About this Manual

The Silicone Molding Design Manual allows designers to access a wealth of free information on silicone that they can incorporate into their designs to improve life science technology.

This manual provides a general overview of silicone rubber elastomers, including physical properties, fabrication methods, and potential advantages for device manufacturing. In addition, it is one of the leading resources in the industry that provides comprehensive information on silicone.

We would like to thank all of the contributors for providing a substantial amount of information and we happily look forward to adding any future papers or articles that can help those in need of silicone resources.

Although every precaution has been taken in the preparation of this manual, we assume no responsibility for errors or omissions. No liability is assumed by us with respect to the use of information contained herein. This publication is designed as guidelines and does not constitute a recommendation of any product that may be involved.

About Albright Technologies, Inc.

Albright Technologies, located in Leominster, MA, specializes in manufacturing prototype and low volume production silicone components for medical, pharmaceutical and life science applications.

Albright Technologies has extensive silicone molding experience and can help with medical silicone material selection and design for manufacturability and scalable molding methods. Albright can also advise on micro tooling and molding, low temperature curing of conductive silicone, silicone optics, bonding of silicone to thermal plastics and metals, as well as designing silicone processing equipment.

Address and Contact:

25 Litchfield Street
Leominster MA, 01453
Tel: 978-466-5870
Fax: 978-466-5901
Web: www.Albright1.com
Email: info@albright1.com
# TABLE OF CONTENTS

**Introduction to Silicone Rubber** ................................................................. 4  
- Silicone Rubber for Medical Device Applications ........................................... 4  
- Silicone Defined ............................................................................................. 4  
- History of Silicones in Medical Devices ......................................................... 5  
- Silicone Chemistry ......................................................................................... 5  

**Types and Properties of Moldable Silicone Rubber** ........................................ 6  
- Chemical Structure and Resistance ................................................................. 6  
- Electrical .......................................................................................................... 7  
- Flammability ..................................................................................................... 8  
- Fungus Resistance ............................................................................................ 8  
- Food Contact Status and FDA Regulations .................................................... 8  
- Mechanical ....................................................................................................... 8  
  A. Compression Set Resistance ........................................................................... 9  
  B. Resistance and Damping Factor ..................................................................... 9  
  C. Hardness Range from ‘0000 shore A’ to ‘70 shore D’ ................................... 9  
  D. Tensile Strength ............................................................................................ 10  
  E. Elongation .................................................................................................... 10  
  F. Bulk Modulus ................................................................................................ 10  
  G. Flex Life ....................................................................................................... 10  
  H. Tear Strength ................................................................................................ 11  
  I. Coefficient of Friction .................................................................................... 11  
  J. Ozone and Oxidation Resistance .................................................................... 11  
  K. Permeability .................................................................................................. 11  
  L. Bondability .................................................................................................... 11  
  M. Radiation Resistance .................................................................................... 12  
  N. Temperature Resistance ................................................................................ 12  
  O. Weather Resistance ...................................................................................... 12  
  P. Bio-testing .................................................................................................... 12  

**Factors in Selecting Medical Silicones** .......................................................... 12  
- Drug Delivery ................................................................................................... 13  
  A. Comparing Silicone Pressure-Sensitive Adhesives to Silicone Gels for Transdermal Drug Delivery ........................................................................................................... 22  
  B. NuSil Technology: Silicones for Drug Delivery Combination Devices ... 30  
  C. Adding Color to Medical Devices .................................................................. 31  
  D. Drug Delivery Market Summary .................................................................... 33  
  E. Understanding the Role of Silicones in Controlled Release Applications ... 38  
  F. Recent Developments in Ultra Low Outgassing Silicones for Space Applications... 42  
  G. A Silicone-Based Ice-Phobic Coating for Aircraft ....................................... 53  

**Optical Silicone** ............................................................................................ 59  

**Aerospace** ..................................................................................................... 78  

**Custom Silicones** ......................................................................................... 86  
- Oil Bleeding Grades of Silicones ....................................................................... 86  
  A. Crosslinking Density ..................................................................................... 86  
  B. Pressure ........................................................................................................ 87  
  C. Storage Time ................................................................................................ 87  
  D. Temperature .................................................................................................. 87  

Medical Sterilization of Silicone Parts. ................................................................. 88

Processing ............................................................................................................... 89
Molding .................................................................................................................. 89
A. Silicone Lost (Disposable) Core................................................................. 89
B. Evaluation of Removal Rate of Cured Silicone Adhesive from Various Electronic
   Packaging Substrates by Solvent and Silicone Digesters for Rework Applications... 90
C. Versatility and Flexibility from Low Outgassing Silicones....................... 96

Hardness Testing of Plastics—Shore Durometer.................................................. 102

Part Design .......................................................................................................... 103
Wall Thickness..................................................................................................... 103
Tolerances and Molded Part Shrinkage.............................................................. 103
Tolerances ........................................................................................................... 103
Shrinkage ............................................................................................................ 103
Coefficient of Thermal Expansion .................................................................. 104
Thermal and Electrical Conductivity ............................................................... 104
Optical Properties .............................................................................................. 104
Radii and Fillets ................................................................................................. 105
Surface Finish .................................................................................................... 105
Draft Angles ....................................................................................................... 105
Undercuts ........................................................................................................... 105
Parting Lines and Gate Location ....................................................................... 105
Over-Molding ..................................................................................................... 105
Heat Aging Effects on Silicone’s Mechanical Properties .............................. 107
   A. Effects on Tensile Strength ...................................................................... 107
   B. Effects on Elongation .............................................................................. 108
   C. Effects on Hardness .............................................................................. 108

Medical Marking ................................................................................................. 109
Laser Marking ..................................................................................................... 109
Inks ....................................................................................................................... 109

Specifying Liquid Silicone Medical Rubber Parts........................................... 110

Examples of Silicone Products ........................................................................ 111
Delta® Valves ..................................................................................................... 111
Silicone for Prosthetics ...................................................................................... 111

Glossary of Silicone Terms .............................................................................. 112

Silicone Rubber Supplies, Molders, Manufacturers and Testers .................. 125
Liquid Silicone Rubber Suppliers ..................................................................... 125
Medical Silicone Molders .................................................................................. 125
Silicone Equipment Manufacturers ................................................................. 1250
Silicone Medical Product Testers ..................................................................... 125

Additional Sources for Information on Silicone Rubber .............................. 125

INTRODUCTION TO SILICONE RUBBER

Silicone Rubber for Medical Device Applications

Selecting an acceptable elastomer for medical and other applications can be a challenge. Product designers, engineers and managers have to evaluate different material properties and manufacturability to assure product reliability and costs. There are many materials and processes to choose from. It is the responsibility of the designer to make the right choice.

Medical grades of silicone are both safe and reliable since they do not melt or promote fire, are short-circuit-proof and have a high dielectric strength. In the event of a fire, they do not generate toxic vapors or residues. Silicone rubber used in medical applications also has the following UNIQUE characteristics and advantages:

- Inert, odorless, tasteless, stainless – (ideal for medical and food applications)
- Hygienic – they give bacteria and fungi little chance to spread.
- Hypo-allergenic
- Extreme temperature applications, -180°F to 600°F (-118°C to 316°C)
- Easy to clean – even with dilute acids such as vinegar.
- Can be steam sterilized and are dishwasher safe.
- Thermal resistance – (special flame retardant compounds are available)
- High resistance to weathering and oxidation
- Excellent electrical qualities – (superior dielectric and insulation characteristics in special compounds)
- Superior resistance to many chemicals
- High resistance to ozone and corona
- Superior water resistance - low water adsorption
- Lime and dirt repellent
- Colorfast and light-stable with FL color pastes
- Highly transparent and have no yellow cast
- Flexibility and Durability
- Fatigue and Compression Set Resistance
- Energy Absorption
- Long Work and Shelf Life
- Can be compounded for special properties

If you need a combination of good mechanical properties and medical safety, then ELASTOSIL® LR liquid silicone rubbers are ideal, thanks to their special chemistry. They contain no organic stabilizers, plasticizers or activators.

Silicone Defined:
Source: Julie M. Stocker

Silicon, silica, silicone-what’s the difference? Silicon is a chemical element, one of the 109 known substances that constitute the universe’s matter. Second only to oxygen in its presence on earth, one-quarter of the earth’s crust is silicon. Carbon is the only element capable of producing more compounds than silicon; thus, silicon possesses immense potential for commercial application. Silicon is one of the premier semi-
conducting elements and is used in many electronic devices, such as transistors and computers.

However, one does not find silicon alone in nature. It always exists as silica or silicates. Silica is silicon dioxide (SiO2), commonly found in sand and quartz. Silicone is a synthetic polymer, or macro-molecule, whose backbone is a repeating chain of Si-O molecules, with various organic groups attached to the silicon. The most common silicone is PDMS, poly-dimethylsiloxane [(CH3) 2Si-O], the foundation of all silicones.

Finally, silicone is also described as an elastomer - a synthetic polymer which behaves much like natural rubber – it can be stretched to several times its size and still snap back to its original length.

**History of Silicones in Medical Devices**

*Sources: Stephen Bruner and John Freedman*


(November 1999)

After extensive use in the aerospace industry in the 1940s, silicones expanded into healthcare and medical applications during the following decade. In 1954, J.D.B. McDougall reported that various tissue cultures taken from warm-blooded animals known to be extraordinarily sensitive to foreign influences showed no deviation from the usual growth picture upon contact with liquid, semi-solid, and rubber-like silicone products. As a result of this work, silicones have been characterized as biologically and toxicologically inert and are now used in a variety of applications including pacemaker leads, hydrocephalus shunts, heart valves, finger joints, and intraocular lenses.

Silicone rubbers were first used in 1960’s for automotive, medical, aerospace and other industrial applications. Silicone became the elastomer of choice because of such properties as:

- a.) inert and stable
- b.) compression set resistance
- c.) hypoallergenic
- e.) electrically non conductive
- d.) wide range of operating temperatures
- f.) variety of durometer choices available

Silicone is widely used in medical applications because it is hypoallergenic and does not produce any extractables like those of other thermoplastic elastomers. Typical medical applications for Silicone are:

- a.) Tubing
- b.) Drains
- c.) Feeding tubes
- d.) Catheters
- e.) Implants for long and short term use.
- f.) Seals and gaskets
**TYPE AND PROPERTIES OF MOLDABLE SILICONE RUBBER**

*Source: Dow Corning, [http://www.dowcorning.com/content/rubber/rubberprop/default.asp](http://www.dowcorning.com/content/rubber/rubberprop/default.asp)*

The unique properties of silicones enable them to be used for a variety of devices and components – Charles Heide

<table>
<thead>
<tr>
<th>Type of Silicone Rubber</th>
<th>Tensile Strength Units: Mpa</th>
<th>Tear Strength Units: kN/m</th>
<th>Elongation Range Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCR – High Consistency Rubber</td>
<td>4 to 13</td>
<td>9 to 55</td>
<td>90 to 1120%</td>
</tr>
<tr>
<td>FSR – Fluorosilicone Rubber</td>
<td>9 to 12</td>
<td>18 to 46</td>
<td>160 to 700%</td>
</tr>
<tr>
<td>LSR – Liquid Silicone Rubber</td>
<td>4 to 12</td>
<td>11 to 52</td>
<td>220 to 900%</td>
</tr>
<tr>
<td>RTV – Room Temperature Vulcanize (160-60)</td>
<td>6</td>
<td>9</td>
<td>370%</td>
</tr>
</tbody>
</table>

**Notes:**
- Base polymer, reinforcing filler, and special additives can change tensile strength significantly.
- Different processing methods and oven cures change the elongation values considerably.

**Chemical Structure and Resistance**


Silicone rubbers are synthetic polymers with an alternating Si-O chain backbone. The molecules will cross link with the addition of a catalyst.

Peroxide catalyst silicones, used in early silicones and still used today, are known to leave an acid residue in the rubber and outgas peroxide byproducts if not fully cured and cross-linked.

Platinum catalyst silicones have become more popular as they, not only do not leave a peroxide bloom, but they also cure faster and are available in an injectable liquid form. Silicones utilizing platinum cure systems are shipped in a two part kit; typically referred to as Part A and Part B. The two parts are mixed in a predetermined ratio, forming a compound ready to be cured.

Platinum-cured silicones are available as a high-consistency rubber, sometimes referred to as gumstock, as well as liquid silicone rubber or LSR.

Silicone resists many chemicals, including water, isopropyl alcohol, some acids, oxidizing chemicals, and ammonia and can meet chemical resistance requirements in elevated temperatures. Liquid silicone can be formulated to enhance its chemical resistance to a given chemical solution. For more information regarding silicone’s resistivity to other chemical compounds please visit:


Avoid using concentrated acids, alkaline, and solvents with silicone. Fluorosilicone rubbers (FSR) resist solvents and fuels and are generally the best silicones to use in corrosive settings. All methyl silicones resist ozone.
The dielectric insulating property of silicone is the best of any of the available elastomers. For example, a half inch thick piece of silicone has the same dielectric properties as that of 18 inches of air. Another useful benefit is that the dielectric and physical properties are not affected by temperature extremes. For more information regarding the dielectric properties of silicone please visit:

http://www.dowcorning.com/content/rubber/rubberprop/elec_dielectric.asp

Examples of electrical engineering applications include:

- Cables and cable terminations
- Corona-resistant insulation tubing
- Keyboards and contact mats
- Conductive profiled seals
- EMI/RFI applications

Here is a Silicone Dielectric Insulator designed for Homeland Security to be used in airport imaging equipment for luggage.

**Silicone Dielectric Insulator**

By: Albright Technologies, Inc.

http://www.Albright1.com/
**Flammability**

Typically silicones are flammable; however silicone rubber can be compounded and fabricated to meet many specifications, including:

- UL-94, V-1 or V-0
- UL Code 62
- BMS 159-C

Silicone can be used to **improve a product flammability rating.**
Silicone can be **formulated to change flammability properties.**

**Fungus Resistance**

When rubber is used in any warm, damp environment, its properties must resist attack by mold or fungus. Although silicone rubber is not antifungicidal, it is not a nutrient for fungi nor is it adversely affected by fungus or mold. With test procedures described in 005272B (USAF), several classes of Military Specification MIL-E, silicone rubber was exposed to chaetomium, globum, aspergillus niger, aspergillus terreus, penicillium lutum, and fusarium moniliforme. None of these microorganisms deteriorated the specimens. In another test, silicone rubber samples were buried in 5 inches of warm (28°C) moist soil for 6 weeks with no evidence of microbial attack. Finally, in a third test, samples were sprayed with a mixed spore suspension of fungi and then placed in a tropical test chamber at 27°C, 90/100 percent relative humidity. None were attacked by mildew.

Silicone can be **formulated to improve fungus resistance properties.**

**Food Contact Status and FDA Regulations**

FDA Regulation - FDA ZZR-765-E Class 2A&B

Silicone can be rated for food contact but special tests should be run.

**Mechanical**


- Very high elongation (up to 1200%)
- Tensile strength (up to 1500 psi)
- Tear strength of silicone is related to the durometer. The higher durometer, the higher tear (typical to 250 ppi)
- Compression Set is as low as 6% at room temperature. The resistance to compression set is maintained at low and elevated temperatures.

The electrical, physical, thermal and chemical resistance properties can be enhanced with special formulations.

*For more information see:*
[http://www.dowcorning.com/content/rubber/silicone-organics.asp](http://www.dowcorning.com/content/rubber/silicone-organics.asp)
A. **Compression Set Resistance**

Compression set of Silastic silicone rubber after various times under compression at room temperature (ASTM D 395)

<table>
<thead>
<tr>
<th>Silastic silicone rubber</th>
<th>Compression set (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After 22 hours</td>
</tr>
<tr>
<td>Extreme low temperature</td>
<td></td>
</tr>
<tr>
<td>(PVMQ)</td>
<td></td>
</tr>
<tr>
<td>General purpose (VMQ)</td>
<td>12</td>
</tr>
<tr>
<td>Fluorosilicone (FVMQ)</td>
<td>6</td>
</tr>
</tbody>
</table>

*These values are not intended for use in preparing specifications.*

**IMPROVED SEALING APPLICATION O RING**

By: Albright Technologies, Inc.

Albright1.com

B. **Resistance and Damping Factor**

Resilience of various types of Silastic silicone rubber

<table>
<thead>
<tr>
<th>Silastic silicone rubber</th>
<th>Bashore Resilience Range (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>General purpose (VMQ)</td>
<td>40 to 65</td>
</tr>
<tr>
<td>High performance (VMQ)</td>
<td>30 to 60</td>
</tr>
<tr>
<td>Fluorosilicone (FVMQ)</td>
<td>10 to 35</td>
</tr>
</tbody>
</table>

*These values are not intended for use in preparing specifications.*

C. **Hardness Range from 0000 shore a to 70 shore D**

The 10 to 80 shore A, durometer hardness range offered by silicone rubber gives the designer freedom to select the desired hardness to best perform a specific function. Variations in blending polymer bases, fillers, and additives permit all intermediate hardness values. And, the length of time and the temperature used for oven curing also change the hardness without destroying other physical characteristics.

The normal hardness tolerance is plus or minus 5 (shore A scale). Mold prototypes in different durometer to see how product performs.
D. **Tensile Strength**

Typical tensile strength ranges are listed here. *(Review the links to each selection guide for more details.)*

- **HCR - High Consistency Silicone Rubber** - typical tensile strength range from 4.0 to 12.5 MPa.
- **FSR - Fluorosilicone Rubber** - typical tensile strength from 8.7 to 12.1 MPa.
- **LSR - Liquid Silicone Rubber** - typical tensile strength range from 3.6 to 11.0 MPa.

Base polymer, reinforcing filler, and special additives, such as fiberglass can change tensile strength significantly.

E. **Elongation**

Generally refers to “ultimate elongation” or percent increase in original length of a specimen when it breaks.

Typical elongation ranges are listed here. *(Review the links to each selection guide for more details.)*

- **HCR - High Consistency Silicone Rubber** - typical elongation range from 90 to 1120%.
- **FSR - Fluorosilicone Rubber** - typical elongation range from 159 to 699%.
- **LSR - Liquid Silicone Rubber** - typical elongation range from 220 to 900%.

*Different processing methods and oven cures change the values considerably.*

The [thermal characteristics section](#) shows that the elongation of silicone rubber varies linearly with temperature, and holds up longer than most other elastomers.

F. **Bulk modulus**

This property refers to the elastic properties of a material when compressed by external pressures. Silicone rubber offers the advantage that under high-pressure it will deform approximately half that of a comparable organic rubber. In addition, at high temperatures, silicone rubber remains stable, while organic rubbers continue to deform. At low temperatures, silicone rubber will remain stable while many organic rubbers suffer from brittle failure.

G. **Flex life**

These properties refer to the ability of the material to undergo extreme flexing, but still retain its original shape without any significant loss of its property profile. Silicone rubber can withstand thousands of cycles over a wide range of temperature making this material ideal for keyboard or exhaust hanger and vibration damping applications. Typically natural rubbers require more energy to deform and breakdown when exposed to ozone and UV light, again silicone rubber remains stable over a wide range of temperatures.

Flexometer tests prove the outstanding crack growth resistance of silicone rubber. When subjected to flexometer test punishment – 18,000 cycles an hour until failure – cut-growth samples of a high-performance silicone elastomer lasts up to 500,000 cycles.
H. Tear Strength

Tear Strength is defined as the resistance to growth of a cut or nick when tension is applied to the cut specimen. High-performance silicone rubber resists tear even when nicked and placed under severe twisting stress.

Typical tear strength ranges are listed here. (Review the links to each selection guide for more details.)

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Typical Tear Strength Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCR</td>
<td>High Consistency Silicone Rubber</td>
<td>9 to 55 kN/m</td>
</tr>
<tr>
<td>FSR</td>
<td>Fluorosilicone Rubber</td>
<td>17.5 to 46.4 kN/m</td>
</tr>
<tr>
<td>LSR</td>
<td>Liquid Silicone Rubber</td>
<td>11 to 52 kN/m</td>
</tr>
</tbody>
</table>

I. Coefficient of Friction

The coefficient of friction of silicone rubber ranges from less than 0.25 to more than 0.75. Steel is about .10. Compared to steel silicone rubber is 2 to 7 times greater. Lower durometers have higher coefficients. The texture can be used to reduce the co-efficient of friction.

Note: Polished surfaces have a higher coefficient of friction. Texture lowers the coefficient of friction.

J. Ozone and Oxidation Resistance

Silicone rubber, when tested for resistance to ozone, shows excellent stability. After both static and dynamic testing for periods of two, four, six, and eight hours, samples had no significant change in durometer hardness, tensile strength, or elongation. Under a magnification of 10, no cracking or checking was visible.

K. Permeability (Gas and Liquid)

Silicone gas permeability is approximately 400 times that of rubber. Gas permeability can be increased by compounding but not decreased.

