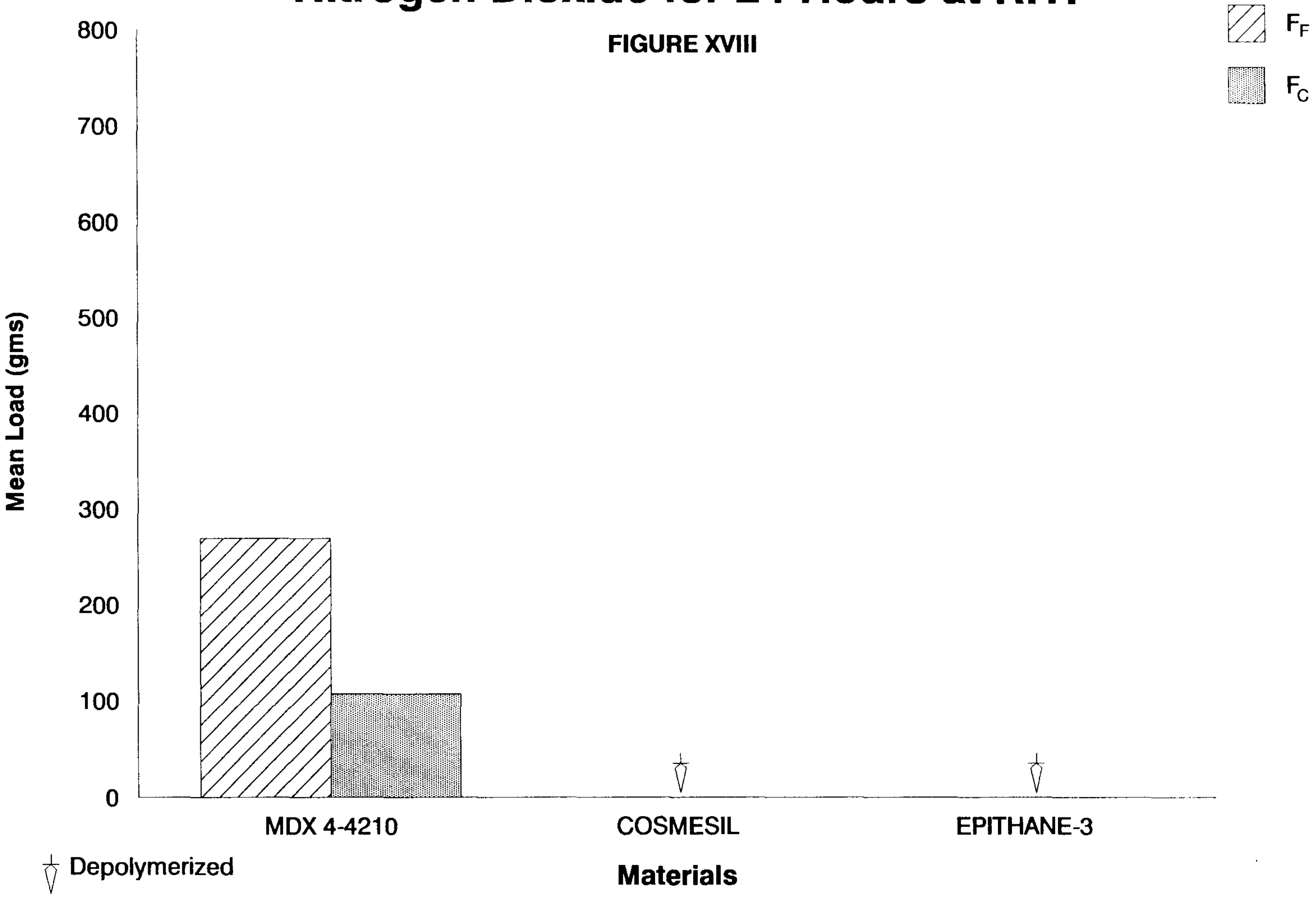
Chlorine for 24 Hours at R.T.

FIGURE XVII



Nitrogen Dioxide for 24 Hours at R.T.

FIGURE XVIII



Control for 24 hours at R.T.

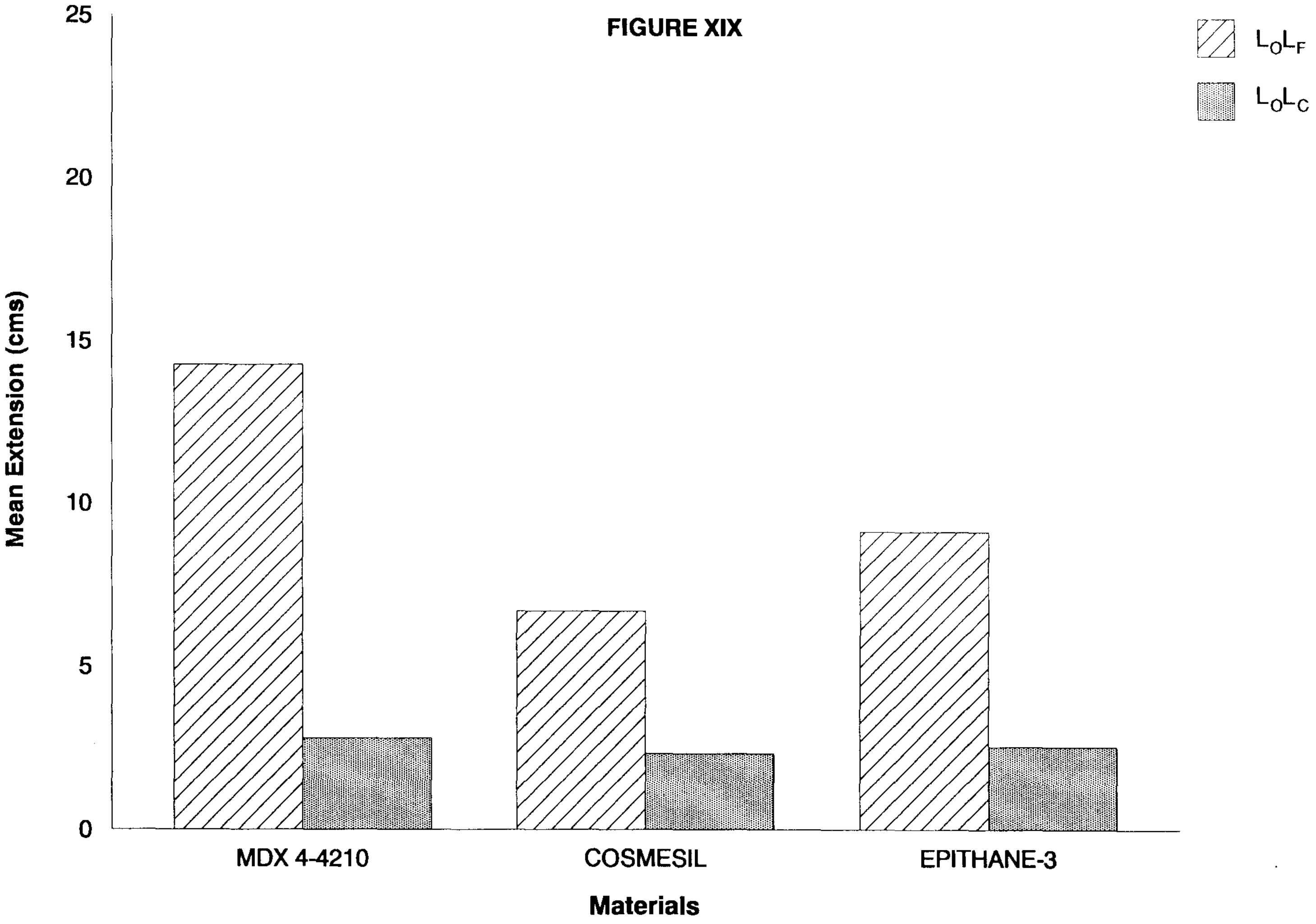


FIGURE XIX

Control for 24 Hours at 60°C