L. Bondability

This property refers to the ability to adhere a rubber to another substrate. Parts fabricated from silicone rubber can be easily bonded to metal, glass, ceramics, silicone-glass laminates, or to silicone rubber itself. Best bonding procedures depend on the exact materials and engineering requirements.

Typically primers are coated onto the substrate to be adhered to, however this involves additional preparation and coating process. Silicone rubber now offers the advantage of incorporating a bonding agent into the rubber, so that when the fabricated part cures it automatically bonds to the substrate. Silicone rubber can be bonded to any porous or non-porous material; the bond formed is highly durable and will readily withstand flex movement at high and low temperatures. Most organic rubbers cannot match the combination of bond and physical properties that silicone rubber offers. The silicone bond to the substrate is stronger than the rubber itself giving the rubber a tearing bond.
M. Radiation Resistance

Radiation causes changes in the properties of silicone rubber similar to those caused by heat aging. As the total radiation dose is increased, hardness of the rubber increases; tensile strength may increase at first, but later decreases sharply; elongation decreases.

These direct effects of radiation are proportional to the total amount of radiation level - as long as the radiation level is low or moderate. However, with high radiation levels, the heating effects cause additional changes.

N. Temperature Resistance

**Temperature extreme stability is silicones most outstanding property.** Under normal operating conditions temperatures as high as 600 F and as low as -150 F do not destroy the physical and electrical properties of silicone. At elevated temperatures, the tensile, elongation, and abrasion resistance of silicone is far superior to that of most organic elastomers.

**Low temperature flexibility is another advantage silicone** has over most organic rubbers. Silicons durometer and modulus show little change at temperatures as low as -100 F.

O. Weather Resistance

Weathering, UV, sunlight and environmental water exposure has less effect on silicone than other materials.

P. Bio-testing


**Biocompatibility.** In extensive testing, silicone rubbers have exhibited superior compatibility with human tissue and body fluids and an extremely low tissue response when implanted, compared with other elastomers. Odorless and tasteless, silicones do not support bacteria growth and will not stain or corrode other materials. They are often formulated to comply with FDA, ISO, and Tripartite biocompatibility guidelines for medical products. Additionally Medical Grade platinum cured silicone meets Class VI medical standards.

Silicone oils, namely dimethicone, simethicone and cyclomethicone are widely used today in cosmetics, antiperspirants in lotions and creams.

**FACTORS IN SELECTING MEDICAL SILICONES**

*Written by: Alastair Winn

Because of their inherently low toxicity, pure silicones present a low risk of unfavorable biological reactions and have thus gained widespread industrial and medical recognition and acceptance. The current health-care market supports a small group of manufacturers of silicone raw materials, companies such as General Electric, Wacker, Bayer, Dow Corning, Rhodia, Shin Etsu, Nusil Technology. The primary differences among these suppliers involve their level of testing and commitment to serving particular applications. Historically, concerns over potential liability have driven most large silicone manufacturers to aggressively exclude themselves from providing silicone intended to be used in the human body for more than 29 days. The author knows of only one supplier willing to continue serving the long-term implantable silicone market: Nusil Technology.
Silicones as a Material of Choice for Drug Delivery Applications

Brian Reilly,  NuSil Technology, brianr@nusil.com / Stephen Bruner,  NuSil Technology
Presented at 31st Annual Meeting and Exposition of the Controlled Release Society, June 12 – 16, 2004
Honolulu, Hawaii

Abstract

This paper will investigate the benefits of using silicone in drug delivery applications. This investigation first provides an overview of how versatile of a material silicone can be to the drug delivery industry. An examination of the chemistry of silicone, the multiple material composition options and various cure chemistries demonstrates how silicone can be tailored to fit specific drug delivery applications. Then, a general investigation of the way a silicone interacts with a drug, in regards to compatibility and potential interactions, exhibits silicone’s ability to deliver pharmaceutical agents. The paper will also review factors that have made silicones the materials of choice in the medical device industry, particularly for long-term implantable devices. Examples of applications demonstrate the reasons for choosing silicone over a different material. The paper will finish with real world examples of current drug delivery applications incorporating a silicone, such as hormone replacement therapies, to manifest the benefits of using silicone in drug delivery applications.

Introductions

The chemistry behind silicone essentially equates to material versatility, and this versatility allows silicone materials to be custom designed to fit drug delivery applications. The polymer chemistry that constitutes silicones allows various types of silicone polymers, which each provide varying properties beneficial to different applications. Silicone chemistry also makes a diverse set of material compositions available for a broad range of applications. Finally, silicone cure chemistry provides options to optimize how a silicone can be used when applied to specific applications.

Polymer Chemistry

The term “Silicone” is actually a misnomer. Normally the suffix ‘-one’ delineates a substance has a double bonded atom of oxygen in its backbone. Scientists initially believed that silicone materials contained double bonded oxygen, hence the use of ‘silicone.’ However, silicones are really inorganic polymers, having no carbon atoms in the backbone, and therefore should be named ‘Polysiloxanes.’ The diagram below shows their typical structure:

R R R R R R

\[ \text{Si-O-Si-O-Si-O-Si-O-Si-O} \]

R=CH₃, phenyl (aromatic carbon ring), F₃CCH₂CH₂, CHCH₂
This structure allows polysiloxanes to be used in a wide array of applications because different types of constituent groups can be incorporated onto the polymer. Different polysiloxanes can provide a variety of excellent elastomic properties that can be chosen according to a specific use. Various types of silicones, or polysiloxanes, and their property advantages include:

**Dimethyl silicones**, or dimethylpolysiloxanes, are the most common silicone polymers used industrially. These types of polymers are typically the most cost effective to produce and generally yield good physical properties in silicone elastomers and gels. The polymer pictured below contains vinyl endgroups that participate in a platinum catalyzed addition reaction (see section on Cure Chemistry for more information).

![Dimethyl silicone structure](image)

**Methyl phenyl silicone** systems contain diphenyldimethylpolysiloxane co-polymers. The steric hinderance of the large phenyl groups prohibit significantly high concentrations of diphenyl units on the polymer chain. The phenyl functionality boosts the refractive index of the polymers and silicone systems that use these polymers. Silicone polymers with diphenyl functionality are useful in bio-photonic applications (e.g., intraocular lenses) where higher refractive index materials can be useful in creating a thin lens. Creating devices with several layers of diphenyl elastomer systems may be useful in controlling release rates of certain drugs. The diagram below shows a typical structure for a methyl phenyl silicone:
Fluorosilicones are based on trifluoropropyl methyl polysiloxane polymers and used for applications that require fuel or hydrocarbon resistance. The trifluoropropyl group contributes a slight polarity to the polymer, resulting in swell resistance to gasoline and jet fuels. However, polar solvents such as methyl ethyl ketone and methyl isobutyl ketone may significantly affect fluorosilicones. While some fluorosilicones contain 100% trifluoropropylmethylpolysiloxane repeating units, other systems contain a combination of the fluorosiloxane units and dimethyl units to form a co-polymer. Adjusting the amount of trifluoropropyl methyl siloxane units in the polymerization phase provides optimal performance in specific applications. The diagram below shows a typical structure for a fluorosilicone:

![Fluorosilicone Structure](image)

**Material Composition**

While the polymer chemistry and structure of silicone provide the different types of silicones outlined above, they also allow those different types of silicones to appear in a wide variety of material compositions. This broad range of material compositions makes silicone a viable option to endless numbers of healthcare and drug delivery applications.

Some silicone material compositions and their typical applications include:

**Silicone Fluids** are non-reactive silicone polymers formulated with dimethyl, methylphenyl, diphenyl, or trifluoropropylmethyl constituent groups. These materials’ viscosity depends largely on molecular weight of the polymer and steric hindrance of functional groups on the polymer chain. Fluids are typically used in lubrication and dampening applications.

**Silicone Gels** contain reactive silicone polymers and reactive silicone crosslinkers. These materials are designed to have a very soft and compliant feel when cured. Typical applications include tissue simulation and dampening.

**Silicone Pressure Sensitive Adhesives** (PSA’s) contain polymers and resins. These materials are designed to perform in an uncured state. PSA’s form a non-permanent bond with substrates such as metals, plastics, glass, and skin.
Silicone Elastomers fall into several categories: high consistency, liquid silicone rubbers, low consistency elastomers, and adhesives.

High consistency elastomers typically contain high viscosity polymers and high levels of reinforcing silica. These materials are clay-like in consistency in their uncured state, and offer good physical properties when vulcanized. High consistency materials can be molded into parts by compression or transfer molding, and are most commonly used for extrusion to yield tubing configurations.

Liquid silicone rubbers, or LSR’s, are elastomers containing medium viscosity polymers and moderate amounts of silica. The cured elastomers have good physical properties. They tend to have an uncured consistency like that of petroleum jelly. These materials can be molded into parts and require the use of liquid injection molding equipment.

Low consistency silicones are pourable systems composed of lower viscosity polymers and reinforcing fillers such as silica or resin. These systems have lower physical properties than high consistency elastomers or LSR formulations, but can be easily processed and molded by manual methods. These materials can be molded into parts by compression molding or used as cured-in-place seals or gaskets.

Adhesives are low consistency elastomers containing lower viscosity polymers, reinforcing silica and adhesion promoters. Silicone adhesives are designed to adhere silicones to various substrate surfaces including metals, glass and certain plastics.

Cure Chemistry
When a manufacturer in the drug delivery industry chooses a material for a specific application, material properties aren’t the only deciding factor. That manufacturer also has to examine how the material is used. Inconvenience in production or material by-products can make a chosen material ineffective for a specific application. Silicones, however, can be designed around various cure chemistries to accommodate different production needs. Silicone systems can cure by platinum catalyzed addition cured systems, tin condensation cure systems, peroxide cure systems, or oxime cure systems. Some of the oldest cure chemistry used with silicones utilizes an acetoxy tin condensation cure system. These systems yield a vinegar-like smell (acetic acid), a byproduct of the reaction. This discussion will focus on platinum systems, tin condensation systems, and peroxide systems.
Platinum catalyzed silicones utilize a platinum complex to participate in a reaction between a hydride functional siloxane polymer and a vinyl functional siloxane polymer. The result is an ethyl bridge between the two polymers. The reaction mechanism is pictured below:

Platinum systems are often cured quickly with heat, but can be formulated to cure at low temperatures or room temperature if necessary. The advantages of these systems include a fast cure and no volatile byproducts. The possibility of inhibiting the cure is the main disadvantage of platinum systems. Inhibition is defined as either temporarily or permanently preventing the system from curing. Some types of inhibitors are purposefully added to these systems to control the rate of cure. However, contact with tin, sulfur, and some amine containing compounds may permanently inhibit the cure. Compounds that inhibit the cure can be identified easily by attempting to cure a platinum catalyzed system in contact with the compound, as inhibition results in uncatalyzed regions of elastomer systems or inconsistency in cure over time.

Tin condensation systems involve hydroxyl functional polymers and alkoxy-functional cross linking compounds. The alkoxy functional cross linker first undergoes a hydrolysis step and is left with a hydroxyl group. This hydroxyl group then participates in a condensation reaction with another hydroxyl group attached to the polymer. The reaction can proceed without the assistance of the tin catalyst, but the presence of the catalyst boosts the rate of reaction. The reaction mechanism is pictured below:

The advantages of condensation systems include the ability to cure at room temperature (useful for temperature sensitive additives) and robust cure systems that are difficult to inhibit. The main disadvantage of condensation systems is the long cure time, as several days are often required to completely cure an elastomer.
Peroxide catalyzed systems, used mostly in high consistency elastomers (see definition below), have a reaction mechanism that involves a peroxide catalyst and either methyl groups or vinyl functional groups. The peroxide catalysts create free radical species of the methyl and vinyl that can then form covalent bonds. Pictured below is the reaction mechanism involving a peroxide catalysis of two methyl groups:

\[
\begin{align*}
   \text{SiCH}_3 & \quad \text{RCOO}^- \\
   \text{SiCH}_3 & \quad \text{RCO}^+ \\
\end{align*}
\]

Peroxide systems are typically robust (not easily inhibited) and offer properties such as low tension set (good for balloon applications). Disadvantages include a lengthy post-curing step at high temperatures in order to remove the reaction’s byproducts. Other disadvantages include the possibility of the catalyst interacting with active agents.

**Discussion**

The versatility of silicones as a material enables them to be a viable option for a broad range of drug delivery applications. Some of silicone’s specific properties and characteristics, such as its interactive chemistry and microporous structure, make them the material of choice for many drug delivery applications. This can be seen when looking at examples of silicones already being used in healthcare and drug delivery applications.

**Interactive Chemistries**

The siloxane polymer backbone of repeating silicon and oxygen atoms creates a potential for interaction. The two free pairs of electrons associated with each oxygen atom can form hydrogen bonds with proton donors. Silicone elastomer systems can be strengthened with silica or resin reinforcement. These systems can result in different degrees of hydrogen bonding.

Despite the ability to form hydrogen bonds, silicone is considered hydrophobic in nature. The methyl constituency on the siloxane polymer backbone creates this effect. This hydrophobicity is ideal for the solubility of pharmaceutical agents having mostly non-polar structures with alcohol or ketone structures. Below are the molecular structures for estradiol, levorphanol, and metronidazole.

---

Estradiol:

Levorphanol:

Metronidazole:

It appears the interaction between the oxygen of the siloxane backbone does have some hydrogen bonding with the alcohol functionality of many active pharmaceutical agents. This is evidenced by a rise in release rates when a fatty acid ester is used in a drug delivery device. The molecular structure of Linoleic Acid is shown below:

\[
\text{CH}_3\text{CH}_2(\text{CH}=\text{CH}_2)_3(\text{CH}_2)_3\text{CH}_2\text{C}=-\text{OH}
\]

It is believed that fatty acid esters increase the hydrophobicity of the siloxane system (3). It can be speculated that the carboxylic acid group competes for siloxane oxygen, thereby reducing the concentration of siloxane oxygen available in the elastomer system. The exact mechanisms and interactions between the silicone polymer backbone and pharmaceutical agents are not known at this point.

**Microporous Structure**

The large atomic volume of the silicon atom, as well as the size and position of constituent groups, explain the virtually complete freedom of rotation around the Si-O-Si bond. Silicone polymers form helixes, and the bond angles of the silicon-oxygen bonds
create large amounts of free volume in silicone elastomers. This free volume, and the high compressibility found in silicones, is associated with their permeability to gases and liquids. The gas permeability of silicone rubber is up to 100 times greater than natural or butyl rubber. Silicone rubbers swell in aliphatic, aromatic and chlorinated hydrocarbon solvents.

Silicone gaskets for industrial applications absorb lubricating oils and will tend to “wet” the surface of the elastomer system after the source of the lubrication is removed (1). NuSil Technology takes advantage of this phenomenon in the various self-lubricating elastomer formulations. Proprietary silicone fluids are incorporated into the elastomer formulation, and migrate to the surface of the molded component after cure.

**Healthcare Applications**
Silicones expanded into healthcare and medical applications in the 1950’s after extensive use in the aerospace industry in the previous decade. Within twenty years, a considerable body of work established that silicone oils and crosslinked siloxane systems did not give rise to harmful consequences when performing subcutaneous, intracutaneous, and intramuscular administrations. In 1954 McDougall reported the cultures of various tissues of warm blooded animals, known to be extraordinarily sensitive to foreign influences, showed no deviation from the usual growth picture on contact with liquid, semisolid, and rubberlike silicone products (10). Silicones have been characterized as biologically and toxologically inert as a result of this work (1). Many applications such as pacemaker leads, hydrocephalus shunts, heart valves, finger joints and intraocular lenses utilize silicone materials.

**Drug Delivery Applications**

*Evaluation and Fabrication*
The first step in determining general compatibility of a silicone with an active agent is determining the solubility of the agent in silicone. Silicone oil can be used to determine if an agent may be soluble in a silicone elastomer system (2). Once solubility has been determined, the active agent can then be tested in the elastomer system to determine the optimal concentration or agent configuration for the target release rate per day and the total number of release days. In some devices, the drug is incorporated into a silicone matrix core or reservoir and the release rate is controlled by an outer layer of silicone (without pharmaceutical agents incorporated) on the device. (3,4,5,6,7).

A general review of those patents listed above suggests that 5% to 50% of the active agent is optimal for release rates of 10 to 500 micrograms of drug per day. These numbers are highly dependent on the type of drug, silicone, and any rate enhancing additives. The release rate is also cited on those patents above and has been characterized as essentially zero order.

**Commercial Applications**
Commercial applications such as Norplant (8) and Femring (9) are examples of clinically successful drug delivery applications that involve silicone materials. Patent number 6,039,968 cites a number of agents that could be used in drug eluting applications. The
drugs cited included antidepressants, anxiolytics, vitamins B6, D, and E, antifungal, opioid analgesics, non-opioid analgesics, and antiviral compounds.

Conclusion

As presented above, an investigation of the chemistry of silicone and silicone materials, interactive characteristics, their extensive use in the healthcare industry and current drug delivery applications show the benefits of using silicone materials in a drug delivery device. The paper explored how versatile a material silicone is and how this can benefit drug delivery. The interaction between drugs, release enhancing agents, and silicone systems was characterized by comparing molecule structures of each. The paper also demonstrated the history of silicone, in various forms, in healthcare applications since the 1950’s. Finally, commercially successful examples of products utilizing silicones demonstrate a commitment to silicone as a material of choice for drug delivery applications.

Bibliography

(3) Nabahi and Shorhre, U.S. Pat. 5,788,980 (August 4, 1998)
(4) McClay and Allen, U.S. Pat. 5,855,906 (January 5, 1999)
(5) Nabahi and Shorhre, U.S. Pat. 6,039,968 (March 21, 2000)
(6) Passmore and Clare and Gilligan and Clare, U.S. Pat. 6,416,780 (July 9, 2002)
(7) Nabahi and Shorhre, U.S. Pat. 6,103,256 (August 15, 2000)
(8) http://www.norplantinfo.com
(9) http://www.femring.com
Comparing Silicone Pressure-Sensitive Adhesives to Silicone Gels for Transdermal Drug Delivery

By Manfred Hof, Polytec PT, Stephen Bruner and John Freedman, NuSil Technology, LLC

Presented at 33 Annual Meeting and Exposition of the Controlled Release Society July 22-26, 2006 Vienna, Austria

Abstract

Transdermal, drug-delivery applications mandate the use of adequate adhesive systems to not only keep the pharmaceutical agent in contact with the intended surface, but to facilitate sustained, controlled delivery. An engineer who must determine which silicone chemistry is optimal for their device has a few options. This paper will investigate the differences in silicone pressure sensitive adhesives (PSAs) and silicone gels for transdermal drug delivery applications. The paper begins with analysis of the chemistry of silicone and silicones. The many variations of the chemistry demonstrate the versatility of using silicone in drug delivery applications. Further exploration of the materials demonstrates fundamental differences between silicone PSAs and silicone gels and the advantages and disadvantages of these materials in use. The findings of the study suggest that silicone gels can offer a compelling alternative to the more traditionally used silicone pressure sensitive adhesives. The paper does recognize that the tradeoffs between ease of use and physical properties need to be considered when evaluating both materials for transdermal drug delivery applications.

Introduction

Since 1979, PSAs have been a mainstay in transdermal, drug delivery. PSAs, provide pharmaceutical companies the means to supply a range of active agents in a non-invasive, controlled-release system and reduce the healthcare industry’s dependence on gastrointestinal and needle-based administrations. The overriding benefits of these systems include improved patient compliance and steady drug levels within the bloodstream.

Estradiol, testosterone, and nitroglycerin are just a few of the compounds currently found in prescribed, transdermal, drug-delivery systems. Over-the-counter (OTC) products such as Dr. Scholl’s Clear Away Wart Remover, Neutrogena’s On-the-Spot Acne Treatment, and several brands of the nicotine patch are examples of how this technology has moved readily into direct consumer applications. Estimates for growth in this area are 12 percent annually (1). Some of the usual adhesives incorporated in transdermal, drug-delivery systems are polyisobutylene (PIB), silicones and acrylic-based PSAs. For this article, silicone-based PSAs are used for comparative purposes. Silicones are good candidates for transdermal, drug-delivery systems because they offer two major benefits to drug-device developers. First, silicones have a more than 50-year history in biomedical applications and, in that time, a considerable body of work has been assembled that characterizes silicones as biologically inert (2). In addition, silicones are ubiquitous in the medical device industry in both long-term, implantable devices and external devices. Second is the compatibility/permeability of silicones with many pharmaceutical agents, not just hormones. Other compatible drugs include antidepressants; anxiolytics; vitamins B6, D, and E; antifungals; opioid and non-opioid analgesics; and antiviral compounds (3).

Siloxane Chemistry

Silicones’ compatibility and permeability with pharmaceutical agents is a function of the siloxane-based polymers and resins used to formulate these systems, and the siloxane polymer backbone of repeating silicon and oxygen atoms creates an interaction potential. The two free pairs of electrons associated with each oxygen atom can form hydrogen bonds with proton donors, often resulting in different degrees of hydrogen bonding with reinforcing fillers. Despite its ability to form hydrogen bonds, silicone is considered hydrophobic in nature. The methyl constituency on the siloxane polymer backbone creates this effect. A vinyl-terminated, dimethyl polysiloxane can be seen in Figure 1.
Figure 1. A vinyl-terminated, dimethyl polysiloxane’s hydrophobicity is ideal for the solubility of pharmaceutical agents.

This hydrophobicity is ideal for the solubility of pharmaceutical agents having mostly non-polar structures. Another characteristic of silicone systems is the large atomic volume of the silicon atom itself, which - along with the size and position of constituent groups - explains the virtually complete freedom of rotation around the Si-O-Si bond. Silicone polymers form helixes, and the bond angles of the silicon-oxygen bonds create large amounts of free volume in silicone elastomers. This free volume, and the high compressibility found in silicones, is associated with their permeability to certain gases and liquids. The gas permeability of silicone rubber is up to 100 times greater than natural or butyl rubber.

In the specific case of drugs or active pharmaceutical molecules, release rates in silicones are determined by the drug’s solubility in a silicone and the diffusion coefficients of those drugs in silicones through the Higuchi equation:\(^{1-5}\) (equation 1 corresponds to a matrix device, and equation 2 corresponds to a reservoir device):

Equation 1: \[ Q = (D_{sil}(2A - C_{sil}) C_{sil}) t^{1/2} \]

Equation 2: \[ Q = ((D_{sil} C_{sil})/ h_{sheath})^t. \]

“Q” is the cumulative amount of drug released per device-unit area, “A” is the drug loading, “C_{sil}” is the drug solubility in the silicone, “D_{sil}” is the diffusivity of the drug in the elastomer, “h_{sheath}” is the thickness of the sheath in cm, and “t” is the time in days. Determination of these values is aided by additional research in this area that relates the molecular weight and melting point of the drugs to release rates\(^4\), as well as demonstrates that the addition of fatty acid esters improve release rates of certain drugs\(^6\). Silicone polymer chemistry can be modified to include different groups on the backbone. For example, trifluoropropyl methyl dimethyl siloxane copolymers are used in applications in which solvent resistance is required, while diphenyl silicone polymers are used in elastomeric formulations, when a high-refractive index is necessary (intraocular lenses or UV and heat protection). The diphenyl and trifluoropropylmethyl functionality may also affect drug solubility and, in turn, affect release rates. The concentration of these groups on the backbone can be easily altered and optimized for specific compounds. A diphenyl polysiloxane structure is seen in Figure 2.

Figure 2. A diphenyl polysiloxane structure can be easily altered and optimized for specific compounds.

---

**Silicone PSAs**

Silicone PSAs incorporate a high-molecular-weight polydimethylsiloxane polymer and a tackifying silicone resin dispersed in a solvent system. The solvent provides the system with viscosity control, as silicone components are virtually impossible to process at room temperature with standard coating equipment. If containing a catalyst, silicone PSAs typically crosslink by curing after removing the solvent. Two systems are currently available: platinum-catalyzed and peroxide-catalyzed.

Platinum catalyzed systems are common in PSAs and utilize vinyl functional polymers, such as those pictured above, and hydride functional crosslinking polymers to cure in the presence of the catalyst. Figure 3 diagrams the cure mechanism of a platinum system. Curing of these PSAs is achieved through multi-zone ovens. The solvent is eliminated by a gradual increase in temperature from 60°C to 90°C.

![Figure 3. Platinum cure mechanism.](image)

Peroxide-cure system employs benzoyl peroxide, or 2,4-dichlorobenzoyl peroxide, as a catalyst to drive a free-radical reaction and achieve cure. Curing is normally performed in a multi-zoned oven. Solvent removal is achieved through a gradual increase in temperature, starting at 60°C to 90°C to ensure that the peroxide catalyst does not cure while solvent is present. The temperature is then increased to 130°C to 200°C, eliminating the peroxide through decomposition. The reaction mechanism is pictured below in Figure 4. A high-crosslink-density PSA can be better achieved through peroxide curing due to the ability to increase peroxide levels up to 4 percent.

![Figure 4. Peroxide cure reaction mechanism.](image)

Tape and adhesive-backed component fabricators take the liquid PSA and either wet coat in sheet form, for small applications, or in roll form (pilot coaters and full-width
production coaters), when large quantities are required. The PSA may be applied on one or both sides of a substrate - such as Kapton®, Mylar®, Nomex®, foils, foams, and rubbers - or it can be coated directly onto a release film. Coat weights on supported film range from 0.0003” to more than 0.010” thick. When the adhesive is coated directly onto a release film, this is called an unsupported PSA transfer film. Common post-production processes include die cutting and laser cutting for later use in component assembly, and automated pick-and-place solutions for difficult-to-apply parts and materials.

Silicone PSAs are not without their drawbacks. As stated above, most PSAs are dispersed in a solvent system to provide viscosity control. The solvent can be problematic and limiting to transdermal, drug-delivery systems. Environmental concerns regarding Volatile Organic Compounds (VOCs) and plant-safety initiatives are costly factors that must be considered. In addition, solvent systems are dynamic, and evaporating solvent can impact viscosity, leading to process variations. PSAs can also limit the transdermal system design, as these materials are typically used in multilaminate, reservoir designs. PSAs that utilize peroxide systems, as mentioned above, require an elevated temperature and may negatively impact active agents. This limitation may require that the PSA is processed in a separate step.

**Silicone Gel Technology**

Silicone gels share the same basic siloxane polymer chemistry as silicone PSAs but lack the silicone resin credited with supplying adhesive strength to the system. Silicone gels are typically composed of two types of siloxane polymers: vinyl-functional polysiloxanes and hydride-functional polysiloxanes. Silicone gels are low-viscosity materials that are not dispersed in solvent systems. These materials do not contain reinforcing fillers, such as silica or silicone resins, found in silicone elastomer systems. As a result, they offer little tensile or tear strength. Typically, gels used in thin-film applications use reinforcing fabrics to add strength.

The tack and adhesion of silicone gels have proven sufficient in transdermal, adhesive-type applications. The testing discussed later in this article illustrates the superior tack properties of silicone gels compared to silicone PSAs. Pfizer’s Scar Solution and Smith & Nephew’s Cica Care are OTC examples of silicone gels used in transdermal applications to treat hypertrophic and keloid scarring.

Silicone gels cure in the presence of platinum catalysts to solid forms that do not flow. Gels can be formulated to cure completely at low temperatures, which may be ideal for pharmaceutical agents that are unstable at higher temperatures. These materials can be utilized in multilaminate, reservoir or monolayer, drug-in-adhesive delivery systems.

**Experimental Methods**

*Comparative Adhesive Properties*

The discussion above provides some basic differences between silicone PSAs and gels from chemistry to supplied forms. The following data was compiled to determine the key property differences between silicone PSAs and gels (and differences in silicone gels with dissimilar compositions). The two properties tested in this study were 90-degree peel strength (NuSil Technology Test Method TM087 Reference ASTM D1876) and tack testing (NuSil Technology Test Method TM103 Reference ASTM D429 Method D).
Because pressure-sensitive system properties are influenced by the thickness or amount of adhesive, care was taken to ensure identical amounts of silicone were used. The materials were prepared per the applicable test method and specific material cure recommendations. Four materials were tested; Table 1 describes the material and characteristics:

<table>
<thead>
<tr>
<th>Material Name</th>
<th>Material Composition</th>
<th>Cure Schedule</th>
</tr>
</thead>
<tbody>
<tr>
<td>MED-1356</td>
<td>Dimethylpolysiloxane PSA, 35% Solids in Ethyl Acetate</td>
<td>37°C for 30 minutes, 150°C for 90 minutes</td>
</tr>
<tr>
<td>MED-1356 (peroxide catalyzed)*</td>
<td>Dimethylpolysiloxane PSA, 35% Solids in Ethyl Acetate, 0.5 pph PD-50S Based on Solids</td>
<td>37°C for 30 minutes 150°C for 90 minutes</td>
</tr>
<tr>
<td>MED-6340</td>
<td>Dimethylpolysiloxane Gel, 0.5 pph PD-50S Based on Solids</td>
<td>100 ºC for 30 Minutes</td>
</tr>
<tr>
<td>GEL-9502-30</td>
<td>Diphenyldimethylpolysiloxane Gel, 100% solids</td>
<td>100 ºC for 30 Minutes</td>
</tr>
</tbody>
</table>

Table 1. The tested materials, as well as their material composition and cure schedule.

**Results and Discussion**

The testing was performed in triplicate for each material, results appear in Table 2:

<table>
<thead>
<tr>
<th>Material Name</th>
<th>Peel Strength Mean (lbf/in)</th>
<th>Peel Strength Standard Deviation (lbf/in)</th>
<th>Surface Tack Mean (psi)</th>
<th>Surface Tack Standard Deviation (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MED-1356</td>
<td>14.7</td>
<td>0.1</td>
<td>2.5</td>
<td>0.8</td>
</tr>
<tr>
<td>MED-1356 (peroxide-catalyzed)*</td>
<td>4.4</td>
<td>0.3</td>
<td>3.4</td>
<td>1.1</td>
</tr>
<tr>
<td>MED-6340</td>
<td>1.3</td>
<td>0.0</td>
<td>5.0</td>
<td>2.1</td>
</tr>
<tr>
<td>GEL-9502-30</td>
<td>1.4</td>
<td>0.2</td>
<td>8.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* MED-1356 product is not supplied as a peroxide-cured product

Table 2. Test results.

From the data, it is apparent silicone gels offer higher tack, but lower peel strength, than PSAs. It also appears that gels containing phenyl functionality gave higher tack and peel
results than the dimethyl gel. The timing of the study prevented a multiple lot measurements of tack and peel but more research is underway to determine the statistical differences between these products. Despite the small sample size, these results are consistent with industry knowledge of these types of products.

Conclusions
The discussion and data presented above provide transdermal, drug-delivery system designers with another choice in pressure-sensitive-type, silicone-based adhesives. Silicones’ historic healthcare use and drug solubility make both silicone PSAs and tacky gels good candidates for certain drug-delivery applications. From the data, it appears silicone gels offer higher tack, but lower peel strength, than PSAs. It also appears that gels containing phenyl functionality gave higher tack and peel results than the dimethyl gel. When considering these results - alongside factors such as drug-release rates, VOC elimination and reservoir/matrix delivery designs it is clear that, no matter which chemistry you choose, tradeoffs must be expected.

Acknowledgements
The authors would like to thank Susan Rhodes of Akron University for her content contributions and expertise in PSA technology, Jim Lambert for his research contributions, and NuSil Technology LLC’s technical healthcare group and commercial testing services for their work.

References
(1) L. Townsend Ferguson, Adhesives In Transdermal Drug Delivery Systems, http://www.adhesivesmag.com/CDA/ArticleInformation/features/BNP_Features_Item article posted 11/01/05
(3) Nabahi and Shorhre, U.S. Pat. 6,039,968 (March 21, 2000)
(6) Nabahi and Shorhre, U.S. Pat. 5,788,980 (August 4, 1998)
(7) B.Reigler, J. Meyer Low Outgas Pressure Sensitive Adhesives for Aerospace Applications, presented at SAMPE Conference, June 2004, NuSil Technology
(8) NuSil Technology’s Test Methods are available by request at www.nusil.com
NuSil Technology: Silicones for Drug Delivery Combination Devices

NuSil Technology is a global leader of silicone-based materials for the healthcare and pharmaceutical industries. For more than 20 years, NuSil has been providing customized silicone solutions for drug delivery and medical devices, including transdermal, transmucosal, and for short- and long-term implantable medical devices. This company is also highly regarded for its extensive level of regulatory product support, especially for silicones used in implantable devices. Recently, NuSil launched a comprehensive line of silicone materials and services intended specifically for use in drug delivery combination medical device applications. Drug Delivery Technology recently sat down with Brian Nash, Vice President of Marketing and Sales at NuSil Technology, for an exclusive interview to discuss how they are providing solutions and meeting the challenges in this competitive and global marketplace.

Q: Why did NuSil decide to create a specialized line of silicone products for drug delivery applications?

A: Drug device combinations are predicted to reach over $11 billion in annual sales by the year 2010, with an average annual growth of 13%. Because combination devices involve regulatory oversight as both a pharmaceutical and a medical device, in 2002, the Office of Combination Products was specifically established to provide specialized regulatory support for this fast-paced industry. NuSil instinctively recognized there was a growing market need to provide dedicated regulatory support for silicone raw materials that are supplied for drug delivery combination devices.

Q: What role do silicones have in drug delivery?

A: As one of the most widely researched biomaterials to date, silicones have a legacy of use in the healthcare industry. Silicone’s history of biocompatibility and unique physical properties has made it a material of choice for both long- and short-term implantable device applications. Silicones have also demonstrated clinical and commercial success in combination devices, such as in products like Norplant® and Femring®. Silicone materials, however, are not only compatible with hormone therapies, but are also compatible with other pharmaceutical agents, such as many antidepressants, antimicrobials, and antiviral compounds, just to name a few. In addition, silicone-based products are used as active ingredients and excipients in pharmaceutical formulations. As an excipient, silicones can be the delivery media of the active agent. In the pharmaceutical industry, simethicones, silicone-based anti-foam agents, are used for gastrointestinal and anti-gas applications as active ingredients and aid in pharmaceutical manufacturing processes.

Q: How has NuSil positioned itself in the industry?

A: High potential liability costs and relatively low volumes of material consumed annually are associated with materials used in long-term implantable devices. This makes supplying silicones for these types of applications economically challenging and unattractive to most silicone manufacturers. We recognized early on there was a critical need to fill this void in this marketplace and have since become an industry leader in the development of customized silicone solutions.”
individualized applications. In addition to being offered an extensive collection of standard elastomers, gels, adhesives, fluids, and lubricants, our customers also have the unique opportunity to work directly with our technical representatives and chemists to custom design formulations for specific applications - all while keeping regulatory concerns in mind. Our personalized approach has allowed us to cater to our customers’ needs in a variety of ways and provide the extensive regulatory support required for these materials.

**Q: What are the benefits of designing a combination device using silicone?**

**A:** Designing a medical or combination device is unquestionably complex. Configurations can range from reservoir designs to drug-in-elastomeric matrix. NuSil is basic, meaning we have the ability to synthesize silicone polymers to adjust physical and chemical properties at the most basic level. Because all silicones begin with polysiloxane polymers, repeating Si-O units, these materials have a wide-range of chemical and physical flexibility. The key to successful drug combination designs is the release of actives, depending specifically on the rate at which the drug permeates the silicone material. This is dependent on two factors: solubility and diffusivity of the active ingredient. Here, we use our many years of experience to modify the backbone chemistry, control the cross-link density, and/or tailor the material to meet the elution requirements of the device. This flexibility offers advantages for maximizing permeation and physical property characteristics.

**Q: How do you aid in the device design?**

**A:** We have been providing technical assistance to design engineers for almost 30 years. Device manufacturers rely on our experience and ability to understand the materials’ inter-property relationships and provide practical solutions to assist in the selection of the optimum material for an intended application. Our integrated approach allows for seamless transitions from conception to design to manufacturing. The ability to develop custom formulations with the appropriate regulatory support potentially shortens the device’s time to market and, in the end, hopefully alleviates some of the accrued cost of qualifying a device.

**Q: What type of regulatory challenges do device manufacturers face using a raw material like silicone? What solutions do you offer to help alleviate these challenges?**

**A:** The regulatory requirements for medical devices and pharmaceuticals are intricate. For medical devices, the US FDA does not directly approve the material used in the device - only the finished product is evaluated for safety and efficacy. This does not, however, imply that biomaterials do not require regulatory support. The Biomaterials Access Act of 1998 places certain requirements on the device manufacturers to demonstrate that the materials used in the device are safe and effective. Pharmaceutical formulations require extensive stability testing; a master validation plan; process information; labeling information; impurity profiles; and references to published safety and efficacy documentation, which must be submitted in the form of a Drug Master File (DMF) to the FDA. Perhaps the most significant requirement is that manufacturing sites producing or handling an active agent must be registered with the FDA.

NuSil is widely recognized for its level of regulatory support and compliance. Our company’s global quality assurance adds value when complex devices are reviewed by different agencies. We provide extensive physical, chemical, and biological testing for materials intended for use in medical devices and for many products, this support has been documented and submitted in the form of Master Access Files (MAFs) to the FDA.

As drug delivery and combination devices continue to become more advanced and specialized for targeted controlled release, we continue to increase our level of regulatory support. Our support for our drug delivery silicones has been expanded from our typical collection of chemical, physical, and bio-testing to include a battery of testing guided by applicable European Pharmacopeia Monographs and customized, certified per-lot features, which include select testing guided by ISO 14949. Unique lot numbers may also be assigned to each uncured silicone part to ensure consistent standard within the pharma industry. This information is all documented in DMFs submitted to the USFDA. We will continue to support customized materials with the same high level of care and support as we do for our standard materials.

**Q: What experience do you have in handling active pharmaceutical ingredients?**

**A:** Since 2004, we have been manufacturing a complete line of digestible simethicone for over-the-counter anti-flatulent products in our FDA-registered facility. We continuously implement cautionary systems that comply with current GMP requirements and associated guidelines. Product quality is assured by the company’s quality system, which begins with an effective design protocol and continues up the supply chain from vendor qualification. Building on this experience, we are currently working with customers to incorporate actives ingredients directly into our silicone products, providing device manufacturers with a one-stop-shop and a potentially cost-saving alternative for a generally complex process.


**ADDING COLOR TO MEDICAL DEVICES**

Summer L. Sivas, Ace Hilmission, Steve Bruner, and Brian Reilly  
NuSil Technology LLC

Medical device companies continue to support the healthcare community by distinguishing models, sizes and improving the aesthetics of the device with the addition of color. Color in medical devices offers a number of benefits in marketing the device. Adding color can help differentiate the product in a competitive marketplace, and the addition of corporate colors can also create a strong tie to the company’s brand. Another factor to consider is the migration of medical devices to home use, emphasizing the need for aesthetics to improve use compliance and other factors.¹

**Coloring Silicone²**

Many applications — such as cosmetic implants, pacemaker leads, hydrocephalus shunts, heart valves, finger joints and intraocular lenses — utilize silicone materials. Adding color to silicone materials that are extruded, molded or calendared is a common manufacturing process for medical devices that utilize silicone parts. Processing and consistency are two major challenges when incorporating pigments into silicone. Typically, coloring silicone materials involves incorporating powdered pigments directly into an uncured elastomer via milling or mixing. Pigments are typically not soluble in silicone, which leads to processing problems. If the pigments are not dispersed homogenously, color variations will result in the cured part. Particulate contamination, handling and additional cleaning of equipment can also add considerable delays in production time, as well as costly maintenance.

The key to color consistency is the accurate addition of pigment(s) to the elastomer and the homogeneous dispersion of those pigments in the elastomer system. An ideal dispersion breaks down the pigments into their primary particle size using high-shear mixing and then disperses the particles homogenously throughout the silicone polymer. This process takes a high level of expertise and high-quality mixing equipment. Colorability is also affected by high pigment powder concentration. The highly filled elastomers tend to be more opaque, drastically changing the color. Another aspect influencing colorability is the thickness of the device, especially for transparent colored silicones.

A more effective alternative to adding color pigments to a silicone polymer directly is to incorporate a color masterbatch prior to the curing stage of the molding or extruding process. In a silicone, color masterbatch pigment is already dispersed in a functional silicone polymer. Typical low-grade masterbatches are simply powders wet-out to be non-dusting materials. While in color-dispersion masterbatches, the pigments are broken down and distributed homogenously in the polymer. The silicone polymers used in the color masterbatches have vinyl functionality and will partake in the cure or tie in with the elastomer system. This leads to two benefits: a reduced effect on the cured physical properties and no “bleeding out” or increase in extractables, which can be experienced when non-functional polymers are used.

NuSil silicone color masterbatches were co-developed with Gayson SDI for coloring low-consistency silicone rubbers (LSRs) and high-consistency silicone rubbers (HCRs). They are offered in an array of both solid colors, including white, black red, orange, yellow green, dark blue and blue and an addition line of translucent colors are available for coloring LSRs. Colors also can be customized or color-matched to fit a variety of device needs. For coloring LSRs used in the injection molding of silicone parts, a low-viscosity masterbatch can be
introduced via a third line prior to the dynamic mixing stage. For HCRs used in tubing extrusion, calendaring and transfer molding applications, a high-viscosity gum polymer masterbatch can be added directly to the elastomer on a two-roll mill during the softening/mixing step. NuSil will also supply most any of its silicone products pre-colored as a ready to use material eliminating any color processing.²

The benefits of using a color masterbatch or colored silicone dispersion will help eliminate particulate contamination in cleanrooms and reduce the costly cleaning time associated with processing powdered pigments. The exceptional color precision will also ensure unparalleled color consistency and improve device esthetics.