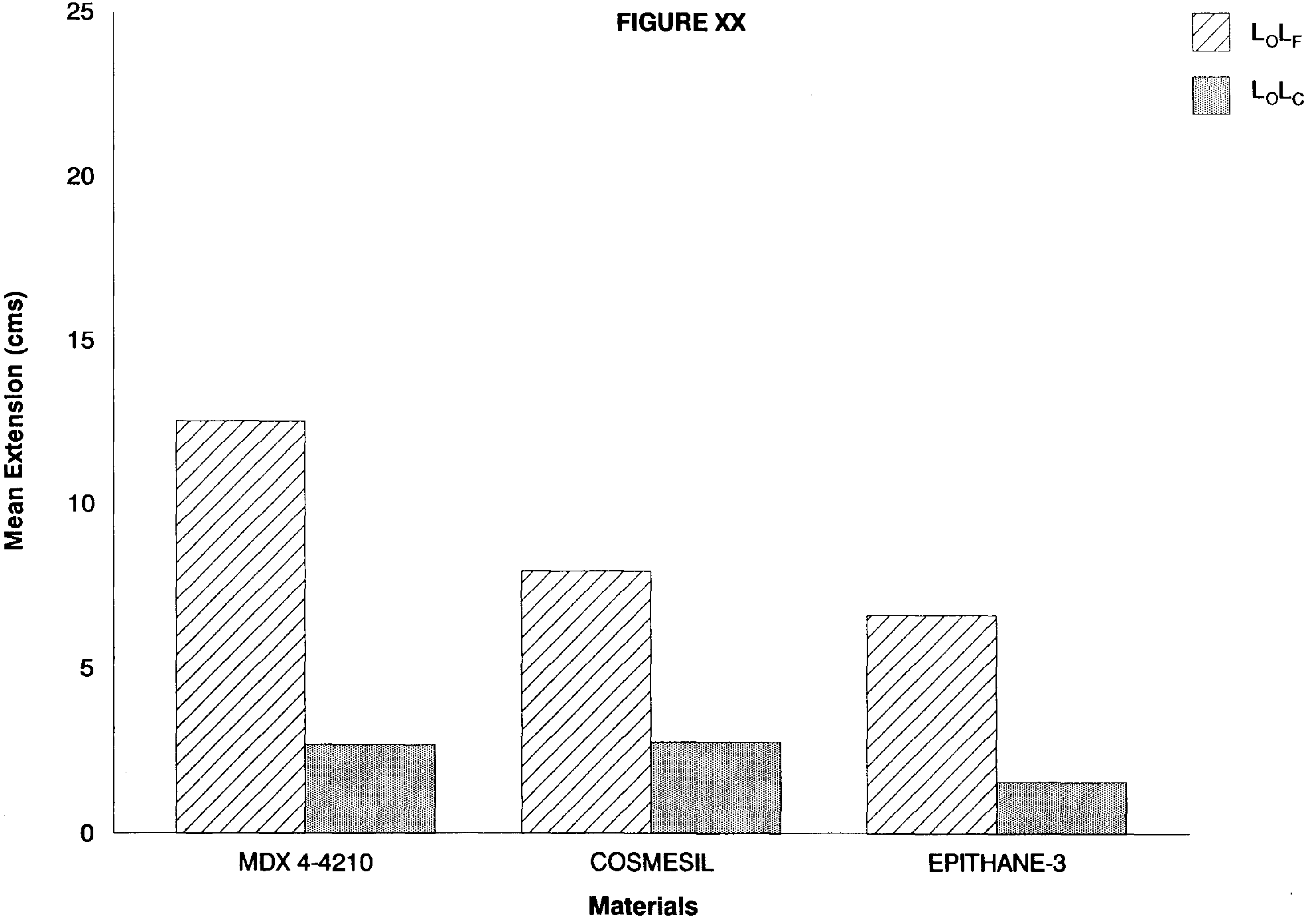
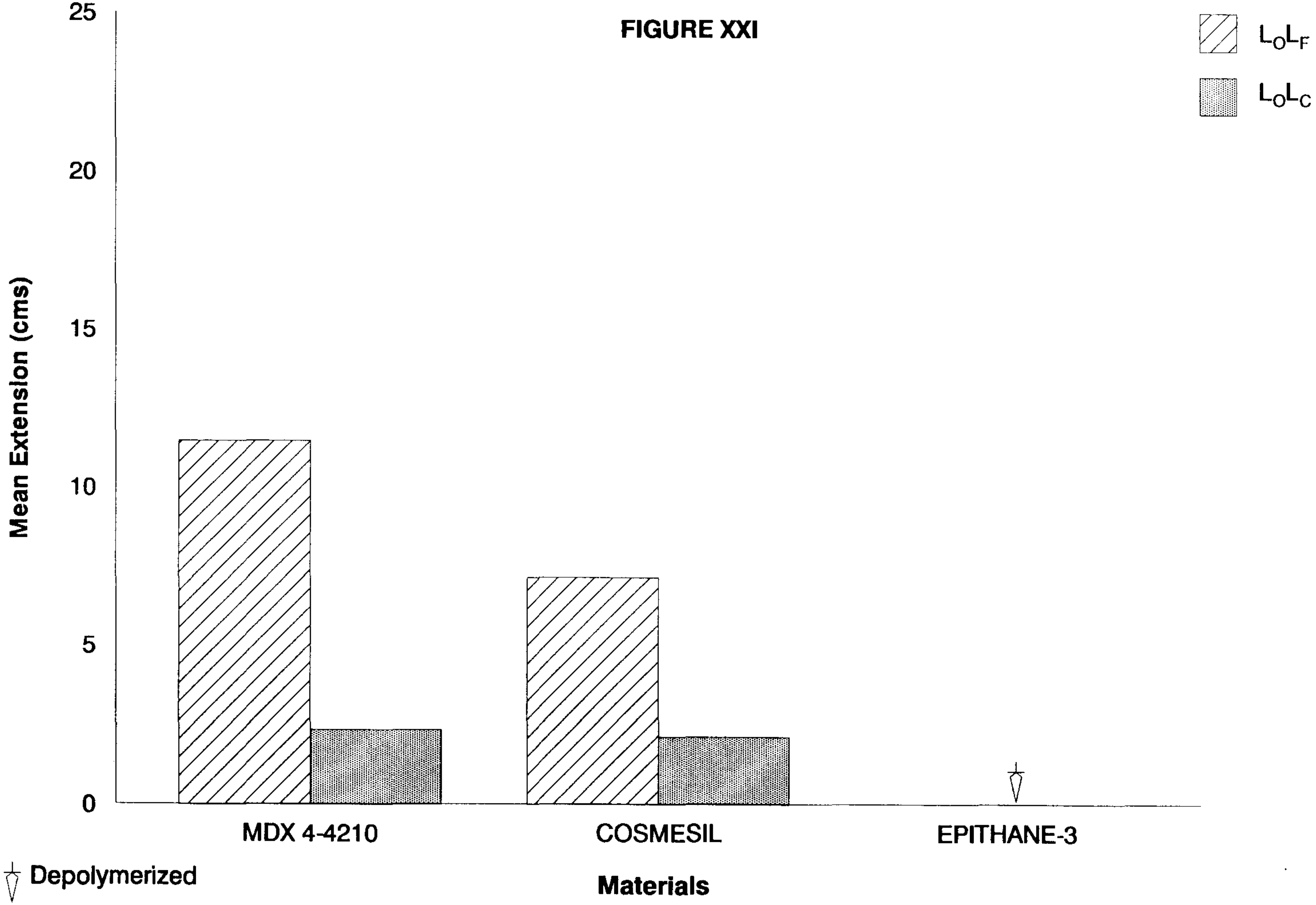


FIGURE XX

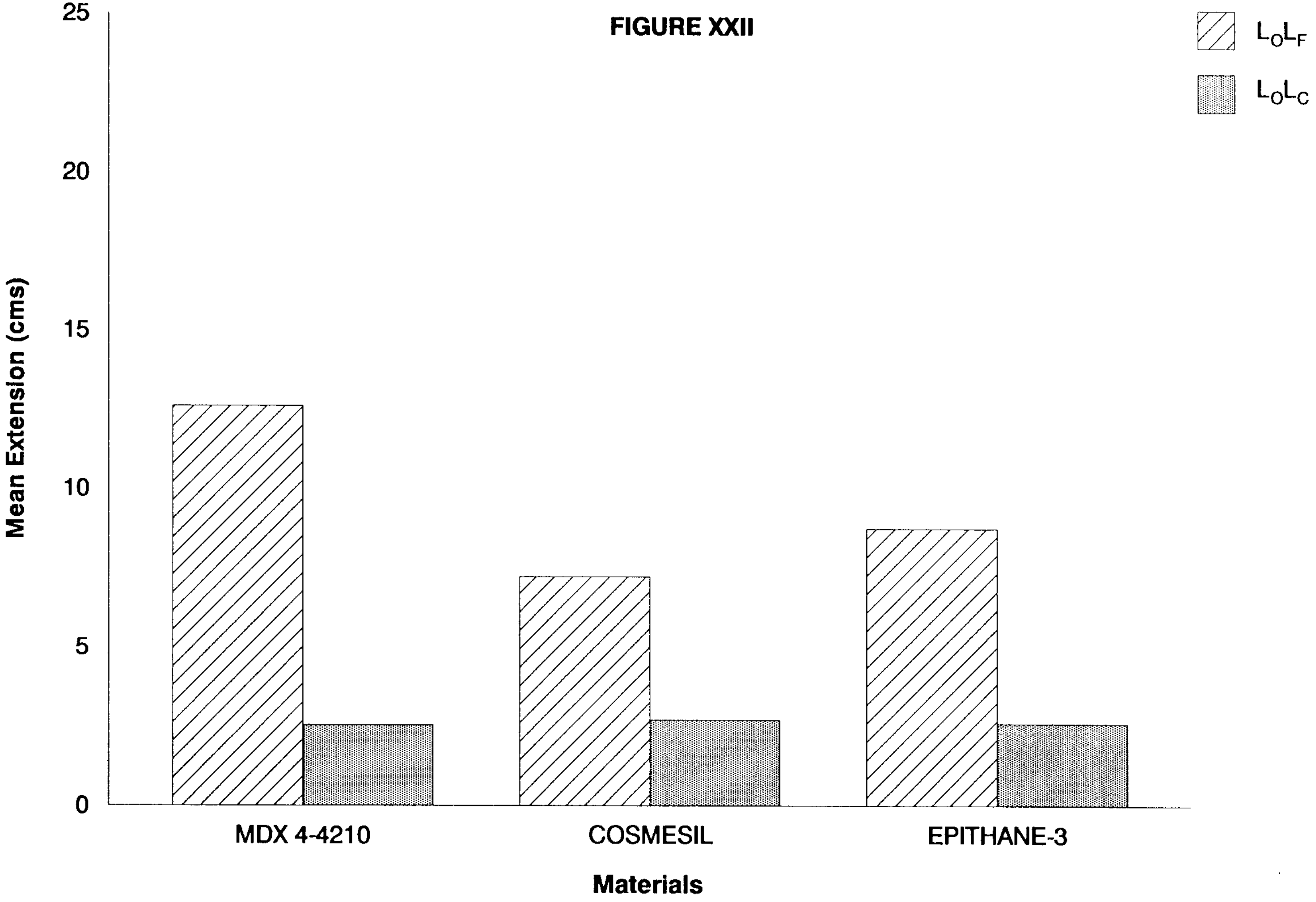
UV Radiation for 500 Hours

FIGURE XXI



Ozone for 24 Hours at R.T.