REGULATORY CONSIDERATIONS FOR COLOR IN MEDICAL DEVICES

What differentiates NuSil’s color masterbatches from other color options in the medical device market is its level of biological testing and support. Silicones expanded into healthcare and medical applications in the 1950s after extensive use in the aerospace industry and have undergone a steady growth in use and importance ever since.³ During the last 20 years, a considerable body of work has established that siloxane systems do not give rise to harmful consequences and have been characterized as biologically inert.⁴

Pigment masterbatches require regulatory support comparable to that provided for the elastomers into which they are incorporated.² NuSil’s line of color masterbatches are supported by U.S. FDA Class VI testing and many ISO-10993 standards. The USP Class VI testing consists of systemic toxicity, intracutaneous reactivity, seven-day muscle implantation, genotoxicity, pyrogenicity and sensitization testing. These products are supported by a comprehensive Master Access Files (MAF) submitted to the United States Food and Drug Administration (FDA). NuSil’s products are also documented quality system certified as conforming to ISO 9001 and adhere to Good Manufacturing Practice.

CONCLUSIONS

The benefits of adding color to medical devices are numerous. Several considerations must be taken into account when adding color to silicone materials used in a device. Processing and, more specifically, concentration accuracy and clean up, are important initial factors to consider. Color consistency in the cured part depends on the optimal filler concentration, material thickness, and cure conditions. Regulatory requirements, as they relate to materials used in medical devices, should be a concern throughout the entire process. When adding color to a material, keeping these factors in mind will ultimately serve to smooth a complicated process.

REFERENCES


**Drug Delivery Market Summary**

**Drug Delivery Summary**

Silicones have been cited as materials regularly used in drug delivery devices. These drug delivery devices incorporating silicones primarily fall into three major categories:

- Implanted delivery devices
- Mucosal delivery devices
- Transdermal delivery devices

Implanted drug delivery devices include spinal treatment devices, ocular treatment devices and contraceptive devices. These delivery configurations typical utilize silicone tubing or molded configurations. The silicone is used to either hold or precisely deliver the drug to a specific location. Liquid silicone rubbers or high consistency silicone rubbers can be molded into precise configurations required by these applications.

Transmucosal drug delivery devices can include silicone elastomer systems with the drug incorporated into the silicone matrix. After the device is placed in contact with the mucosal membrane, the drug elutes from the device at a controlled rate. A non-medicated sheath is cited (References 12,11,7) as a means to control the initial burst of drug from the device. Drugs can be incorporated into liquid silicone rubbers and molded into various configurations.

Transdermal delivery devices are primarily skin patches in configuration. The drug may be incorporated directly into the adhesive of the patch or may exist as a separate layer. Silicone pressure sensitive adhesives have been used in these applications because of the low skin sensitization, oxygen and drug permeability properties they offer. Silicone materials used in medical device configurations can also be treated with drug infused coatings.

**Materials**

NuSil Technology offers a complete line of off the shelf silicones and offers customized versions of the following materials types:

<table>
<thead>
<tr>
<th>Silicone Type</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Silicone Rubber</td>
<td>Molded Parts</td>
</tr>
<tr>
<td>High Consistency Rubbers</td>
<td>Molded Parts, Extruded Tubing</td>
</tr>
<tr>
<td>Pressure Sensitive Adhesives, Gels</td>
<td>Temporary Adhesives</td>
</tr>
</tbody>
</table>

Two types of liquid silicone rubbers are cited as candidates for transmucosal drug delivery systems, non-acetoxy RTV silicones and platinum catalyzed silicones.
## Drugs or Active Agents

The table below is a list of drugs cited (References 5-14) as candidates for incorporation into a silicone transmucosal drug delivery device. These same citations list typical amounts of 5 to 15% by weight of the drug for release rates of 10 to 500 micrograms per day in a 30 to 60 day time frame. Rate enhancing additives can improve release rates significantly (Reference 9) and are listed below the table. Release rates are essentially zero order. Particle sizes, where applicable, are cited as below 200 microns for the most effective release rates. References for these drugs are listed in the references section under transmucosal drug delivery.

<table>
<thead>
<tr>
<th>Indication Category</th>
<th>Active Ingredient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antidepressants / Anxiolytics</td>
<td>17.beta.-estradiol</td>
</tr>
<tr>
<td></td>
<td>Progestertone</td>
</tr>
<tr>
<td></td>
<td>Medroxyprogesterone</td>
</tr>
<tr>
<td></td>
<td>Norethisterone</td>
</tr>
<tr>
<td></td>
<td>Trimegesteron</td>
</tr>
<tr>
<td></td>
<td>Norethisterone acetate</td>
</tr>
<tr>
<td></td>
<td>Mifepristone</td>
</tr>
<tr>
<td></td>
<td>Ethinyl estradiol</td>
</tr>
<tr>
<td>Anxiolytics</td>
<td>Fluphenazine</td>
</tr>
<tr>
<td></td>
<td>Flupentixol</td>
</tr>
<tr>
<td></td>
<td>Haloperidol</td>
</tr>
<tr>
<td></td>
<td>Buspiron</td>
</tr>
<tr>
<td></td>
<td>Alprazolam</td>
</tr>
<tr>
<td></td>
<td>Trifluoperazine</td>
</tr>
<tr>
<td>Vitamin B6</td>
<td>Pyrodoxine</td>
</tr>
<tr>
<td></td>
<td>Pyridoxal</td>
</tr>
<tr>
<td></td>
<td>Pyrdoxamine</td>
</tr>
<tr>
<td>Vitamin D</td>
<td>Cholecalciferol</td>
</tr>
<tr>
<td></td>
<td>Dyhydrotachysterol</td>
</tr>
<tr>
<td></td>
<td>Ergocalciferol</td>
</tr>
<tr>
<td></td>
<td>Alfacalcidol</td>
</tr>
<tr>
<td>Vitamin E</td>
<td>d-alpha Tocopherol</td>
</tr>
<tr>
<td>Opioid Analgesics</td>
<td>Buprenorine</td>
</tr>
<tr>
<td></td>
<td>Levorphanol</td>
</tr>
<tr>
<td></td>
<td>Phenoperidine</td>
</tr>
<tr>
<td></td>
<td>Fentanyl</td>
</tr>
<tr>
<td></td>
<td>Methadone</td>
</tr>
<tr>
<td>Non-Opioid Analgesics</td>
<td>Mefanamic Acids</td>
</tr>
<tr>
<td>Antiviral</td>
<td>Acyclovir</td>
</tr>
<tr>
<td></td>
<td>Vidarabine</td>
</tr>
<tr>
<td></td>
<td>Arildone</td>
</tr>
<tr>
<td></td>
<td>Idoxuridine</td>
</tr>
<tr>
<td></td>
<td>Cestrinone</td>
</tr>
<tr>
<td></td>
<td>Mifepristone</td>
</tr>
<tr>
<td>Antifungal</td>
<td>Clotrimazole</td>
</tr>
<tr>
<td></td>
<td>Enconazole</td>
</tr>
<tr>
<td></td>
<td>Itraconazole</td>
</tr>
<tr>
<td></td>
<td>Metronidazole</td>
</tr>
</tbody>
</table>
Rate Enhancing Additives

Silicone polymers are relatively hydrophobic and it’s thought the list of compounds below can increase the rate of release. The typical amount by weight added to the elastomer system is cited at 5 to 20%.

<table>
<thead>
<tr>
<th>Rate Enhancing Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acid esters –</td>
</tr>
<tr>
<td>Isopropyl myristate</td>
</tr>
<tr>
<td>Caproic acid</td>
</tr>
<tr>
<td>Lauric acid</td>
</tr>
<tr>
<td>Oleic acid</td>
</tr>
<tr>
<td>Linoleic acid</td>
</tr>
<tr>
<td>Adipic acid</td>
</tr>
<tr>
<td>Lanolic acids</td>
</tr>
</tbody>
</table>

NuSil Technology / Drug Delivery

NuSil Technology is actively involved in the development of custom materials for the drug delivery industry. Our customers range in size from Fortune 500 to start-up ventures. NuSil’s focus on silicone materials and chemistry can help customers prototype devices quickly. We have worked extensively with major pharmaceutical customers to supply materials for several commercially successful drug delivery devices on the market today.

Please contact a NuSil Technology technical sales representative regarding additional resources on silicone’s use in drug delivery applications at 805-684-8780.
References

Transdermal Drug Delivery:


(2) Studen, J.R., Method and Composition for the Treatment of Scars. U.S. Patent 6,337,076

Implanted Drug Delivery Devices:

(3) Segal, M., Patches, Pumps, and Timed Release FDA Consumer (October 1991)

(4) DiCosmo, F. and Ditizio and Valerio Drug Delivery via Therapeutic Hydrogels U.S. Patent 6,228,393

Transmucosal Drug Delivery Devices:


(7) Nabahi, Shorhe Intravaginal Drug Delivery Device U.S. Patent 6,039,968


(9) McClay A Intravaginal Drug Delivery Devices for the Administration of 17.bets.-oestradiol Precursors U.S. Patent Number 5,855,906

(10) Zimmerman I, Windt F, Reck HJ Vaginal Ring U.S. Patent 4,822,616

(11) Passmore C, Gilligan C Intravaginal Drug Delivery for the Administration of Testosterone and Testosterone Precursors U.S. Patent 6,416,780

(12) Nabahi, Shorhe Intravaginal Drug Delivery Device U.S. Patent 6,103,256

(13) Nabahi, Shorhe Intravaginal Drug Delivery Device U.S. Patent 5,788,980

(14) Saleh SI, Nash HA, Bardin WC, Harmon T Intravaginal Rings with Insertable Drug Containing Core U.S. Patent 6,126,958
Warnings About Product Safety:

NuSil Technology believes that the information and data contained herein is accurate and reliable; however, it is the user’s responsibility to determine suitability and safety of use for these materials. NuSil Technology can not know the specific requirements of each application and hereby makes the user aware that it has not tested or determined that these materials are suitable or safe for any application. It is the user’s responsibility to adequately test and determine the safety and suitability for their application and NuSil Technology makes no warranty concerning fitness for any use or purpose. There has been no testing done by NuSil Technology to establish safety of use in any medical application.

NuSil Technology has tested its materials only to determine if the product meets the applicable specifications. (Please contact NuSil Technology for assistance and recommendations when establishing specifications.) When considering the use of NuSil Technology products in a particular application, you should review the latest Material Safety Data Sheets and contact NuSil Technology for any questions about product safety information you may have.

No chemical should be used in a food, drug, cosmetic, or medical application or process until you have determined the safety and legality of the use. It is the responsibility of the user to meet the requirements of the U.S. Food and Drug Administration (FDA) and any other regulatory agencies. Before handling any other materials mentioned in the text, you should obtain available product safety information and take the necessary steps to ensure safety of use.

Patent Warning:

NuSil Technology disclaims any expressed or implied warranty against the infringement of any patent. NuSil Technology does not warrant that the use or sale of the products described herein will not infringe the claims of any United States patents or other country’s patents covering the product itself or the use in combination with other products or in the operation of any process.
Understanding the Role of Silicones in Controlled Release Applications

Nathan Wolfe, Technical Sales
Alex Kurnellas, Technical Writer

As one of the most widely researched biomaterials to date, silicone has an approximate 50-year legacy of use in the healthcare industry. This history of biocompatibility has made silicone a material of choice for both long and short-term implantable device applications. The last twenty years have seen the emergence of targeted release and combination product applications. These technologies evolved as the result of pharmaceutical and medical device manufacturers seeking novel ways to achieve their therapies. So, raw materials that were formerly chosen for their performance capabilities in medical device applications are now tasked with maintaining those requirements but also with meeting a host of new performance expectations that are specific to drug delivery applications. Faced with these new challenges few raw materials have succeeded in transitioning quite as well as silicone. This is because silicones possess certain dynamic characteristics which allow them to be compounded in with a host of actives. These same unique characteristics also allow them to release those actives from a molded/extruded device in a predictable way – whether that application is for transdermal, transmucosal, short or long-term human implantation. This article will highlight key attributes of certain silicones as well as key considerations when selecting a silicone.

When designing a drug delivery application with silicone, the first question to be answered relates to the product’s basic design. Generally speaking there are two configurations to choose from: matrix and reservoir.

A matrix design is where the active is mixed homogenously into the silicone and then molded, extruded, etc. into the desired geometry. A good example of this might be a central venous catheter impregnated with actives intended to combat infection.

Reservoir configurations are the other primary device design. A reservoir device is one where an active is concentrated in a void in the center of a molded silicone part. A good example of this would be several early-generation contraceptive devices that were implanted just under the skin; small silicone tubes were molded or extruded, cured, filled with active and then sealed with silicone adhesives.

It’s important to understand the impact that the design of a part or device has on how the active will be
released. Generally speaking, matrix designs release the most active initially and then the release rate tapers off whereas reservoir devices will exhibit an initial spike and then normalize into a lower but consistent release rate.

If it is decided that a matrix design is ideal, there are a number of considerations that must be evaluated. The first order of business is to establish that the active in question is appropriately soluble in silicone. As most silicones are hydrophobic in nature it is important to either know or establish the extent to which the active in question is hydrophobic/lipophilic. If an active is extremely polar and, subsequently, hydrophilic, it will not readily dissolve into most traditional silicone formulations. As a direct result of insolubility a matrix design would no longer be an option.

Once solubility is established the next question has to do with how one wishes to process the part/device in question. If the design relies upon heat curing the molded or extruded silicone part then the matrix design may not be an option if the active in question is heat sensitive. Here again, understanding the chemical characteristics of the API is key and the specific temperature threshold must be determined. Perhaps the desire is to mold a matrix design and the drug is found to be robust relative to temperature, there still remains the potential that the platinum catalyzed, heat accelerated silicone will be inhibited by the active in question; it has been observed that some actives common to combination products are chemically very similar to an inhibitor often used to control the work time (pot life) of platinum systems. This can result in excessive work times or even failure of a part to cure. In such instances one option is to mold with rapidly curing moisture sensitive cure chemistries. However, it’s important to note that these concerns are specific to matrix designs and not reservoir.

All this having been said, it’s understandable to wonder how an active moves, (or diffuses) through a cured silicone medium at all. To better understand this phenomenon it is necessary to cover some basics of silicone chemistry.

To start with, silicone is an inorganic polymer, having no carbon atoms in its backbone. However, because the pendant groups off this backbone do contain carbon atoms it is fair to classify silicone as an “organo-polysiloxane”. It is these organic pendant groups that make silicone hydrophobic. A typical silicone polymer structure is shown below.
The constituent if the polymer is functional or non-functional. If a polymer only contains non-functional pendant groups (methyl, fluoro and/or phenyl), the polymer is essentially nonreactive, not easily crosslinked and generally only used as a fluid. While non-functional silicone fluids can be used as excipients to facilitate the diffusivity and ultimate elution of certain APIs through a device or part molded from a silicone elastomer, this article limits its scope to drug delivery applications relying simply on curable silicone chemistry.

Accordingly a closer look will now be taken at silicone gels, liquid silicone rubber elastomers (LSRs) and high consistency rubber elastomers (HCRs).

Silicone gels are polymers – similar to fluids – except that they contain reactive groups, which allow the polymers to crosslink. Because the degree of crosslinking (or crosslink density) tends to be minimal and because these materials tend to have little or no filler (silica, resin, diatomaceous earth, etc.) silicone gels cure into a soft and compliant gel-like rubber. Typical applications include tissue simulation.

Liquid silicone rubbers, or LSR’s, are elastomers containing medium viscosity polymers and moderate amounts of silica. They tend to have an uncured consistency like that of petroleum jelly and the cured elastomers have good physical properties. These materials can be molded into parts and require the use of liquid injection molding equipment.

High consistency elastomers typically contain high viscosity polymers and sometimes contain higher levels of reinforcing silica. These materials are clay-like in consistency in their uncured state, and offer good physical properties when vulcanized. High consistency materials can be molded into parts by compression or transfer molding and are most commonly used for extrusion to yield tubing configurations.

All of the above silicons rely upon the same basic repeating siloxane polymer and for each the pendant groups may be customized. Gels are loosely crosslinked, with little or no filler. LSRs have more crosslinking and more filler. Lastly, HCRs, are basically the same as LSRs except their polymers are of a much higher molecular weight.

Due to the fact that all of the above rely on the same basic siloxane polymer they all benefit from a unique characteristic that is inherent to these polymers – a lot of empty space. Specifically, the large atomic volume of the silicon atom, as well as the size and position of the applicable pendant groups, result in bond angles that yield a high degree of free volume. This free volume then provides what may be considered “microporous pathways” for liquids and gasses (including water vapor) to migrate through a cured silicone medium.

Now that the means by which actives can move through silicone have been established, a closer look will be taken at the factors that control their diffusivity and rate of release. While we’ve talked briefly about how matrix and reservoir designs impact release rates, there are other factors to be considered in how an active will move throughout a cured silicone system and release into or onto the body. When considering diffusivity, one must realize that variables associated with both the active and the silicone medium have a part to play. On a very basic level the molecular weight and/or the molecular volume (or spatial dimensions) of an active will have an impact on how readily it migrates through a cured silicone. The bulkier the molecule the slower the progress. Similarly, the amount of crosslinking that a given silicone formula provides will impact diffusion and release. The more
functional groups on the polymer (and often the lower the molecular weight of the polymer) will yield a greater crosslink density and, in effect a denser web through which to pass.

Then there are also filler levels to consider. Silicone elastomers are most commonly filled with silica, which provides the mechanical, rubber-like strength of an elastomer, as opposed to the soft and easily torn consistency of a silicone gel. The greater the loading of a reinforcing filler, such as silica, the greater the steric hindrance to slow down the active. However, it’s not simply the steric hindrance of the reinforcing filler; the pendant groups coming off the backbone of the polymers themselves will also impact the progress of an active. Moreover, very large groups such as diphenyl, will provide a much greater degree of hindrance than smaller groups such as dimethyl. Lastly, there is the polarity of the pendant groups versus the polarity of the active to be considered. Slight inconsistencies in polarity may result in further slowing of the active through the silicone.

All of the above variables may be controlled through custom formulation to optimize the diffusivity and permeability of an active through a silicone.

Silicones are well established as the elastomeric biomaterials of choice for long-term implants, and are also ideal for use as platforms for drug delivery. As indicated above, a host of APIs are soluble in silicones. Additionally, the material’s inherent microporous structure provides a means of transporting soluble APIs through the cured material and delivering them to their targeted location. Lastly, silicone chemistry offers a variety of methods by which to control permeation and elution rates. Taken as a whole, these characteristics distinguish silicone as a versatile raw material that is tailor-made to facilitate the needs of the emerging targeted-release and combination product markets.
Recent Developments in Ultra Low Outgassing™ Silicones for Space Applications

Bill Riegler(1), Brian Burkitt(2), Vincent Malave(3), Roy Johnson(4), and Rob Thomaier(5)

NuSil Technology, Product Director – Engineering Materials, 1050 Cindy Lane, Carpinteria, CA 93013, USA,
+1.805.684.8780, billr@nusil.com

(2) NuSil Technology, Technical Sales Supervisor
(3) NuSil Technology, Technical Sales
(4) NuSil Technology, Chemist
(5) NuSil Technology, Research Director

Presented at the 11th Japan International SAMPE Conference (JISSE-11)
November 25-27, 2009, Tokyo, JAPAN
ABSTRACT

On spacecraft, silicones are imperative materials for use as protective coatings, encapsulants, adhesives, and sealants. Silicones also provide broad operating temperature ranges and are excellent materials for CTE mismatch in bonding applications. Nonetheless, there is concern that silicones may contribute to contamination of sensitive equipment when exposed to harsh environments and vacuum conditions. Contamination from polymeric materials usually results from outgassing of low molecular polymers not crosslinked into the polymer matrix. Subsequently, these contaminants may condensate on nearby surfaces during thermal cycling.

Controlled volatility silicones formulated to reduce the levels of outgassed materials have been in use for decades. These materials are required to meet standards set by NASA and the European Space Agency (ESA), including <1 % Total Mass Loss (TML) and <0.1 % Collected Volatile Condensable Material (CVCM) in accordance with ASTM E 595. However, many skeptics feel these regulations are outdated and may not be stringent enough. In response to this criticism and concern, NuSil developed a line of Ultra Low Outgassing™ silicones. These new materials achieve TMLs ≤ 0.1% and CVCM ≤ 0.01%. NuSil recently expanded this line, by developing two ultra low outgassing silicone elastomers with improved physical properties: SCV-2585 and Developmental Material LSR2-9860-30 (a microballoon and iron oxide filled version of SCV-2585). In this study, these 2-part, platinum cure, RTV silicones are compared to standard low outgassing materials, CV-2289 and CV10-2568. The physical properties are compared looking for any property losses, and the TML’s and CVCM’s are compared and analyzed according to ASTM E 595 standards and the outgassing kinetics from ASTM 1559 experiments. This paper is the effort of ongoing work based on the SAMPE Japan 2007 ‘Best Paper Award’, “Ultra Low Outgassing™ Silicone Materials”.