FIGURE XXII



Simulated Sebum for 24 Hours at 60°C

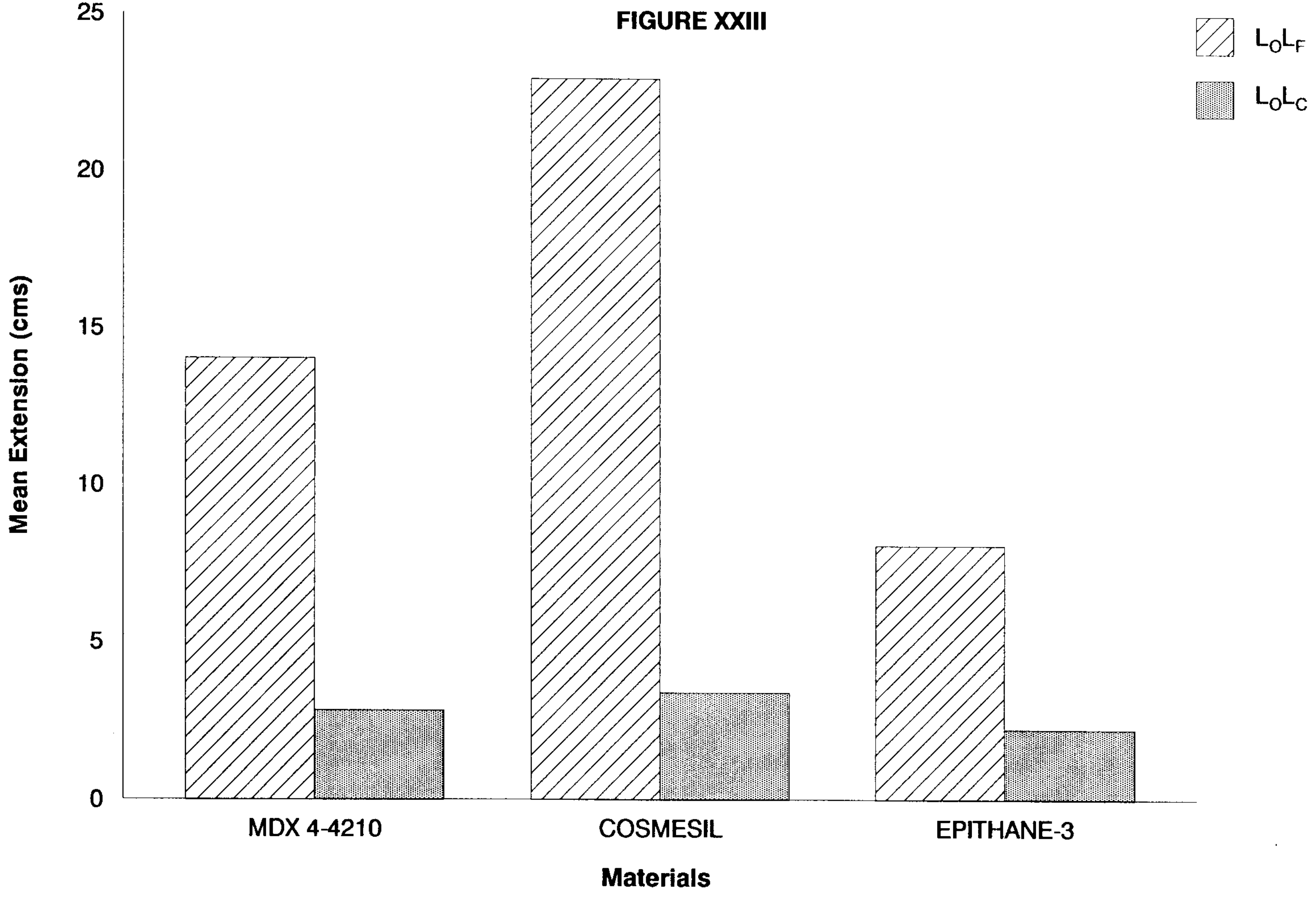
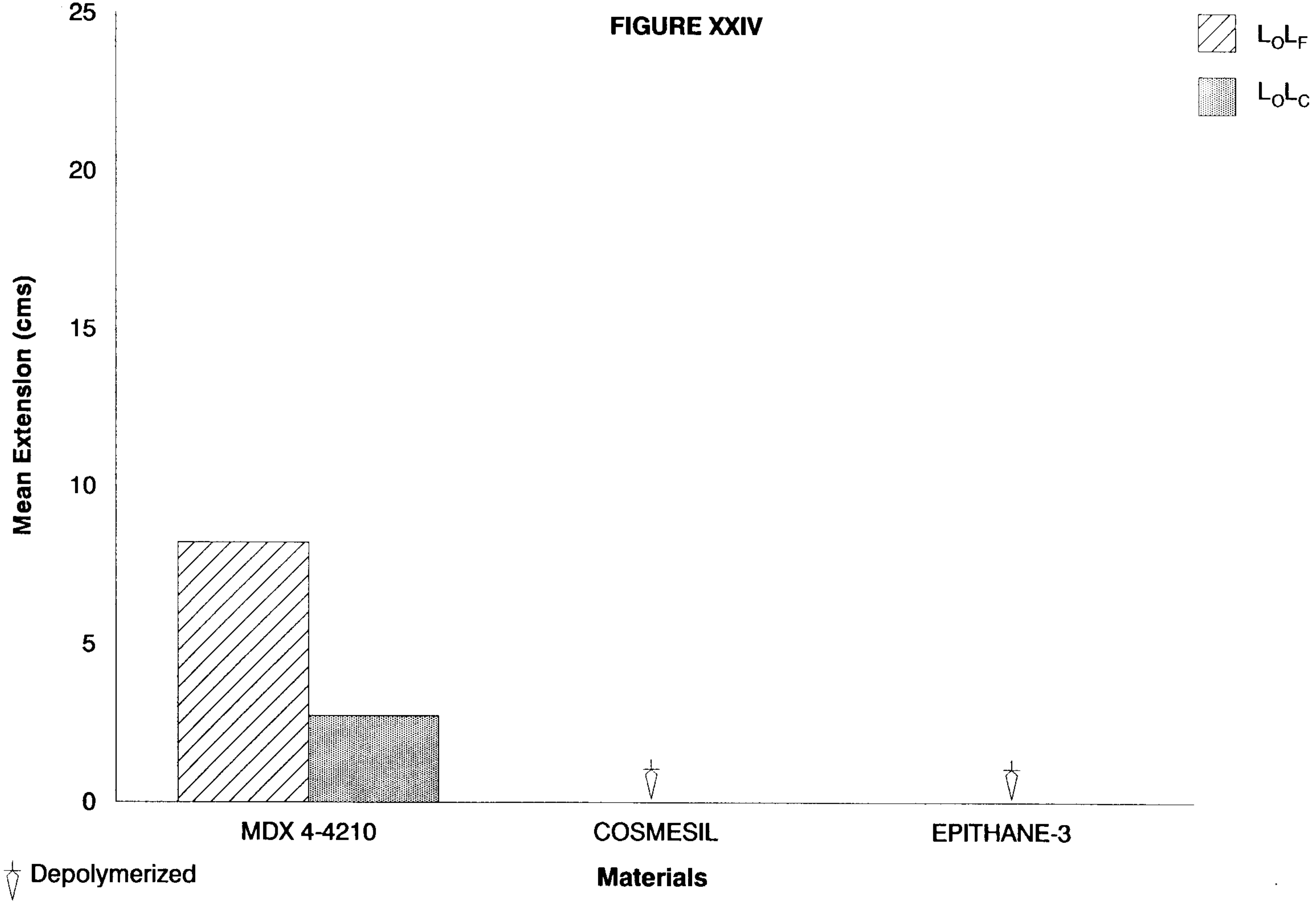