1. INTRODUCTION

1.1 Situation Background and Overview of Contents

With the large amounts of adhesive/sealants currently utilized on spacecraft, manufacturers must pay close attention to the materials’ outgassing levels and carefully monitor their cumulative contaminant levels. Selecting a material with outgassing levels that exceed the industry standard of ≤ 1 % TML and ≤ 0.1% CVCM could prove beneficial for many reasons. For instance, by employing materials with lower outgassing levels manufacturers could use more of a material when necessary for mechanical reasons or as required by production techniques. An Ultra Low Outgassing™ material keeps processing time down as no additional conditioning is required to achieve the desired outgassing values, nor are the physical properties altered in the conditioning. In addition, if device contamination is based on cumulative contaminant levels from all material within the device’s vicinity, using a material with exceptionally low levels of outgassing could allow use of other materials with higher outgassing levels in the same vicinity.

An exemplary potential application for using Ultra Low Outgassing™ materials can be found in solar cell arrays. The lower outgassing level produces lower contamination, subsequently producing a potential more efficient solar cell by extending the life of a cell, especially in Low Earth Orbit (LEO) where equipment is exposed to the detrimental effects of molecular oxygen. The spacecraft could potentially last longer in space, therefore displacing the huge cost to build and transport spacecraft over longer periods of time.

In recent years, the industry need for lower levels of outgassing led to the development of several silicone material systems that exceed the standard criteria for outgassing and meet the Ultra Low Outgassing™ requirements of ≤ 0.1 % TML and ≤ 0.01 % CVCM. Originally, these materials were all resin-reinforced silicone elastomers. While silica-reinforced systems generally have improved physical properties over resin-reinforced systems, silica contains a volatile component and chemists were initially unable to develop a silica-reinforced material that met the Ultra Low Outgassing™ requirements. Extensive research and development provided SCV-2585, the first silica-reinforced Ultra Low Outgassing™ silicone system. This report compares the cured physical properties of a standard silica filled, low outgassing material, CV-2289, with SCV-2585. CV-2289, like all CV- materials, meets the NASA standard of <1% TML and <0.1% CVCM. The outgassing profiles of each material based on ASTM E 1559 test method are examined in detail.

The next hurdle to jump was incorporating “fillers” into the silica-reinforced Ultra Low Outgassing™ silicone system. Iron oxide is a common “filler” incorporated into material systems because it aids in thermal stability and has a long
space flight heritage. One issue with filling a material with iron oxide is that iron oxide significantly increases the material’s specific gravity. Subsequently, a “filler package” utilizing iron oxide and microballoons is incorporated into materials. The microballoons not only offset the increase in specific gravity from the iron oxide, but reduce the material’s specific gravity to less than that of the unfilled material.

To date, CV10-2568 is a widely used low outgas silicone material for space applications offered by NuSil Technology. It incorporates the iron oxide/microballoon filler and is an ideal material for bonding, sealing, or potting due to its silica-reinforcement and subsequent mechanical properties. This includes low density and low modulus for CTE mismatch and excellent thermal stability over a broad operating temperature range required for materials used in extreme environments such as space, where thermal temperatures can range from -115°C to 300°C.

Nevertheless, a low modulus silica reinforced, iron oxide and microballoon elastomeric silicone that meets Ultra Low Outgassing™ requirements has not previously been achieved. This report compares the cured physical properties of the CV10-2568 with a comparable Ultra Low Outgassing™ developmental iron oxide and microballoon filled silicone elastomer, LSR2-9860-30. The outgassing profiles of each material based on ASTM E 1559 test method are examined in detail.

2. EXPERIMENTATION

Table 1. List of material samples used and their basic chemical makeup.

<table>
<thead>
<tr>
<th>SILICONE PROPERTY</th>
<th>CV-2289</th>
<th>SCV-2585</th>
<th>CV10-2568</th>
<th>LSR2-9860-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>SILICONE POLYMER</td>
<td>DIPHENYL-DIMETHYL</td>
<td>DIPHENYL-DIMETHYL</td>
<td>DIPHENYL-DIMETHYL</td>
<td>DIPHENYL-DIMETHYL</td>
</tr>
<tr>
<td>CURE MECHANISM</td>
<td>2-PART ADDITION CURE</td>
<td>2-PART ADDITION CURE</td>
<td>2-PART ADDITION CURE</td>
<td>2-PART ADDITION CURE</td>
</tr>
<tr>
<td>Mix ratio (A:B)</td>
<td>(1:1)</td>
<td>(1:1)</td>
<td>(1:1)</td>
<td>(1:1)</td>
</tr>
<tr>
<td>REINFORCING FILLER</td>
<td>SILICA</td>
<td>SILICA</td>
<td>SILICA</td>
<td>SILICA</td>
</tr>
</tbody>
</table>

2.1 Materials

Table 1. List of the materials that are compared in this study.

2.1.1 Processing for Controlled Volatility

The critical contaminating species typically outgassed from silicone materials are primarily caused by the low to middle molecular weight silicone cyclics and polymers that are not covalently bonded into the silicone matrix. These species are eliminated in NuSil CV materials to prevent subsequent outgassing and contamination.

A refinement process can remove low to middle molecular weight linear and cyclics from the polymer formed during the polymerization process. To produce the Ultra Low Outgassing™ materials, SCV-, extensive processing time is needed to achieve lower levels.
2.2 Methods

2.2.1 ASTM E 595

This test method is used to determine the volatile content of materials when exposed to a vacuum environment (i.e. space). The two parameters measured are TML and CVCM. Water vapor recovery (WVR) is an additional parameter that can also be obtained after the completion of the exposures and measurements required for TML and CVCM.

2.2.2 ASTM E 595 Test Parameters

Each material sample is preconditioned at 50 % relative humidity and ambient atmosphere for 24 hours. The sample is weighed and loaded into the test chamber within the ASTM E 595 test stand. The sample is then heated to 125°C and vacuum is pulled to less than 5x10^{-3} torr. These conditions are held for 24 hours. The volatiles that outgas under these conditions escape through an exit port, and condense on a collector plate maintained at 25 C. Once the test is complete, the samples are removed from the chamber and the collector plate and samples are then weighed.

2.2.3 Data Analysis

The CVCM is the quantity of material outgassed from the sample that condenses on the condenser plate and is presented as a percentage calculated from the difference in mass on the collector plate before and after the test. The percent TML, the percent total mass of the material outgassed from the initial sample is calculated from the mass of the sample measured before and after the test.

After the specimen is weighed to determine the TML, the WVR can be determined. The specimen is stored at 50% humidity for 24 hours at 25°C to permit sorption of water vapor. The specimen is then weighed again which is then subtracted by the mass determined after vacuum exposure to obtain the WVR.

2.2.4 ASTM E 1559

OSI laboratories conducted ASTM E1559 experiments and provided test reports. The isothermal outgassing test apparatus is explained in detail by Garret et al. and will only be discussed here briefly. The material sample can range from 0.5 g to 10 g and is placed in a temperature-controlled effusion cell in a vacuum chamber. All samples are preconditioned in accordance with ASTM E 595 unless otherwise specified.

Outgassing flux leaving the effusion cell orifice condenses on four Quartz Crystal Microbalances (QCMs) that are controlled at selected temperatures. The QCMs and effusion cell are surrounded by liquid nitrogen shrouds to ensure the molecular flux impinging on the QCMs is due only to the sample in the effusion cell. The TML and outgassing rate from the sample are determined as functions of time from the mass deposited on an 80 K QCM and normalized with respect to the initial mass of the sample.

The amount of condensable outgassing species (VCM), is measured as a function of time from the mass collected on the 298 K QCM. After the outgassing test is complete, the QCMs are then heated to 398 K at a rate of 1K/min. As the QCM heats the deposited material evaporates. The species that evaporate can be analyzed by a quadruple mass spectrometer to quantitatively determine the species observed.

2.2.4.1 ASTM E 1559 Sample Preparation

The CV-2289 and SCV-2585 samples were cured at 150°C for 15 minutes into discs 1.49 inches in diameter by 0.125 inches thick. CV10-2568 and LSR2-98960-30 were cured at 150°C for 30 minutes into discs. The surface area is calculated for both faces and the edge of the disc.

One of the supplied discs of material was placed in the effusion cell as the test sample. The samples were tested with no additional preconditioning.

2.2.4.2 Test Parameters

The following parameters were set for each sample:
2.2.5 Data Analysis

2.2.5.1 Outgassing Rate

The outgassing rates for species condensable on the warmer QCMs can be calculated from curve fits to the data. The total outgassing rate from the 80 K QCM then can be compared to the outgassing rates for species condensable on the warmer QCMs to determine the rates of very high volatility species (water and solvents) and the rates of the remaining species (high, medium, and low volatility).

3. RESULTS AND DISCUSSION

3.1 Comparison of Physical Properties

In Table 2 the results for the typical material properties for each sample were measured according to ASTM protocols, are listed and compared. These properties were measured at NuSil Technology.

Table 2. Typical Physical Properties Evaluated for Silicone Elastomers

<table>
<thead>
<tr>
<th>ASTM</th>
<th>Typical Property</th>
<th>CV-2289</th>
<th>SCV-2585</th>
<th>CV10-2568</th>
<th>LSR2-9860-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncured</td>
<td>Viscosity, cP</td>
<td>50,000</td>
<td>50,000</td>
<td>102,000</td>
<td>300,000</td>
</tr>
<tr>
<td></td>
<td>Worktime, hrs</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Cured</td>
<td>Cure Time</td>
<td>15min @ 150°C</td>
<td>15min @ 150°C</td>
<td>30min @ 150°C</td>
<td>30min @ 150°C</td>
</tr>
<tr>
<td></td>
<td>Specific Gravity</td>
<td></td>
<td></td>
<td></td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Durometer, Type A</td>
<td>30</td>
<td>36</td>
<td>40</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Tensile, psi</td>
<td>650</td>
<td>650</td>
<td>235</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>Elongation, %</td>
<td>350</td>
<td>300</td>
<td>170</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>Lap Shear, psi</td>
<td>525</td>
<td>500</td>
<td>175</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>% TML</td>
<td>0.52</td>
<td>0.06</td>
<td>0.54</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>% CVCM</td>
<td>0.05</td>
<td>0.01</td>
<td>0.06</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>% WVR</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
</tbody>
</table>
3.2 % Total Mass Loss

3.2.1 Comparison of % TML from ASTM E 595 and %TML at the end of the ASTM E 1559 Test

The %TML of each sample for the results obtained from ASTM E595 is compared to the results obtained from ASTM E1559.

![Comparison of % TML for each sample from ASTM E 595 and ASTM E 1559 at the end of the test.](image)

Fig. 1: Comparison of % TML for each sample from ASTM E 595 and ASTM E 1559 at the end of the test.

3.2.2 % TML ASTM E 1559

3.2.2.1 Amount of TML Due to Different Outgassed Species

The volatility of a material is directly related to its molecular weight (MW): the lower the molecular weight, the higher the volatility, and vice versa. Molecular weight ranges for the species in the different volatility categories can be estimated based upon engineering experience related to species condensability and mass spectrometer data. The "extremely low molecular weight" group of species in Table 3 is primarily due to water and solvents, highly volatile materials. The "low molecular weight" species most likely have molecular weights of 50 to 200 amu, the "medium molecular weight" species fall in the 200 to 400 amu range, and the "high molecular weight" species have estimated molecular weights above 400 amu and are the least volatile of all the species.

Table 3. Cumulative Amounts of Estimated Volatility of Different Outgassed Species

<table>
<thead>
<tr>
<th>ASTM E 1559</th>
<th>% TML at end of test</th>
<th>Extreme low MW</th>
<th>Low MW</th>
<th>Medium MW</th>
<th>High MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone Material</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CV-2289</td>
<td>0.43 100%</td>
<td>0.09</td>
<td>0.19</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td>SCV-2585</td>
<td>0.08 100%</td>
<td>0.076</td>
<td>0.00</td>
<td>0.0031</td>
<td>0.00091</td>
</tr>
<tr>
<td>CV10-2568</td>
<td>0.30 100%</td>
<td>0.10</td>
<td>0.12</td>
<td>0.07</td>
<td>0.006</td>
</tr>
<tr>
<td>LSR2-9860-30</td>
<td>0.07 100%</td>
<td>0.06</td>
<td>0.006</td>
<td>0.008</td>
<td>0.0005</td>
</tr>
</tbody>
</table>
3.2.3 **Total Mass Loss as a Function of Test Time**

Fig. 2 & 3 is a plot of the TML of each sample over the 72 hour period. After the initial loss and compared to CV-2289 & CV10-2568 respectively, the *Ultra Low Outgassing*™ materials, SCV-2585 & LSR2-9860-30, show relatively no mass loss over the entire course of the experiment.

**Figure 2: Total Mass Loss of CV-2289, SCV-2585 as a function of time**

**Figure 3. Total Mass Loss of CV10-2568 and LSR2-9869-30 as a function of time**

3.3 **% Volatile Condensable Material (ASTM E 1559)**

Figures 4 & 5 are plots of the volatile condensable material from the 298 QCM as a function of time.
Fig. 4 & 5. Volatile Condensable Materials from CV-2289 & SCV-2585, CV10-2568, & LSR2-9860-30 condensed on the 298 K QCM

3.4 Comparison of the Total Outgassing Rate as a Function of Time

Fig. 6 & 7 shows the total outgassing rate data as a function of test time for CV-2289, SCV-2585, CV10-2568, & LSR2-9860-30. These outgassing rates are for species condensable at 80 K and thus would not include certain gases such as nitrogen and oxygen.
3.3 Desorption Rate at 80 K QCM

The QTGA test data can be used to determine the relative amounts of the species outgassed. Recall that at the conclusion of the isothermal outgassing test, the 80 K QCM is heated at increments of 1K/min while the outgassed species that deposit on the surface evaporate from the crystal. As the temperature of the QCM is increased during QTGA, the collected species will evaporate from the QCM in order of their relative volatilities. As the temperature of the QCM increases, the evaporation rate of the species also increases until it reaches a peak. The slope of the leading edge is characteristic of the species being volatilized. In Fig. 8 & 9, the QTGA data for all materials are plotted together as evaporation rate from the QCM as a function of QCM temperature.
**QTGA Data:** Evaporation Rate from the 80 K QCM of the Collected Outgassed Material as a Function of QCM Temperature

![Graph 1](image1)

![Graph 2](image2)

Fig. 8 & 9. QTGA Data: Evaporation Rate from the 80 K QCM of the Collected Outgassed Material as a Function of QCM Temperature
4. Conclusions

As devices and processes become more advanced and sensitive to molecular contamination, more details of characterization of the construction materials must be obtained. Ultra Low Outgassing™ specification requirements of ≤ 0.1% TML and ≤ 0.01% CVCM can be useful in the overall management of outgassing species. The results from kinetic outgassing data allow engineers to better predict the levels of contamination, migration, and deposition once the materials are in space. Achieving these lower levels does not compromise physical properties and thus a broad range of silicone elastomers with unique and specific properties can be developed. We have shown that the addition of unique filler packages such as iron oxide and microballoons do not change the outgassing kinetics.

5. REFERENCES

4. OSI Labs

5.1 Biography

Bill Riegler is the General Manager Asia for NuSil Technology, the eighth largest silicone manufacturer in the world. Bill has been in the silicone industry for almost twenty five years with various positions at NuSil and the silicone division of Union Carbide, which became the OSi Specialties Group of GE Silicones, now Momentive.

Bill has a B.S. in Chemistry from the University of California at Santa Barbara and a Masters in Business from Pepperdine University.

He began his career in Research and Development and held several technical sales positions before managing NuSil’s domestic technical sales force & Engineering Materials Product Line. Bill is now directing NuSil’s worldwide efforts into Asia for Healthcare & Engineering Materials, which includes the Aerospace, Photonics and Electronics Industries.
A Silicone-Based Ice-Phobic Coating for Aircraft

Summer L. Sivas, Ph.D., Technical Specialist,
Bill Riegler, Product Director-Engineering Materials,
Rob Thomaier, R&D Director,
NuSil Technology LLC, Carpinteria, CA., U.S.
Kelly Hoover, Senior Engineer, Pratt & Whitney, East Hartford, CT., U.S.

ABSTRACT

The problem of ice build-up in an engine or on the leading edges of a plane is a significant problem in the aircraft industry. Ice build up can affect many aspects of flying such as lift, drag, and thrust. Under the direction of Pratt & Whitney in 2004, the Department of the Army, Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, NH, U.S, performed adhesion strength tests designed to measure the adhesion strength of ice to several different commercially available ice-phobic coatings. The results show that the silicone material, R-2180, dropped the adhesion strength by a factor of 40 over bare steel and aluminum surfaces. These results were the lowest mean failure stress that CRREL has ever seen at 37 kPa while Teflon was previously the lowest tested value measured at 238 kPa.

Key words: Silicone coating, ice-phobic coating, de-icing

1. INTRODUCTION

1.1 Background. Ice control is a significant and practical concern spanning over many industries. To address these issues the U.S. Army Corps of Engineers of the Department of the Army has written a twenty-chapter manual to provide guidance in this area.1 Titled Ice Engineering, this manual covers ice buildup on lock walls, hydropower intakes, navigation channels, hydraulic systems, etc. Ice engineering is not only a structural engineering concern in cold regions but also a major area of significance in the aircraft industry affecting many aspects of flying. For instance, when ice builds up on the wings or leading edges of airplanes it may decrease lift and increase drag. In fact, wind tunnel tests have shown that very thin ice sheets can reduce lift by as much as 30% and drag by 40%.2 These consequences of ice build-up are extremely hazardous and may occur during any season, anywhere in the country. In order to avoid hazardous situations the Federal Aviation Administration (FAA) has administered Airworthiness Directives (Ads), like Docket # FAA-2004-19078, that identifies the limitations of certain commercial aircraft to icing problems.

Controlling ice from building up on static surfaces is not a trivial task. There are multiple ways to control ice build up on an aircraft and often more than one is used for maximum benefit. The most effective approach is to keep the temperature of the surface above 0°C. Often times the aircrafts are stored in heated hangars or heaters are built into areas where ice tends to form. Chemicals such as derivatives of glycol ethers have also been used to de-ice aircrafts, as they effectively lower the freezing point. Recently, however, Canada has banned 2-methoxyethanol as a de-icing chemical because of environmental concerns.3 Unfortunately, both these solutions are costly and impractical in many situations.
An ideal and more economical de-icing solution would be to apply a material that prevents ice from building in the first place rather than taking it off after the fact. However, this is a difficult undertaking considering that the adhesion strength of the ice must be less than the shear stress that the ice exerts on the substrate. In general terms adhesion is defined as the physical and chemical bonding of two substrates. Substrates that have reactive groups available for bonding like OH or C=O groups on glass, plastics, and aluminum make this chemical attraction greater through van der Waals forces or weak hydrogen attraction. Substrates with limited available bonding sites make adhesion difficult, such as Acetal, Nylon 24, or PTFE. Numerous other substrates fit somewhere in-between. Currently there are many materials commercially available and marketed as ice-phobic. Many of these materials have been tested and ranked by the 1998 study by Haehnel and Mulherin. More recently, another round of materials were tested and reported in Laboratory Ice Adhesion Test Results for Commercial Icephobic Coatings for Pratt & Whitney at CRREL, including a silicone coating from NuSil Technology, LLC.

1.2 Silicone Chemistry. Silicone, or more appropriately named ‘Polyorganosiloxanes’, are over sixty years old. The diagram below shows a typical structure, Figure 1, where the R groups represent functional organic constituent groups such as methyl, phenyl or trifluoropropyl.

Silicones have very unique properties compared to organic based rubbers. Their ability to remain elastic at low temperatures and resistance to breakdown at high temperatures make its use valuable in harsh environments. The typical glass transition point (Tg) of many silicones is less than -115 °C. Other properties silicone offers are low modulus, resistance to moisture (< 0.4 %), high dielectric strength of 500 V/mil, low shrinkage (< 1%), low ionic content (< 20 ppm) and formulation flexibility.

Unlike one-part moisture cure silicone adhesives, this mechanism involves no leaving group allowing these systems to cure in closed environments. Most platinum systems can fully cure at room temperature in twenty-four hours, or the cure can be accelerated with heat.

2. EXPERIMENTAL

Twelve replicates each of six different ice-phobic coatings were spray applied to aluminum test piles. The tested coatings are given in Table 1. Each sample was rinsed at least two times with isopropyl alcohol except for the Microphase Coatings, Cary, NC based on the companies recommendation prior to ice adhesion tests.

<table>
<thead>
<tr>
<th>Table 1:</th>
<th>Sample Name</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>MegaGuard LiquiCote</td>
<td>KissCote, Inc</td>
<td>Microphase Coatings</td>
</tr>
<tr>
<td>Phasebreak B-2</td>
<td>Microphase Coatings</td>
<td></td>
</tr>
<tr>
<td>ESL</td>
<td>S&amp;A Fernandina, Inc.</td>
<td></td>
</tr>
<tr>
<td>RIP-4004</td>
<td>21st Century</td>
<td></td>
</tr>
<tr>
<td>Urethane-51PC951</td>
<td>NuSil Technology</td>
<td></td>
</tr>
</tbody>
</table>
The adhesion strengths of listed ice-phobic coatings were tested and compared using a CRREL developed test method to measure the bond strength of ice to a substrate adapted from the Zero-Degree Cone Test for adhesive joints. A schematic of the test stand is shown in Figure 3. Ice is grown in a gap between two concentric, cylindrical surfaces. The force required to push the inner cylinder out of the ice collar is measured determining the adhesive strength. An O-ring placed at the bottom of the inner cylinder, keeps any water from leaking out while it is freezing. The samples are frozen for eight hours at -10°C and allowed to rest for another 40 hours. The samples are then tested on the equipment with a constant rate of 0.06 mm/min until the ice adhesion fails.

![Zero-Degree cone test configuration](image)

**Figure 3.** Zero-Degree cone test configuration (left) and instrumental sample pile and mold in testing machine (right).

### 4. RESULTS AND DISCUSSION

Laboratory Ice Adhesion test results for commercial ice-phobic coatings, Table 1, were tested for Pratt & Whitney. These materials include: MegaGuard LiquiCote; Phasebreak B-2; Microphase ESL; RIP-4004, 51PC951; and R-2180. Load-displacement plots for each test performed were collected and are available with the CRREL report. Figure 5 summarizes these results. The Y-axis describes the shear stress required for ice release, the value that is calculated from the measured maximum load required to remove the ice from the surface. The mean and standard deviation were derived from 12 replicates. The error bars indicate the range in stress values for each group of samples.

Prior to this study, Teflon consistently expressed the lowest failure values of 238 kPa. However, it is apparent that the silicone polymer, R-2180, demonstrates the least amount of nominal stress of 37 kPa compared to the other commercially available icephobic coatings tested. Phasebreak B2 and ESL also had low adhesion strength at 117 and 295 kPa respectively. However, both coatings show high variability and standard deviation. These discrepancies are associated with
the observation that the ice was in various states of solidification. It was observed in the CRREL report that several of the replicates from both Phasebreak B-2 and ESL had observable traces of unfrozen water on the top and bottom of the samples. These materials are suspect to inconsistencies due to solutes leaching from the coatings into the water that lower the freezing point of the surrounding water. It would be valuable to determine if these coatings would stabilize if the tests were conducted under conditions where the ice completely freezes at lower temperatures.

![Ice Adhesion Test Data](image)

**Figure 4:** Laboratory Ice Adhesion test Results for Commercial Ice-phobic Coatings for Pratt & Whitney, May 2004, CRREL.²

A comparable study conducted by the US Army Corps of Engineers of the Department of the Army evaluated the adhesion strengths of several commercially available materials, coatings, and paints known to have low friction or non-stick properties, see Figure 5. In this test the coatings were applied over samples having highly durable Corp paints previously applied because it was considered highly unlikely that the low-adhesion coatings would actually replace the existing paints and more likely would be applied directly over the Corps paints. Similar to the results presented in this study, R-2180 again performed superior to the other coatings and materials tested. In fact, it decreased the adhesion strength over bare steel by a factor of 40.
Figure 5. Ice adhesion test results for construction materials and commercial coatings from DOA Manual; R-2180 is on the far right. Error bars represent the range in data.1

Another critical issue addressed is how well a coating will perform after exposure to extreme environmental conditions and wear. Figure 6 shows how R-2180 performs after exposure to various environmental conditions including physical wear, thermal cycling, humidity cycling, and salt spray. The durability of R-2180 coated aluminum pins were tested by roughening the surface with sand paper prior to CRREL ice adhesion to simulate the influence of wear. Figure 6 shows that although the worn R-2180 surface does not perform as remarkably as a freshly applied coating of R-2180, it still outperforms the Teflon. Furthermore when coated pins were exposed to extreme thermal conditions, humidity cycles, and sprayed with a salt-water solution prior to ice adhesion testing, R-2180 continues to perform better than Teflon (Figure 5).

Figure 6: Post Conditioning Ice Adhesion Pin Testing at CRREL.4
5. CONCLUSIONS

Ice build up is a serious problem and major economic impact in the aircraft industry resulting in multiple efforts to understand and improve the problem. Tests performed by the Department of the Army, Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory (CRREL) have shown that the R-2180 silicone coating significantly reduces ice adhesion when applied on aluminum surfaces compared to other commercially marketed ice-phobic coatings and other materials known to have non-stick properties. In particular, R-2180 performed almost 10 times better than many other commercially available materials typically used for aircraft purposes. In addition, R-2180 silicone coating continues to show favorable performance after wear and exposure to extreme environmental conditions such as heat, humidity, and salt water. It is believed that surface energy of the material or coating can have a dramatic effect on ice adhesion and perhaps a complex interaction between the ice and the silicone coating that reduces adhesion. Thus it would be valuable in future studies to measure the surface energies of the several materials tested to determine any correlation between the ice adhesion and surface energy of the coating.

6. REFERENCES

(3) CNN online, December 11, 2006, Canada Bans Ethylene Glycol Monomethyl Ether.
(4) Laboratory Ice Adhesion test Results for Commercial Icephobic Coatings for Pratt & Whitney, May 2004, CRREL.
Using Optical Index Matching Silicone Gels to Improve Outdoor Viewing and Ruggedness of Displays

Bill Riegler and Michelle Velderrain

NuSil Technology LLC
1050 Cindy Lane
Carpinteria, CA 93013
Portable computing, military environments, and demanding outdoor activities like fire rescue require a reliable and accurate display. Most commercial, off-the-shelf displays are not produced for direct viewing outdoors. The bright ambient light outdoors can cause high reflection losses and subsequently “display washout.” Companies can increase display brightness, however this typically results in added power consumption and poor aspect ratios.

An alternative and growing trend is use of optical index matching silicone gels to reduce reflection losses and also aid in durability. Commercial displays typically have the display protected by a coverglass with a small air gap between the display and the coverglass (see Figure 1). This gap leads to reflection loss as much as 8.5%, dependent on the difference of refractive indices between the surfaces. This reflection loss can be decreased by filling the gap with an optical index matching silicone gel, thus greatly increasing viewing outdoors in bright ambient light.

These optical index matching silicone gels are especially designed for protection of sensitive photonics assemblies. The encapsulation materials help improve impact resistance and protect the assembly from dust and mechanical and thermal shock. Optical silicone gels are also transparent and their softness easily allows the LCD panel to be disassembled for rework.

There are several materials to choose from depending on the refractive index matching: 1.52 to match BK7 glass or 1.46 to match silica glass. In addition, these materials bond well to glass and other substrates used in the display.

Most optical silicones cure at room temperature within 24 hours, or heat can be used to accelerate the cure. Curing at lower temperatures minimizes stress on the display by reducing the thermal expansion between materials with different Coefficients of Thermal Expansion (CTE). No UV exposure or temperature bake is required to initiate the cure process. These materials also remain fluid for at least eight hours. The long pot life and low viscosity enable the materials to wet out and fill in voids in complex assemblies and permit time for any trapped air bubbles to float to the surface and escape (see Table

![Diagram of optical index matching silicone gels](image-url)
Epoxy and acrylate encapsulants have also found use for gap filling in displays. However, these materials' rigid nature causes cracking when thermally cycled and they yellow when exposed to UV light from the sun.

<table>
<thead>
<tr>
<th>Properties</th>
<th>LS-3246</th>
<th>LS-3252</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncured</td>
<td>RI = Fused Silica Glass</td>
<td>RI = BK7 Silicate Glass</td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td>1000</td>
<td>425</td>
</tr>
<tr>
<td>RI, 589nm</td>
<td>1.46</td>
<td>1.52</td>
</tr>
<tr>
<td>Work Time, hr</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Cure</td>
<td>24 hr @ 25°C</td>
<td>24 hr @ 25°C</td>
</tr>
<tr>
<td>Durometer,’00’</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Operating Temp, °C</td>
<td>-115 to 200</td>
<td>-115 to 200</td>
</tr>
</tbody>
</table>

Table 1. Physical properties of optical silicone gels

These optical gels have specialized optical properties that allow them to provide the needed optical benefits for displays (see Figures 1-2).

Figure 1: Optical Absorption vs. Wavelength
In the future, touch screens will become more prevalent, creating further potential material demands to protect against hand oils, dirt and rain. These ever-changing challenges will keep the material scientist busy in the laboratory inventing the next generation of optical index matching silicone gels.

*Bill Riegler has a BS in Chemistry and is the General Manager Asia for NuSil Technology LLC, a leading global specialty silicone manufacturer.*

*Michelle Velderrain has a BS in Chemistry and is the Senior Technical Specialist for NuSil Technology LLC, a leading global specialty silicone manufacturer.*
Optical Silicones for use in Harsh Operating Environments

By Bill Riegler, Product Director-Engineering Materials, Stephen Bruner, Marketing Director, Rob Thomaier, Research Director, NuSil Technology, Carpinteria, CA.

Optical Polymers, Gels, and Thermosets for Index Matching Applications

A poster presentation at Optics East, Philadelphia, PA, October 25-28, 2004
Abstract

The optics industry widely uses silicones for various fiber optic cable potting applications and light emitting diode protection. Optics manufacturers know traditional silicone elastomers, gels, thixotropic gels, and fluids not only perform extremely well in high temperature applications, but also offer refractive index matching so that silicones can transmit light with admirable efficiency. However, because environmental conditions may affect a material’s performance over time, one must also consider the conditions the device operates in to ensure long-term reliability. External environments may include exposure to a combination of UV light and temperature, while other environments may expose devices to hydrocarbon based fuels. This paper will delve into the chemistry of silicones and functional groups that lend themselves to properties such as temperature, fuel, and radiation resistance to show why silicone is the material of choice for optic applications under normally harmful forms of exposure. Data will be presented to examine silicone’s performance in these environments.

Discussion

Industry Background

The production of electronics and sensors used in harsh environments is expected to be an $887 million dollar market by 2008. Today’s electronics and sensors encounter a variety of harsh environments, including: extremes in temperature or pressure, chemical aggressiveness, acceleration/deceleration, radiation, cyclic operation and shock. Devices employed in such environments must endure these harsh conditions, enabling them to perform their functions over time. A brief list of current optical sensing technology and developing applications is listed below:

- Vision sensors for industrial applications that include the identification and measurement of production outputs, verify accurate assembly, and guide production equipment.
- Weather satellites employ the use of optical sensors technologies that continuously expose their position-sensors to sunlight or radiation. These sensors operate under extremely high temperatures in order to sense the satellite is in its proper position.
- The Department of Energy’s National Energy Technology Laboratory is developing novel sensors able to withstand high temperatures and harsh environments. These microsensors will be used in fuel cell, turbines, gasification, and combustion systems.
- NASA’s Marshall Space Flight Center utilizes the Advanced Video Guidance Sensor in conjunction with a computer program for the autonomous rendezvous of a spacecraft with a target satellite.
- NASA is investigating hybrid Peizoelectric/fiber optic sensors for aerospace, aeronautical and automotive applications.

**Polymer Chemistry**

The term “Silicone” is actually a misnomer. Normally the suffix ‘-one’ delineates a substance has a double bonded atom of oxygen in its backbone. Scientists initially believed that silicone materials contained double bonded oxygen, hence the use of ‘silicone.’ However, silicones are really inorganic polymers, having no carbon atoms in the backbone, and therefore should be named ‘Polysiloxanes.’ The diagram below shows their typical structure:

\[
\begin{align*}
  & \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
\sim \sim \sim \sim \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si}\end{align*}
\]

\[\text{R}=\text{CH}_3, \text{phenyl (aromatic carbon ring), } \text{F}_3\text{CCH}_2\text{CH}_2, \text{CHCH}_2\]

This polymeric structure allows polysiloxanes to be used in a wide array of applications because it allows different types of polysiloxanes groups to be incorporated. Different polysiloxanes can provide a variety of excellent properties that can be chosen according to the specific application, temperature stability (-115 to 260°C), fuel resistance, optical clarity (with refractive indexes as high as 1.60), low shrinkage (2-%), and low shear stress. Different types of silicones, or polysiloxanes, and their property advantages include:

*Dimethyl silicones*, or dimethylpolysiloxanes, are the most common silicone polymers used industrially. These types of polymers are typically the most cost effective to produce and generally yield good physical properties in silicone elastomers and gels. The polymer pictured below contains vinyl endgroups that participate in a platinum catalyzed addition reaction (see section on *Cure Chemistry* for more information).

For optics purposes, all dimethylpolysiloxanes have a refractive index of 1.40, 25°C at 598nm.
Methyl phenyl silicone systems contain diphenyldimethylpolysiloxane co-polymers. The phenyl functionality boosts the refractive index of the polymers from 1.40 upwards to 1.60. There are limitations, the steric hinderance of the large phenyl groups prohibit significantly high concentrations of diphenyl units on the polymer chain. Silicone polymers with diphenyl functionality with refractive index of 1.43 to 1.46 are useful in bio-optic applications (e.g., intraocular lenses) in creating a thin lens. The diagram below shows a typical structure for a methyl phenyl silicone:

![Methyl phenyl silicone structure](image)

Fluorosilicones are based on trifluoropropyl methyl polysiloxane polymers and historically are used for applications that require fuel or hydrocarbon resistance. The trifluoropropyl group contributes a slight polarity to the polymer, resulting in swell resistance to gasoline and jet fuels. For optic applications, the refractive index is 1.38 at 25°C at 598nm. While some fluorosilicones contain 100% trifluoropropylmethylpolysiloxane repeating units, other systems contain a combination of the fluorosiloxane units and dimethyl units to form a co-polymer. Adjusting the amount of trifluoropropyl methyl siloxane units in the polymerization phase provides optimal performance in specific applications. The diagram below shows a typical structure for a fluorosilicone copolymer:

![Fluorosilicone copolymer structure](image)

Material Composition
Silicone materials, with the chemistries described above appear in a wide variety of material compositions. This broad range of material compositions makes silicone a
viable option to endless numbers of optic applications. Some silicone material compositions and their typical applications include:

Silicone Fluids are non-reactive and reactive silicone polymers formulated with dimethyl, methylphenyl, diphenyl, or trifluoropropylmethyl constituent groups, with refractive index ranging from 1.38 to 1.60. These materials’ viscosity depends largely on molecular weight of the polymer and steric hinderance of functional groups on the polymer chain and can range from 100cP (a light oil) to 20,000cP (like honey). Fluids are typically used to fill air gaps in high temperature lens assemblies in order to displace dust, permit cooling action or reduce interfacial reflections. Fluids can also be used to fill lenses or microchannel waveguides because of the small thermo-optic coefficient of -2 to 5 x 10^-4°C. Optical fluids can be used as the working medium in bubble-action optical switches or attenuators.

Silicone Thixotropic Gels are comprised of an optical fluid immobilized in a nanoparticle powder. These gels have no curing characteristics and by nature they are thixotropic and do not have well-defined viscosities. At rest they are mechanically stable and will not migrate. Due to the index matching limitations of the nanoparticle powder, these materials are available at 1.46 to 1.59 refractive indices only. Their primary use is for improving the return loss in a single mode mechanical fiber splice.

Silicone Curing Gels contain reactive silicone polymers and reactive silicone crosslinkers in a two-part system. When mixed together these materials are designed to have a very soft and compliant feel when cured and will stick to substrates without migrating. Viscosities can be adjusted with the molecular weight of the polymers from 200 – 10,000cP. Depending on the functionality of the polymer, optical index matching can be formulated from 1.38-1.57. For HBLED applications this allows for the optimal light to come out of the die while protecting it from dust, moisture, vibration and changes in temperature. The yield strength of the gel is low enough to permit wire bonds to slice through during thermally induced micromotion without risking wire bond failure. Steps need to be taken to manufacture these materials with minimal outgassing and low ionic species. Other applications besides encapsulating HBLEDs include potting of packaged modules such as transponders, transceivers and detector arrays.

Silicone Thermosets fall into two categories, moldable elastomers and adhesives. Like the Gels, these two-part systems contain reactive polymers and crosslinkers that cure up to a rubbery type hardness. Most will cure at room temperature, however some need heat to cure. To impart increased physical properties, sometimes these materials have higher viscosities. The moldable materials can be casted or injection molded into optical lenses. They have inherently stronger physical properties than the gels and can work as excellent adhesives in optical applications. Special versions of these can be produced to have extremely low outgassing for electronic and aerospace applications. These also can have the broad refractive index range of 1.38 – 1.57.

Silicone resins, also called Polysilsesquioxanes, are highly crosslinked siloxane systems with the empirical formula:
R - Si - O$_{1.5}$

Both the Polysilsesquioxane and T-resin names can be derived from the empirical formula. The root “sesqui” indicates the one and a half stoichiometry of the oxygen bond to silicon. T-resin indicates the trisubstitution of silicon by oxygen. Silicone resins are also named by the organic, or “R,” group.

Sample Resin Structures:

These materials when cured can give very hard durometers, Shore D. The phenyl content can be adjusted providing refractive index from 1.40-1.57.

*Cure Chemistry*

When a manufacturer in the optics industry chooses a material for a specific application, material properties aren’t the only deciding factor. That manufacturer also has to examine how the material is used. Inconvenience in production or material by-products can make a chosen material ineffective for a specific application. Silicons, however, can be designed around various cure chemistries to accommodate different production needs. Silicone systems can cure by platinum catalyzed addition cured systems, tin condensation cure systems, peroxide cure systems, or oxime cure systems. Some of the oldest cure chemistry used with silicons utilizes an acetoxy tin condensation cure system, such as used in household bathroom caulk. These systems yield a vinegar-like smell (acetic acid), a byproduct of the reaction. For various reasons as described below, platinum systems are the most appropriate for optics applications.
Tin condensation systems involve hydroxyl functional polymers and alkoxy- functional crosslinking compounds. The alkoxy functional crosslinker first undergoes a hydrolysis step and is left with a hydroxyl group. This hydroxyl group then participates in a condensation reaction with another hydroxyl group attached to the polymer. The reaction can proceed without the assistance of the tin catalyst, but the presence of the catalyst "boosts the rate of reaction. The reaction mechanism is pictured below:

\[
\text{OR} \quad \text{RO-Si-OR} \quad + \quad 4\text{OH} \quad \xrightarrow{\text{Moisture}} \quad \text{Tin} \quad \text{O-Si-O} \quad + \quad 4\text{ROH}
\]

The main disadvantages of condensation systems are the leaving group, shrinkage and long cure time, as several days are often required for to completely cure an elastomer.

Peroxide catalyzed systems, have a reaction mechanism that involves a peroxide catalyst and either methyl groups or vinyl functional groups. The peroxide catalysts create free radical species of the methyl and vinyl that can then form covalent bonds. Pictured below is the reaction mechanism involving a peroxide catalysis of two methyl groups:

\[
\text{RCOOCR} \quad \xrightarrow{\Delta} \quad \text{RCO}^+ \quad + \quad \text{OCR} \quad + \quad \text{SiCH}_3 \quad + \quad \text{RCO} \quad \xrightarrow{\text{SiCH}_2} \quad \text{SiCH}_2\text{SiCH}_2 \quad + \quad \text{CH}_2\text{Si}
\]

Disadvantages include a lengthy post-curing step at high temperatures in order to remove the reaction’s byproducts. Other disadvantages include the possibility of the catalyst interacting with active agents.

Platinum catalyzed silicones utilize a platinum complex to participate in a reaction between a hydride functional siloxane polymer and a vinyl functional siloxane polymer. The result is an ethyl bridge between the two polymers. The reaction mechanism is pictured below:
Platinum systems are often cured quickly with heat, but can be formulated to cure at low temperatures or room temperature if necessary. The advantages of these systems include a faster cure and no volatile byproducts. The possibility of inhibiting the cure is the main disadvantage of platinum systems. Inhibition is defined as either temporarily or permanently preventing the system from curing. Some types of inhibitors are purposefully added to these systems to control the rate of cure. However, contact with tin, sulfur, and some amine containing compounds may permanently inhibit the cure. Compounds that inhibit the cure can be identified easily by attempting to cure a platinum catalyzed system in contact with the compound, as inhibition results in uncatalyzed regions of elastomer systems or inconsistency in cure over time.
Typical Testing For Optical Materials

Index Matching
Optical sensing devices operate most efficiently when photons can pass freely through the optics of the device. For this reason, components used in the assembly of the optics should have similar refractive indexes. The refractive index of silicone that can be effective in harsh operating environments can range from 1.38 to 1.60. We describe some of the testing methods to characterize silicones for optical applications.