FIGURE XXIII

Chlorine for 24 hours at 24 R.T.

FIGURE XXIV



Nitrogen Dioxide for 24 Hours at R.T.

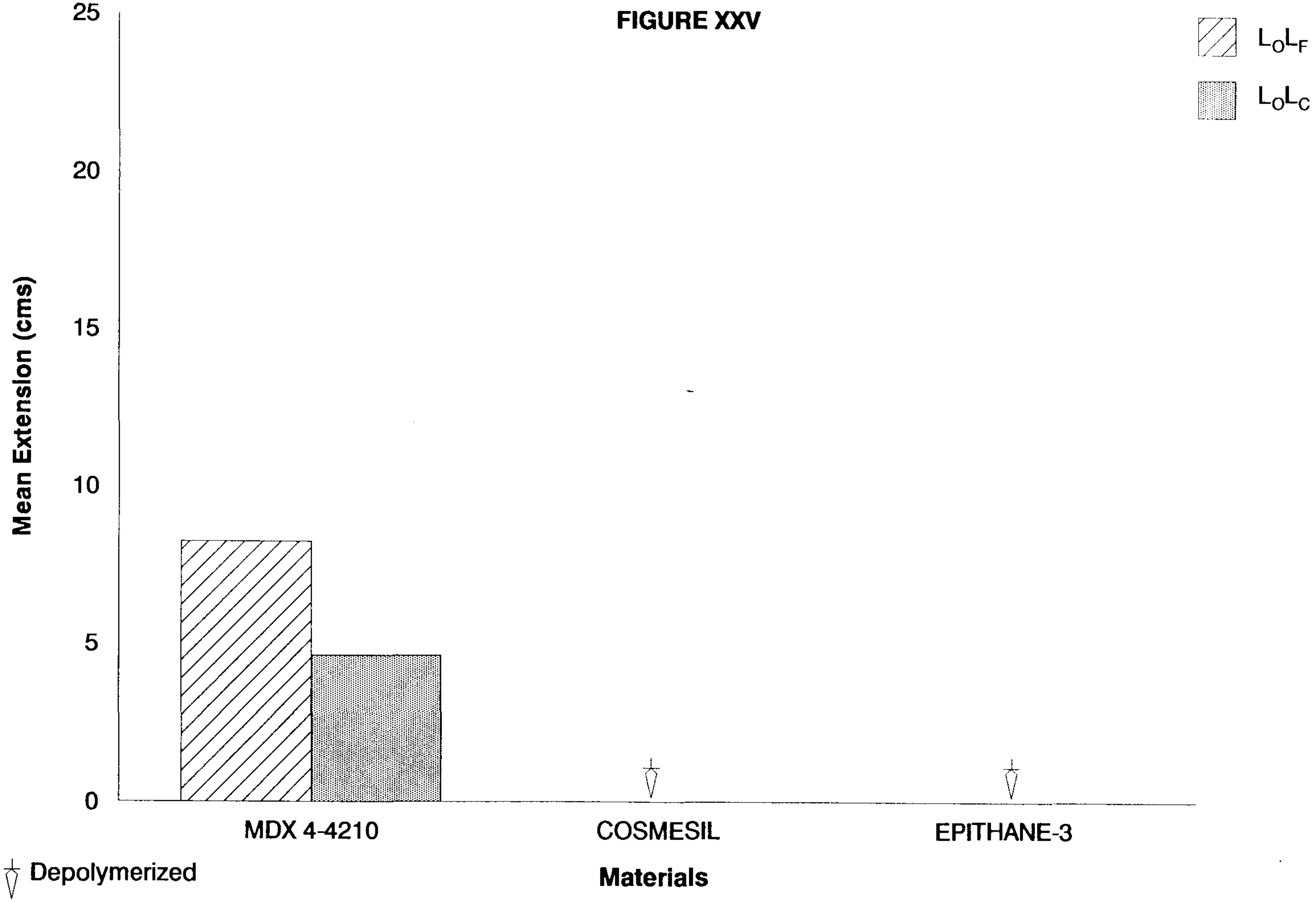


FIGURE XXV

DISCUSSION

The supposition that facial prostheses worn over an extended time are exposed to uv (solar) radiation, ozone, sebaceous oils (sebum), chlorine and nitrogen dioxide, seems legitimate. It can be further theorized, that exposure to these environmental factors results in degradative changes in the polymer structure of the material, resulting in the ultimate deterioration of the prostheses. It was felt that these effects should be studied as a possible link to the conundrum of degradation of facial prosthetic materials.