Refractive Index, the measurement of the speed of light traveling through a transparent material. It is measured at 589 nanometer (nm) wavelength (a.k.a. “the Sodium D line”, or “nD”) with a refractometer using the method of the American Society for Testing and Materials’ ASTM D-1218 at a fixed temperature of 25.0°C. As previously mentioned, silicones have a refractive index range of 1.38-1.60.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Acronym</th>
<th>Tradenames</th>
<th>nD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td>1.34</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>PTFE</td>
<td>Teflon®</td>
<td>1.34</td>
</tr>
<tr>
<td>Magnesium Fluoride</td>
<td>MgF2</td>
<td></td>
<td>1.38</td>
</tr>
<tr>
<td>Fused quartz</td>
<td></td>
<td></td>
<td>1.46</td>
</tr>
<tr>
<td>Acrylate</td>
<td>PMMA</td>
<td>Plexiglass®</td>
<td>1.49</td>
</tr>
<tr>
<td>Cyclic Olefin</td>
<td>COC</td>
<td>Topas®</td>
<td>1.53</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>PC</td>
<td>Lexan®</td>
<td>1.59</td>
</tr>
<tr>
<td>Aluminum Oxide</td>
<td>Sapphire.ruby</td>
<td></td>
<td>1.76</td>
</tr>
</tbody>
</table>
Refractive index versus change in temperature, is conducted at 25°C to 50°C in 5-degree steps. Data is reported as shown in the graph below, and the least squares linear regression fit to the data for the thermo-optic coefficient (in units of dn/dT) is also calculated and provided on the chart.
**Refractive Index versus change in Wavelength**, data are measured at 411nm, 589nm, 833nm, 1306nm and 1550nm at 25.0°C and presented as shown in the graph below. Coefficients are also printed on the plot for a Sellmeier dispersion curve fit.

---

**Refractive Index vs. Wavelength (25°C)**

*Lightspan Encapsulation Gel*

*LS-3252, Lot# 11031-0313*

---

**Dispersion curve fit:**

\[ n = 1.495 + (1.096e+4)^{-2} + (-1.660e+9)^{-4} + (2.072e+14)^{-4} \]

**Measured Data:**

<table>
<thead>
<tr>
<th>(nm)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>411</td>
<td>1.5443</td>
</tr>
<tr>
<td>589</td>
<td>1.5174</td>
</tr>
<tr>
<td>833</td>
<td>1.5075</td>
</tr>
<tr>
<td>1306</td>
<td>1.5008</td>
</tr>
<tr>
<td>1550</td>
<td>1.4987</td>
</tr>
</tbody>
</table>

---

*Lithium niobate 3252, Lot# 11031-0313*
Optical Absorption versus change in Wavelength, is measured across the wavelength range of 300nm to 1700nm, with 2nm resolution, using a spectrophotometer with the sample temperature at 25°C. The graph is presented below:

![Optical Absorption vs. Wavelength](image)

**Results**

The general properties of silicones, by product type, are described briefly above. For our purposes, we will present and discuss data that relates specific properties of silicones that are useful in harsh operating environments. While the stability of the siloxane bond bodes well for silicone material performance in a diverse range of operating conditions, we have chosen to focus on three types of environments that can adversely affect materials in a sensor assembly; extreme temperatures, exposure to fuels, and radiation exposure.

**Extreme Temperatures**

Extreme temperatures can cause outgassing of volatile components with temperatures ranging from -115°C to 260°C. In closed electronic and opto-electronic systems, volatile components can contaminate sensitive components. Smaller electronic
packages with higher voltage requirements can produce excessive heat, and any components containing volatile chemical species can outgas under these conditions. Electronic systems can contain a variety of components at various operating temperatures. Cooler components behave like a cold soda can on a warm humid day, as they can become a conduit onto which these volatile components re-condense.

Traditionally, applications on satellites and shuttles employ low outgassing materials, as these applications encounter extraterrestrial environments that cause outgassing. These environments typically undergo extreme temperature cycling in a vacuum. The ASTM test method E595 provides a standard for testing all silicone materials for extraterrestrial use. Total Mass Loss (TML) and Collected Volatile Condensable Material (CVCM) testing can be useful in screening low outgassing materials from other materials. NASA has set current limits of Total Mass Loss not to exceed 1.0% and Collected Volatile Condensable Materials not to exceed 0.1%. The materials listed below demonstrate the physical similarities between low outgassing silicone materials and other silicone materials:

<table>
<thead>
<tr>
<th>Clear Encapsulants:</th>
<th>CV-2500</th>
<th>R-2615</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive Index @ 25°C</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td>Durometer, Type A</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>900psi</td>
<td>1100psi</td>
</tr>
<tr>
<td>Elongation</td>
<td>150%</td>
<td>100%</td>
</tr>
<tr>
<td>Volume Resistivity</td>
<td>1x10^15</td>
<td>1x10^15</td>
</tr>
<tr>
<td>Collected Volatile Condensable Material</td>
<td>0.01%</td>
<td>0.80%</td>
</tr>
<tr>
<td>Total Mass Loss</td>
<td>0.05%</td>
<td>0.25%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>High Temperature Clear Encapsulants:</th>
<th>CV16-2500</th>
<th>R-2655</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive Index @ 25°C</td>
<td>1.43</td>
<td>1.43</td>
</tr>
<tr>
<td>Durometer, Type A</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>500psi</td>
<td>800psi</td>
</tr>
<tr>
<td>Elongation</td>
<td>100%</td>
<td>125%</td>
</tr>
<tr>
<td>Collected Volatile Condensable Material</td>
<td>0.01%</td>
<td>0.87%</td>
</tr>
<tr>
<td>Total Mass Loss</td>
<td>0.05%</td>
<td>2.03%</td>
</tr>
</tbody>
</table>

Another factor to consider is the coefficient of thermal expansion or CTE in electronic packages. Silicone materials typically have large CTE values compared to filled and unfilled epoxies. This large CTE, combined with and related to low modulus values, creates an environment where low stress is imparted on mismatched CTE components. This low stress results in fewer component fractures over large temperature ranges.

**Radiation**

Applications that are exposed to radiation, such as weather sensors, can adversely affect the materials used. Silicone materials are affected as well by radiation but these effects can be minimized with adjustments to the type of polymer used. Radiation can create free radical groups on polymers within the elastomeric matrix. These free radicals
readily form linkages to other polymers creating a higher crosslink density. A higher crosslink density in silicone systems generally translates to higher durometer or hardness, higher modulus and lower elongation. As briefly described above, higher modulus values can create stress in temperature cycling applications where CTE mismatches are observed. While the increase in modulus from radiation exposure may still be lower than epoxies, certain silicone chemistries can be effective in resistance to radiation. Several sources point to phenyl based silicones as having greater stability than standard polysiloxane systems. Walter Noll states, “resistance increases with increasing content of phenyl groups, copolymers with diphenylsiloxane units and methylphenylsiloxane units have proved particularly suitable”. In potting applications where elongation is not a significant factor, like electric wire and cable, electrical properties are “little affected by radiation” Handbook pg 16. The table below demonstrates the radiation resistance of phenyl containing silicone rubbers (PMQ) compared to dimethyl silicone rubbers (VMQ).

**Radiation Resistance Silicone Rubber**

<table>
<thead>
<tr>
<th>Dosage (Rads)</th>
<th>Elongation (%)</th>
<th>Tensile (psi)</th>
<th>Elongation (%)</th>
<th>Tensile (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>200</td>
<td>1200</td>
<td>600</td>
<td>1200</td>
</tr>
<tr>
<td>5 x 10^6</td>
<td>130</td>
<td>1000</td>
<td>450</td>
<td>1100</td>
</tr>
<tr>
<td>5 x 10^7</td>
<td>50</td>
<td>900</td>
<td>225</td>
<td>900</td>
</tr>
<tr>
<td>5 x 10^8</td>
<td>20</td>
<td>600</td>
<td>75</td>
<td>850</td>
</tr>
</tbody>
</table>

**Fuel Resistance**

When we refer to fuel resistance, we are specifically citing the resistance of silicones to swell when put in contact with hydrocarbon based fuels and fluids. While silicone materials do not undergo structural breakdown when exposed to hydrocarbon-based compounds, some systems expand several times their original size and could create problems in lens and other potting applications. Fluorosilicones, with the chemistry described above, perform effectively in a fuel and fluid environment by retaining geometry and resisting absorption of hydrocarbons. The table below lists one fuel (JP 5) and two hydraulic fluids (Hydrol and Skydrol) common to the aerospace industry. The table also lists the percentage of trifluoropropylmethylsiloxane units used in the polymer of the elastomer system tested. The results are listed as the percent swell after exposure:

<table>
<thead>
<tr>
<th></th>
<th>JP5</th>
<th>Hydrol</th>
<th>Skydrol</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 Mole %</td>
<td>28% Swell</td>
<td>43% Swell</td>
<td>4 % Swell</td>
</tr>
<tr>
<td>50 Mole %</td>
<td>6% Swell</td>
<td>28% Swell</td>
<td>3% Swell</td>
</tr>
<tr>
<td>100 Mole %</td>
<td>16% Swell</td>
<td>5% Swell</td>
<td>6% Swell</td>
</tr>
</tbody>
</table>
The table demonstrates that different fluorosilicone compositions perform optimally in different systems and we point out that more trifluoropropylmethylsiloxane units are not always better.

**Conclusion**

Silicone elastomers, gels, thixotropic gels, and fluids not only perform extremely well in high temperature applications, but also offer refractive index matching so that silicones can transmit light with admirable efficiency. The examples of emerging and existing sensor technology provided the basis on which optics engineers must also consider the conditions the device operates in to ensure long-term reliability. External environments may include exposure to a combination of UV light and temperature, while other environments may expose devices to radiation and hydrocarbon based fuels. This paper demonstrated that the chemistry of silicones and functional groups that lend themselves to properties such as fuel and radiation resistance show why silicone is the material of choice for optic applications under normally harmful forms of exposure.

**References**


NEW LOW STRESS FILM ADHESIVE FOR AEROSPACE APPLICATIONS REQUIRING LOW OUTGASSING

Bill Riegler, Product Director-Engineering Materials, 
Dee Anne Long, R&D Supervisor, 
NuSil Technology LLC, Carpinteria, CA. 
1050 Cindy Ln, Carpinteria, CA, US 93013

Presented at the 2006 SAMPE Conference, May 1-4, Long Beach, CA.
ABSTRACT

Low stress liquid adhesives based on silicone chemistry have been used for years in the aerospace industry requiring low outgas, ASTM E-595 requirements (1). The applications include coverglass adhesives, mirror bonding, potting of electronic parts and many more. Silicones are valued for their dependability during extreme temperature cycling and inherently low modulus characteristics. Aerospace Engineers working on applications that require precision bond lines for adhesion or sealing applications have struggled with liquid silicone systems. The lack of uniform bond thickness and mess / clean-up issues result in significant process inefficiencies.

Film adhesive technology solves many of these problems. Films can be produced to an exact thickness specified by the customer. If many of the same components are going to be adhered to, a die cut of the film could be obtained and reproduced to improve the efficiency of applying adhesive. Mess and clean-up are non-existent.

The problem until recently is that low stress, low outgassing silicone film adhesive versions were not available. This paper will characterize new film adhesives and compare with similar liquid materials; CTE, High/low temperature resistance, adhesion, etc. The possibility for future novel applications will also be discussed.

KEY WORDS: Silicone Polymers, Film Adhesives, Outgassing

1. INTRODUCTION

The National Aeronautics & Space Administration (NASA) recommends all adhesives used in extraterrestrial environments be tested by ASTM E-595 (2). This test method is primarily a screening technique and very useful in identifying materials with relatively low potential for contamination, verifying material quality, and aiding in material selection and qualification for space applications. The criteria used for acceptance or rejection of material is determined by the user and based upon specific component and system requirements. Historically a maximum Total Mass Loss (TML) of 1.00% and a maximum Collected Volatile Condensable Materials (CVCM) of 0.10% have been used as screening levels for rejection of materials.

Film adhesives are a whole category of adhesives defined as adhesives with a specified and consistent bond thickness that does not change (3). They often require heat or an activator to instigate the chemical reaction for cure.

2. SILICONE CHEMISTRY

Silicone adhesives are over sixty years old (1), and oddly enough, ‘silicone’ is a misnomer. Normally the suffix ‘-one’ delineates a substance having a double bonded atom of oxygen in its backbone. Scientists initially believed that silicone materials contained double bonded oxygen, hence the use of ‘silicone.’ However, scientists have found that silicones are really inorganic polymers, having no carbon atoms in the backbone, and therefore should be named ‘Polyorganosiloxanes.’ The diagram below shows their typical structure (FIGURE 1):

---

Polysiloxanes offer excellent elastomeric properties, a wide range of temperature stability (-115 to 260°C when phenyl substituted), fuel resistance (when Trifluoropropyl substituted), optical clarity (with refractive indexes as high as 1.60), low shrinkage (<1%), and low shear stress. Silicons are used in a wide array of applications due to these property advantages (4).

One-part adhesives are the most common silicone adhesive and are used in diverse applications from bathtub caulking to adhering pace maker leads. These one-part adhesives are based on acetoxy (alkyltriacetoxyisilane) or alcohol (alkoxy) crosslinked cure systems. The following demonstrates the reaction, which requires water to cure:

Addition cure adhesives, based on a two-part platinum catalyst system, do not require moisture or open air to cure. Both parts generally contain a vinyl functional silicone polymer with the platinum catalyst added to the material’s Part A and a hydride functional crosslinker and inhibitor added to Part B. Often both parts contain reinforcing fillers, pigments and special additives such as barium sulfate for radio-opacitity or boron nitride for thermal conductivity. The cure involves the direct addition of the hydride functional crosslinker to the vinyl functional polymer forming an ethylene bridge crosslink (See Figure 2).
Unlike one-part silicone adhesives, this mechanism involves no leaving group allowing these systems to cure in closed environments. Most platinum systems can fully cure at room temperature in twenty-four hours, or the cure can be accelerated with heat.

3. FILM ADHESIVE CHEMISTRY

A film adhesive is manufactured very similar to a low outgassed addition cure liquid adhesive. A polymer is made to meet the ASTM E-595 outgas limits, < 1.0% TML and <0.1% CVCM. These polymers used as the primary building block, are created with polyorganosiloxane cyclic and short-chained siloxane oligmers (see Figure 3). The use of catalysts can polymerize polysiloxane cyclics into linear, high molecular weight silicones at low temperatures and pressures.

![Figure 3, Octamethyltetrcyclosiloxane](image)

**Figure 3, Octamethyltetrcyclosiloxane**

![Figure 4, Hexamethyldisiloxane](image)

**Figure 4, Hexamethyldisiloxane** $\text{H}_3\text{C} - \text{Si} - \text{O} - \text{Si} - \text{CH}_3$

This is an equilibrium reaction, and in the presence of an end blocking or chain terminating species such as hexamethyldisiloxane (Figure 4), the reaction begins with an increase in viscosity. This increase in viscosity occurs primarily because the rate of cyclic opening and polymerizations is greater than that of the end blocking molecule scission. The polymer chain forms and breaks through the course of the reaction. Typical reactions take several hours to reach equilibrium. The product of the polymerization reaction is a mixture of cyclics, short-chained linear molecules and higher molecular weight polymers. The length of the polymers, or molecular weight, is normally distributed, and gel permeation chromatography will show a bimodal distribution with a smaller, low molecular weight peak, representing cyclics and very short chained linear, and a larger peak, representing the larger molecular weight polymers (See Figure 5). The species represented in the smaller peak and the lower molecular weight portion of the larger peak can outgas in extreme operating environments. Following E-595, CV- materials, these species are eliminated to prevent contamination.
A distillation process known as wiped film evaporation can remove low molecular weight fractions of polymerizations. The wiped film apparatus is typically an evacuated chamber with heated walls and a central cooling finger designed for condensing low molecular weight molecules. After the polymerization reaction is complete, the material is driven into the heated chamber and wiped onto the heated chamber walls. This exposes a thin film of the polymerization to heat under vacuum conditions. Higher molecular weight silicones continue to migrate down (or wipe down) the chamber wall, while the low molecular silicones condense on the cold finger and are routed to a collection vessel. Depending on the type of equipment, several attempts may be required to remove a sufficient amount of low molecular weight silicone species to pass the low outgassing requirement of E-595.

Once the low outgassed polymer is produced, silica is added as a reinforcing filler to improve the physical properties of the adhesive. Crosslinker and inhibitor are added to this silica filled base and calendared into a sheet. The catalyst, in the activator Part B, is applied to both the substrate and the film adhesive if possible. The film adhesive is then laid onto the substrate as smoothly as possible with a weight or roller added to apply some pressure. See Figure 6 for a diagram.

The activator with the catalyst diffuses throughout the silicone sheet and allows cure. Thin films can also be cured at room temperature.

4. LOW OUTGAS TESTING

As mentioned in the Abstract, ASTM E-595 is used to verify all silicone adhesives for extraterrestrial use. The test involves each material sample undergoing preconditioning, conducted at 50% relative humidity and ambient atmosphere for twenty-four hours. The sample is weighed and loaded into a compartment (see Figure 7) within a test stand (Figure 8). The sample is then heated to
125°C at less than 5 x 10⁻⁵ torr for 24 hours. Any volatile components of the sample outgas in these conditions. The volatiles escape through an exit port, and if condensable at 25°C, condense on a collector plate maintained at that temperature. The samples are post-conditioned in 50% relative humidity and ambient atmosphere for a twenty-four hour minimum. The collector plate and samples are then weighed again to determine the percentage of weight change, determining TML% and CVCM%. Standard criteria for low outgas materials limit materials’ Total Mass Loss (TML) to 1.0% and Collected Volatile Condensable Material (CVCM) to 0.10%. To adhere to these requirements, NuSil Technology performs this as a standard, lot-to-lot test.

5. FILM ADHESIVE TESTING

Because these film adhesives are used as adhesives, testing related to the adhesive strength of these materials on substrates is primary. ASTM D-1002, Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading, was used as our test method reference. This standard has been approved for use by the Department of Defense (5).

An aluminum panel is cut into a lap configuration, 1 inch wide by 4 inches long. Six strips of each substrate were prepared to make 3 test panels. Panels were cleaned with isopropanol to remove
dirt, grease or particulates. The activator, Part B is added to one square inch area on one end of each lap panel as described above and let to sit for at least 30 minutes. The film adhesive was placed on the panels, covering the applicator. The two panels were pressed together forming a sandwich (See Figure 9). This sandwich then has a 1lb weight placed on it for 30 minutes. The panels were then placed in an air-circulating oven set at 65°C for a four-hour cure. The equipment used to test for lap shear value was an ISTRON Model 1011 with MTS data acquisition and 1000-lb load cell installed (See Figure 10).

![Figure 9 - Lap Panel configuration](image)

![Figure 10. Instron 5500 Series Tabletop model for 450 lb to 11,500 lb capacities. New model updating the 1011.](image)

### 6. COMPARISON WITH LIQUID ADHESIVES

<table>
<thead>
<tr>
<th></th>
<th>Low outgas Film Adhesive (6)</th>
<th>Low outgas Liquid Adhesive (7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>NA</td>
<td>12000cP</td>
</tr>
<tr>
<td>Thickness, inches</td>
<td>0.010-0.014</td>
<td>NA</td>
</tr>
<tr>
<td>Work time</td>
<td>4 hrs min</td>
<td>20 hrs</td>
</tr>
<tr>
<td>Durometer</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Lap Shear, psi</td>
<td>150</td>
<td>250</td>
</tr>
<tr>
<td>Tensile, psi</td>
<td>800</td>
<td>400</td>
</tr>
<tr>
<td>Tear, ppi</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>TML</td>
<td>0.20</td>
<td>0.3</td>
</tr>
<tr>
<td>CVCM</td>
<td>0.05</td>
<td>0.09</td>
</tr>
</tbody>
</table>
7. CONCLUSION

The development of a low outgas silicone film adhesive, combining the low outgas properties needed from a material used in space with the consistent bond thickness and no mess of a film adhesive, was concluded and characterized. The low outgassing requirements of 1% or less Total Mass Loss (TML) and 0.1% or less Collectable Volatile Condensable Materials (CVCM) were achieved. When compared to liquid adhesives most properties are very similar with the exception being tensile and tear which are greater. The use of a thicker base in the film adhesive allows for this increased strength. The thicker the bondline the greater the lap shear strength. The aerospace industry now has a thermally reliable, low outgassed film adhesive that can be used in a variety of applications common to satellite manufacturing. The material comes in a number of forms and thicknesses. Future work could be performed to incorporate electrically and/or thermally conductive fillers into the base to develop further unique films.