This investigation sought to discern if the degradation of facial prosthetic materials was caused by environmental factors. Limited number of studies have reported the effects of uv radiation on facial prosthetic materials.[28,45,46]. This study is unique in some aspects, since several of the environmental factors that the facial prosthetic materials were exposed to, have not been tested before or reported in the literature.

Sebum, a mixture of lipids is secreted by human sebaceous glands.[48,49] It was felt that facial oils (sebum) might penetrate and interact with the polymer structure of these facial materials, resulting in degradative changes. Sebum composition is highly variable, but typically consists of squalene, steryl esters, triglycerides, free sterols, free fatty alcohols and wax monoesters.[50-54] The presence of fatty acids, palmitic, stearic and linoleic acid have been reported in human sebum.[52] For the purpose of this investigation, sebum was simulated using a combination of fatty acids, palmitic and linoleic acids and tripalmitin. 10% by weight of palmitic acid ($CH_3 (CH_2)_{14} COOH$) and 2% by weight of tripalmitin ($C_{51} H_{98} O_6$) was dissolved in 88% by weight of linoleic acid ($C_{18} H_{32} O_2$). This combination of fatty acids was tested in a pilot study that preceded this investigation.

Tear characteristics peculiar to silicones (Cosmesil, MDX 4-4210) and polyurethanes (Epithane-3) have been observed.[22,23,34] With an increase in load, the silicones have a tendency to tear at a point, referred to as the initial tear "blip" (**FIGURE X**).[22] For the purpose of this study, that point was termed "critical". The initial tear load (grams) and the initial tear length (centimeters) were termed $F_{Critical}$ (F_C) and $L_0L_{Critical}$ (L_0L_C) respectively. With the progressive increase in load, the silicone specimens exhibit a stretching and tearing component towards a point referred to as maximum load.[22] This point, where failure occured was termed "final". The final tear load (grams) and the final tear length (centimeters) were termed F_{Final} (F_F) and L_0L_{Final} (L_0L_F) respectively. Polyurethane specimens (Epithane-3) exhibit a minimal stretching component (**FIGURE XI**), thus the F_C and F_F values in the control specimens were very similar (**TABLE VI**).

It can be argued that the significance of tear patterns from the clinical standpoint is moot, since the occurrence of an initial tear "blip" in the material would make the prosthesis unserviceable. During the pilot study, MDX 4-4210, Cosmesil and Epithane-3 exhibited significantly different tear patterns. More importantly there was a marked change in the tear pattern between the control specimens and those exposed to the environmental factors. This assessment albeit anecdotal and purely qualitative, is important. The supposition that exposure to the environmental factors caused irreversible changes in the material chemistry, resulting in "aberrant" tear patterns, seems logical. It was hoped that quantitative data to support this theory would be found in the collected test results.

The materials in the control group at room temperature had significantly different ($\alpha = 0.01$) mean values for the parameter F_C. The material with the highest mean value was Cosmesil and MDX 4-4210 had the lowest. The control group at 60° C was included in the experimental method to obtain baseline data and to make a comparative evaluation of the mean values in the simulated sebum at 60^{o} C group. The mean values of all the parameters were lower in the control group at 60^{o} C, when compared to the mean values at room temperature. A notable exception to this trend were the F_C, L_0L_C, F_F and L_0L_F values of Cosmesil. These values were consistently higher than the means at room temperature. The manufacturer's have recommended increasing the mold temperature to accelerate the polymerization process but have never correlated higher temperature to improved tear propagation resistance. The fact that the specimens have been stored in the mold for 24 hours at room temperature prior to subjecting them to the 60^{o} C environment rules out the accelerated polymerization explanation.

Chlorine for 24 hours at room temperature, nitrogen dioxide for 24 hours at room temperature and uv radiation for 500 hours were the environments (in descending order) that caused the most significant changes in the exposed specimens. MDX 4-4210 was the material that was least affected by these environments.

Cosmesil and Epithane-3 were affected by chlorine for 24 hours at room temperature and nitrogen dioxide for 24 hours at room temperature. Both the materials were depolymerized after being exposed to these environments. There were color changes observed in specimens from both materials. Exposure to the chlorine environment resulted in specimens changing color to greenish-white and exposure to the nitrogen dioxide environment caused color changes in the specimen to brownish-red. The specimens were tacky and mushy to touch and thus could not be placed in the Instron machine grips.

MDX 4-4210 had significantly lower mean values for all the parameters tested after being exposed to chlorine for 24 hours at room temperature. *Chen*[3] conducted a survey which revealed that patients use soap and water, alcohol, cleaning cream, benzine and even gasoline to clean their facial prostheses. Facial materials come in contact with chlorine (an additive to water) while cleaning the prostheses and these results should be a warning to patients vis á vis cleansing the prostheses with harsh chemicals. Chlorine is also present in swimming pool water. Although the likelihood of patients wearing this prostheses and engaging in recreational activity like swimming is remote, concentration of chlorine in pool water could be high enough for the fumes to affect bystanders.

MDX 4-4210 had significantly lower mean values for F_F and L_0L_F after being exposed to nitrogen dioxide for 24 hours at room temperature. The mean values for parameters F_C and L_0L_C were higher than the control group. A possible explanation for this phenomenon is that the extension (L_0L_C) includes a large stretching component observed prior to the initial tear "blip" (F_C). This results in significantly higher F_C and L_0L_C values. Once the initial tear "blip" occurs, there is rapid failure of the material resulting in a reduced maximum load value (F_F) and a reduced final extension value (L_0L_F). Thus the F_C and F_F values are very similar when compared to the disparate control F_C and F_F values.

Nitrogen dioxide is present in pollutants like automobile emissions. The need to warn patients of the effect of nitrogen dioxide on facial prosthetic materials is important because of the ubiquitous nature of automobile emissions in contemporary society.

Epithane-3 was affected by uv radiation for 500 hours. The specimens were discolored greyish-black and were tacky to touch. The depolymerized specimens were discolored as early on as 200 hours of exposure. The specimens were depolymerized by 350 hours of exposure and had to be removed from the color stability test apparatus as the specimens were totally destroyed. MDX 4-4210 and Cosmesil had lower mean values for all the parameters tested. It should be noted that MDX 4-4210 had almost a 50% drop in mean values for the F_C and F_F parameters after exposure to uv radiation.

There were no "dramatic" trends observed in the specimens exposed to ozone for 24 hours at room temperature, as was seen in the specimens exposed to chlorine, nitrogen dioxide and uv radiation. However there were more subtle yet significant changes observed in Cosmesil and Epithane-3. There was a statistically significant drop in mean values for the F_C and F_F parameters after exposure to ozone for 24 hours. Although the L_0L_C and L_0L_F values were not significantly different, the drop in mean values for the F_C and F_F parameters in Cosmesil and Epithane-3 signifies an initial tear "blip" at reduced load and reduced maximum load.

MDX 4-4210 was not significantly affected after being exposed to ozone, however degradation of the material should not be ruled out. This is because there were certain limitations to the equipment used for this experiment. Ozone is colorless in nature and thus it's flow is very difficult to monitor. Further studies with an ozone generator equipped with a flow regulator is warranted. Also the fact that ozone is not very stable and reverts back to oxygen, makes the calibrated storage of ozone very difficult.

There were no clear trends revealed after the specimens were exposed to the simulated sebum for 24 hours at 60^{o} C. However, an interesting observation needs to be noted. There was a significant difference in the value of parameter F_C after Cosmesil was exposed to simulated sebum. There was almost a four fold decrease in the mean value for F_C and a significant increase in values for L_0L_C, L_0L_F and F_F. This can be interpreted to mean that there was a decrease in the load value for the initial tear "blip" (F_C) and an increase in the extension values, resulting in an increase in the stretching component (L_0L_C and L_0L_F). The fact that parameter F_F shows a significant increase over the control values is difficult to explain, more so since the values for F_C reveals a significant drop in value when compared to the control. It should be pointed out that the sebum used in this experiment was simulated to represent the sebaceous secretions and that a study more representative of these secretions may be possible. However, the multitude of variations observed and the logistics of collecting these secretions in infinitesimal quantities makes this an arduous task. Thus this approach was precluded from the present study and simulated sebum was used.

SUMMARY AND CONCLUSIONS

This study evaluated the serious problem of degradation of facial prosthetic elastomers in a service environment. The resulting database gives us insights and a better understanding, while selecting from the myriad of facial prosthetic materials available today.

MDX 4-4210, Cosmesil (silicone) and Epithane-3 (polyurethane) were evaluated using standard specimens as defined by ASTM specifications D 1938 ("pants tear test"). Baseline data was determined on freshly prepared specimens. Additional samples were prepared and exposed to uv radiation, simulated sebum, ozone, chlorine and nitrogen dioxide. The specimens were tested for tear propagation resistance by a single-tear method as per ASTM specifications D 1938. The specimens were aligned so that their major axes coincided with an imaginary line joining the centers of the grips. Using a grip separation speed of 10 inches / minute, the specimens were tested on an Instron testing machine.

Test results revealed significant differences in the tear characteristics between silicones and polyurethanes. Differences in tear patterns were observed between the control and the specimens exposed to the environmental factors. The environmental factors affected the polyurethane Epithane-3 the most and silicone MDX 4-4210 the least. When exposed to chlorine and nitrogen dioxide, Cosmesil and Epithane-3 were degraded to a point where sample testing was not possible. When exposed to uv radiation, Epithane-3 was depolymerized and could not be tested. Simulated sebum and ozone affected Cosmesil and Epithane-3 but no clear trends were observed.

Based on the results of this investigation the following conclusions can be made:

1. It can be concluded that environmental factors do have an effect on facial prosthetic elastomers and that this might play a role in degradation of the prosthesis in a service environment.

2. The results reveal that the silicones as a group are more resistant to environmental degradation when compared to the polyurethanes and axiomatically the material of choice clinically.

3. MDX 4-4210 had the lowest initial tear "blip" in the control samples yet was affected the least by the environmental factors. Epithane-3 was the least resistant to the effects of environmental degradation as it was affected the most.

4. Patients should be warned vis á vis the degradative potential of environmental factors like solar (uv) radiation, ozone, skin oils, nitrogen dioxide and chlorine.

5. More research needs to be conducted using materials that have not been tested in this study. Ozone and sebum should be considered to have degradative effects and more elaborate testing with these environmental factors is warranted.

6. A desperate need for the design and development of a completely new polymer system with maxillofacial restoration as it's end use. However, many might find the need for major investment in research and development required to design this material to fulfill exacting demands in a relatively small market, unjustifiable.

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The thesis is therefore accepted in partial fulfillment of the requirements for the degree of Master of Science.

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