8. REFERENCES

(2) Something about NASA E-595
(3) Definition of film adhesive
(6) Product Profile for NuSil Technology LLC CV-2680-12
(7) Product Profile for NuSil Technology LLC CV-2-2289-1

Bill Riegler is the Product Director-Engineering Materials for NuSil Technology LLC, the eighth largest silicone manufacturer in the world. Bill has been in the silicone industry for over twenty years with various positions at NuSil and the silicone division of Union Carbide, which has now become a part of GE Silicones. Bill has a B.S. in Chemistry from the University of California at Santa Barbara and a Masters in Business from Pepperdine University.
He began his career in Research and Development and held several technical sales positions before managing NuSil's domestic technical sales force. Bill is now directing NuSil’s worldwide efforts into the Aerospace, Photonics, and Electronics industries.

Dee Ann Long is an R&D Supervisor at NuSil Technology. A Chemical Engineering Major from the University of California at Santa Barbara, with seven years of silicone experience, particular experience with film adhesives.
**CUSTOM SILICONES**

All properties of silicones can be customized to enable unique capabilities. Silicone Solutions product line is comprised of all custom developed silicone products. These have been developed to meet previously unmet customer needs. Some are LSR’s and HCR’s. Many are adhesives, sealants, coatings and gels. The unique aspects of the non-LSR’s can be implemented into LSR and HCR products formulations. For a full listing of the product line, check-out [http://www.siliconesolutions.com](http://www.siliconesolutions.com). Silicone Solutions offers consulting and custom silicone products to industry, government and academia.

Additional capabilities include enabling: extremely high elongation, lubricity, unprimed adhesion to unusual substrates, unique rheologies, customized cure schedules, very high temperature resistance and thermal stability, very low modulus, non-bleeding gels and smart silicones.

Silicone combined with barium can be used as an x-ray marker. This application will verify the location of a medical device in the body.

### A. Oil Bleeding Grades of Silicones

**Source:** Wacker Chemie AG, [http://www.wacker.com](http://www.wacker.com)

Self-lubricating liquid silicone rubbers from the ELASTOSIL® LR series are treated with special silicone fluids (methylphenylsilicone fluids). These fluids can be dispersed homogeneously in the rubber where, after vulcanization, they produce a self-lubricating effect that is useful for installation and assembly applications.

Physically, the incompatibility of the silicone fluid in the rubber stems from the differences in chemical potential between the liquid and solid phases in the system. This potential gradient induces passive migration of the silicone fluid. The bleeding or diffusion behavior of the oil-bleeding grades depends on the following parameters:

- Temperature
- Viscosity
- Particle cross-section or size
- Pressure

Fluctuations in the bleeding behavior of silicone rubber articles can lead to considerable difficulties. Especially when single-wire seals or cable bushing mats are fabricated in automatic processes. For this reason, certain inter-related factors must be taken into account when self-lubricating liquid silicone rubbers are being processed:

**Crosslinking Density**

The distance between particles depends on the crosslinking density in the silicone rubber. And this, in turn, can be controlled via different processing parameters:

- by the vulcanization conditions: injection pressure, mold temperature and heating time.
- by the hardness of the rubber: filler and crosslinker content.
- by the color: the pigment incorporated.

However, the crosslinking density is easily kept constant by using a special rubber blend and an appropriate window in a state-of-the-art process.
**Pressure**
Aside from the oil content of the rubber blend, the pressure depends on the article’s design and the storage conditions. Small molded articles, especially, are frequently tightly packed in plastic bags and stored for protracted periods of time. Such conditions can readily cause bleeding.

**Storage Time**
Not only temperature and pressure, but the storage duration as well affect the oil content at the surface of silicone rubber articles. It is therefore imperative that storage conditions be optimized.

**Temperature**
The storage temperature has a considerable influence on the speed of the diffusion process. Diffusion occurs much faster at high temperatures than at low ones. Therefore, seasonal temperature fluctuations can affect bleeding behavior. Especially if the finished silicone rubber articles are not stored under controlled conditions: whereas in winter it might seem that a silicone rubber article bleeds hardly at all, a similar article in summer could be extensively wetted with silicone fluid.
Medical Sterilization of Silicone Parts

Silicone Parts can be sterilized via EtO gas, gamma or E-beam irradiation, steam autoclaving, and various other methods.

<table>
<thead>
<tr>
<th>Issue Date: August 14 2006</th>
<th>Project: E-Beam Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Wacker Lab Work Request

<table>
<thead>
<tr>
<th></th>
<th>LR 2003/05</th>
<th>LR 2003/08</th>
<th>LR 2004/05</th>
<th>R 407/00</th>
<th>R 407/00</th>
<th>R 407/00</th>
<th>R 460/05/06</th>
<th>R 460/05/06</th>
<th>R 460/05/06</th>
<th>R 460/05/06</th>
<th>R 460/05/06</th>
<th>R 460/05/06</th>
<th>R 460/05/06</th>
<th>R 460/05/06</th>
<th>R 460/05/06</th>
<th>R 460/05/06</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Original Physical Properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength, MPA</td>
<td>10.00</td>
<td>10.09</td>
<td>10.02</td>
<td>10.18</td>
<td>10.09</td>
<td>9.99</td>
<td>10.17</td>
<td>1477</td>
<td>1475</td>
<td>1474</td>
<td>1468</td>
<td>1475</td>
<td>1474</td>
<td>1474</td>
<td>1474</td>
<td>1474</td>
</tr>
<tr>
<td>Modulus ≥ 50% Elongation, MPA</td>
<td>0.30</td>
<td>0.75</td>
<td>2.73</td>
<td>0.46</td>
<td>1.08</td>
<td>2.17</td>
<td>0.46</td>
<td>0.99</td>
<td>2.55</td>
<td>1.47</td>
<td>1.24</td>
<td>0.75</td>
<td>1.08</td>
<td>1.24</td>
<td>2.55</td>
<td>1.47</td>
</tr>
<tr>
<td>Tensile Strength, Lb/In²</td>
<td>54</td>
<td>109</td>
<td>396</td>
<td>67</td>
<td>157</td>
<td>314</td>
<td>66</td>
<td>143</td>
<td>389</td>
<td>213</td>
<td>180</td>
<td>108</td>
<td>108</td>
<td>180</td>
<td>213</td>
<td>180</td>
</tr>
<tr>
<td>Modulus ≥ 50% Elongation, Lb/In²</td>
<td>0.55</td>
<td>1.75</td>
<td>4.44</td>
<td>0.78</td>
<td>1.85</td>
<td>3.06</td>
<td>0.90</td>
<td>1.72</td>
<td>4.09</td>
<td>1.49</td>
<td>2.51</td>
<td>0.99</td>
<td>1.72</td>
<td>1.49</td>
<td>4.09</td>
<td>1.49</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>821</td>
<td>453</td>
<td>111</td>
<td>781</td>
<td>472</td>
<td>361</td>
<td>748</td>
<td>692</td>
<td>358</td>
<td>219</td>
<td>279</td>
<td>463</td>
<td>463</td>
<td>279</td>
<td>463</td>
<td>279</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.11</td>
<td>1.133</td>
<td>1.175</td>
<td>1.111</td>
<td>1.163</td>
<td>1.195</td>
<td>1.104</td>
<td>1.144</td>
<td>1.164</td>
<td>1.108</td>
<td>1.115</td>
<td>1.223</td>
<td>1.115</td>
<td>1.223</td>
<td>1.115</td>
<td>1.223</td>
</tr>
</tbody>
</table>

### E-Beam Treatment 10.0 MR

<table>
<thead>
<tr>
<th>Appearance notes</th>
<th>Durometer Change, points</th>
<th>15</th>
<th>10</th>
<th>4</th>
<th>13</th>
<th>8</th>
<th>2</th>
<th>8</th>
<th>7</th>
<th>3</th>
<th>12</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength, %</td>
<td>-22.7%</td>
<td>-29.0%</td>
<td>-28.2%</td>
<td>-28.4%</td>
<td>-30.8%</td>
<td>-28.4%</td>
<td>-28.4%</td>
<td>-28.4%</td>
<td>-28.4%</td>
<td>-28.4%</td>
<td>-28.4%</td>
<td>-28.4%</td>
<td>-28.4%</td>
</tr>
<tr>
<td>Modulus Change, %</td>
<td>-42.2%</td>
<td>-34.9%</td>
<td>-36.3%</td>
<td>-36.2%</td>
<td>-36.2%</td>
<td>-36.2%</td>
<td>-36.2%</td>
<td>-36.2%</td>
<td>-36.2%</td>
<td>-36.2%</td>
<td>-36.2%</td>
<td>-36.2%</td>
<td>-36.2%</td>
</tr>
<tr>
<td>Modulus ≥ 50% Elongation, %</td>
<td>0.30</td>
<td>0.75</td>
<td>2.73</td>
<td>0.46</td>
<td>1.08</td>
<td>2.17</td>
<td>0.46</td>
<td>0.99</td>
<td>2.55</td>
<td>1.47</td>
<td>1.24</td>
<td>0.75</td>
<td>1.08</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>821</td>
<td>453</td>
<td>111</td>
<td>781</td>
<td>472</td>
<td>361</td>
<td>748</td>
<td>692</td>
<td>358</td>
<td>219</td>
<td>279</td>
<td>463</td>
<td>463</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.11</td>
<td>1.133</td>
<td>1.175</td>
<td>1.111</td>
<td>1.163</td>
<td>1.195</td>
<td>1.104</td>
<td>1.144</td>
<td>1.164</td>
<td>1.108</td>
<td>1.115</td>
<td>1.223</td>
<td>1.115</td>
</tr>
</tbody>
</table>

### E-Beam Treatment 40.0 MR

<table>
<thead>
<tr>
<th>Appearance notes</th>
<th>Durometer Change, points</th>
<th>38</th>
<th>25</th>
<th>9</th>
<th>31</th>
<th>15</th>
<th>10</th>
<th>26</th>
<th>18</th>
<th>7</th>
<th>25</th>
<th>16</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength, %</td>
<td>-49.4%</td>
<td>-35.9%</td>
<td>-33.7%</td>
<td>-34.8%</td>
<td>-35.5%</td>
<td>-35.5%</td>
<td>-35.5%</td>
<td>-35.5%</td>
<td>-35.5%</td>
<td>-35.5%</td>
<td>-35.5%</td>
<td>-35.5%</td>
<td>-35.5%</td>
</tr>
<tr>
<td>Modulus Change, %</td>
<td>-245.5%</td>
<td>-153.2%</td>
<td>-108.6%</td>
<td>-223.9%</td>
<td>-246.2%</td>
<td>-229.6%</td>
<td>-152.2%</td>
<td>-153.2%</td>
<td>-152.2%</td>
<td>-151.4%</td>
<td>-37.1%</td>
<td>130.0%</td>
<td>-191.7%</td>
</tr>
<tr>
<td>Modulus ≥ 50% Elongation, %</td>
<td>1.35</td>
<td>1.90</td>
<td>5.90</td>
<td>1.49</td>
<td>3.97</td>
<td>7.14</td>
<td>1.56</td>
<td>2.88</td>
<td>5.13</td>
<td>2.01</td>
<td>2.86</td>
<td>2.17</td>
<td>1.56</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>-89%</td>
<td>-89%</td>
<td>-71%</td>
<td>-94%</td>
<td>-91%</td>
<td>-90%</td>
<td>9.9%</td>
<td>-90%</td>
<td>-90%</td>
<td>-90%</td>
<td>-90%</td>
<td>-90%</td>
<td>-90%</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.92</td>
<td>0.75</td>
<td>0.32</td>
<td>0.47</td>
<td>0.62</td>
<td>0.25</td>
<td>0.57</td>
<td>0.67</td>
<td>0.35</td>
<td>0.57</td>
<td>0.37</td>
<td>0.47</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Molding

Today, the most commonly used methods of molding liquid silicone rubbers are injection and compression molding.

The silicone molding process is different from that of thermoplastics in a few different aspects. To mold a part, thermoplastic resin is heated in the barrel, and injected into a cold mold. Silicone molding of a part requires the liquid rubber to be kept cool in the barrel and injected into a heated mold. The design and fabrication of the silicone tooling is very different from that of thermoplastic tooling as well. Tolerances, venting, and part ejection are examples of tooling design aspects that differ. Although the tooling design is different, optimizing such processing variables such as temperature, pressure, and time are essential in both thermoplastic molding and silicone molding processes.

Here are a few examples of Silicone Molding:

A. **Silicone Lost (Disposable) Core**

The Y Boot Design requires no flash at the cores intersection therefore a disposable core is used. This type of silicone molding is possible because of the elasticity of silicone.

*See the sample included in the Designers Tool Kit (received at Medical Design Part Conference).*

---

**Silicone Y Boot**

Molded with Lost (Disposable) Core

*By: Albright Technologies, Inc.*

Evaluation of Removal Rate of Cured Silicone Adhesive from Various Electronic Packaging Substrates by Solvent and Silicone Digesters for Rework Applications

Michelle Velderrain and Marie Valencia
NuSil Technology LLC
1050 Carpinteria, CA 93013
(805) 684-8780, http://www.nusil.com
As presented at the 40th International Symposium on Microelectronics
San Jose Convention Center, San Jose, CA

Abstract

Reworking electronic packages is an integral process related to diagnostics and salvaging valuable materials. It is a meticulous and time-consuming procedure that requires some knowledge of the package material composition to determine compatible cleaning solutions and processes. Silicone adhesives are being used more frequently due to their ability to minimize shear stress during temperature cycling. A common method for removing silicone adhesive is by swelling in solvent and removing by mechanical methods taking care not to damage fragile materials and leave minimal residue. Silicone digesters (emulsifiers) are another means of removing cured silicone. They are comprised of weak acids or bases and remove silicone by breaking the siloxane bonds that make up the polymer matrix. They are able to penetrate into areas that are difficult, or impossible to reach, greatly reducing the risk of causing damage due to mechanical removal. The purpose of this study is to evaluate the rate of silicone removal by solvents and silicone digesters on silicones bonded to copper and aluminum. The removal rate was determined by developing a rating system based on time intervals where silicone was observed to delaminate or dissolve. Silicone adhesives and Thermal Interface Materials (TIMs) were used in the evaluation of two commonly used solvents and two commercially available silicone digesters. Copper and aluminum panels were evaluated by using a ~0.5 mm thick layer of silicone to bond 2 panels together. The samples were placed in cleaning solution for 24 hours at 40 degree Celsius and evaluated at specific intervals for any changes in appearance of silicone. Based on the performance of combinations of silicone, substrate and cleaner, the engineer can chose which method is best for reworking based on their own assembly configuration and materials.

Key words: Silicone, rework, adhesive, TIM, silicone emulsifier, low modulus

Introduction

Rework is an integral process to the electronics industry in order to diagnose failures and salvage valuable materials within the package. This involves compatible cleaning solutions and processes for reworking assemblies. removing the adhesives through mechanical or chemical methods without damaging sensitive components. There are several types of adhesives used in microelectronic packaging. This can make it challenging in choosing applications is hydrosilation (also known as Platinum cure or Addition Cure). The
Silicone adhesives are gaining popularity for use in microelectronic hybrid assemblies due to their inherently low elastic modulus. This low modulus provides stress relief during thermal cycling between substrates with different Coefficients of Thermal Expansion (CTE) such as copper and aluminum.

Silicone adhesives can be formulated to have a variety of mechanical and chemical properties that can influence the chemicals and processes one would use for rework. The chemical compatibility of the substrates that the package is composed of must also be considered (as well as any other associated hazards) when choosing the applicable method for rework. To better understand how various chemicals can affect silicones, it is important to understand their general composition.

What mainly defines silicone adhesives is the silicone polymer. This is characterized by the siloxane bond (-Si-O-Si), where the silicon atom will have at least one bond to an organic molecule. This is commonly referred to as polyorganosiloxanes, (-R₂SiO-)ₙ. The most common organic group found on the silicon atom for adhesives is methyl (CH₃). There are other organic groups that can be reacted onto the silicon atom giving the silicone different chemical and physical properties such as solvent resistance and increased thermal stability. Other functional groups will be present based on the specific cure chemistry for a particular formulation.

The most commonly used cure mechanism for microelectronic other is alkoxy and requires moisture to cure and the cure rate is dependent on available and exposed surface area. The platinum cure system allows the cure reaction to be accelerated by heat and is also desirable since there are no chemicals released during the curing reaction as there are with alkoxy cure systems. Other advantages to platinum cure systems for electronics is they are have relatively good shelf stability compared to one part alkoxy and need only ppm levels of platinum metal to function.

Silicone polymers alone have weak mechanical properties when crosslinked into a cured matrix, so they are reinforced with fillers (commonly fumed silica) and/or silicone resins to increase the elastic strength of the cured silicone rubber. These methods of reinforcing the silicone affect how the silicone adhesive flows and mechanical properties. How the silicone flows is directly related to how it is dispensed and processed, where the cured properties will dictate performance in the application. Silicone adhesives that contain silicone resins have a rheology similar to honey—they can coat a substrate by flowing around intricate design patterns. Adding silica will give the adhesive shear thinning properties (a.k.a. thixotropic) and will not flow without shear. These are used as glob tops and in other applications where the adhesive does not need to flow. Silicones also have intrinsically high dielectric strength that can be optimized to have electrical or thermally conductive properties by adding ceramic or metallic fillers. This allows them to be used in many applications ranging from a dam and fill application to
Thermal Interface Materials (TIMs) where the silicone adhesive matrix can be > 80 % filler (w/w).

There are generally two methods to remove the silicone for rework and each has its own set of challenges. Historically, soaking microelectronic assemblies in solvents, such as xylene, has been used to swell and soften the silicone to allow removal by mechanical tools. This method may cause damage to the substrates and assembled package due to the intricate and compact nature of microelectronic assemblies. It may also fail to remove any remaining silicone residues on substrate surfaces. The use of silicone digesters (also known as silicone emulsifiers) is becoming a popular method to remove silicone. The digesters are comprised of weak acids or bases that cleave the siloxane bonds and revert the cured silicone matrix back into discrete polyorganosiloxane molecules. Using silicone digesters can greatly reduce the need for additional mechanical methods to remove silicone, and thus decreases the potential for damaging the part as well as leaving minimal silicone residues on the substrate [1].

Experimental Evaluation

Testing was conducted to evaluate individual combinations of silicones, substrates and cleaning solutions. The substrates and silicones chosen for the experiment are commonly used in microelectronic assemblies (Figure 1).

Figure 1: Applications for Silicone Adhesives in Microelectronic Packaging

The removal rate was determined by developing a rating system based on time intervals where silicone was observed to delaminate or dissolve (Table 1).

Table 1. Removal Rate Ranking System

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Complete digestion/delamination time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt; or = 3 hr</td>
</tr>
<tr>
<td>2</td>
<td>3 hr &lt; Time &lt; 8 hr</td>
</tr>
<tr>
<td>3</td>
<td>8 hr &lt; Time &lt; 24 hr</td>
</tr>
<tr>
<td>4</td>
<td>&gt; 24 hr</td>
</tr>
</tbody>
</table>

The silicones, solvents and silicone emulsifiers chosen for evaluation are listed in Table 2.

Table 2. Silicones, solvents and silicone emulsifiers evaluated

<table>
<thead>
<tr>
<th>Silicone Sample ID</th>
<th>Silicone Type</th>
<th>Solvent Type</th>
<th>Silicone Emulsifier Sample ID</th>
<th>Silicone Emulsifier Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFA</td>
<td>Silica Filled Adhesive</td>
<td>IPA</td>
<td></td>
<td>Commercially available</td>
</tr>
<tr>
<td>TIM</td>
<td>alumina Thermal Interface Material</td>
<td>Xylene</td>
<td></td>
<td>Commercially available</td>
</tr>
<tr>
<td>DA</td>
<td>silver filled Die Attach</td>
<td>D1</td>
<td></td>
<td>1 % TBAF (tetra-n-butylammonium fluoride trihydrate) in Dowanol PMA</td>
</tr>
<tr>
<td>RFA</td>
<td>Resin Filled Adhesive</td>
<td>D2</td>
<td></td>
<td>Commercially available</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1 % TBAF (tetra-n-butylammonium fluoride trihydrate) in Dowanol PMA (propylene glycol methyl ether acetate) solution that was prepared by our laboratory [4].

The silicone was cured between 2 panels of the substrate in question per the manufacturer’s instructions under constant pressure and to achieve a cured silicone diameter of 6-7 mm with a thickness of 0.5 mm. Substrates were not exposed to any surface treatments to improve adhesion, but were wiped with IPA prior to applying silicone to remove any oily residues. Cured silicone/substrate sample panels were placed in each cleaning solution at 40° C and monitored over time for changes in appearance and/or delamination.

Experiments were initially performed in ambient conditions, but it was found that the elevated temperature did accelerate the delamination and/or digestion process and 40° C was below the boiling points of solvents and solutions being evaluated. Observations were made every hour for 8 hours and then once at 24 hours.

The combinations of silicone, substrate, and cleaner were rated based on time to demonstrate delamination or silicone emulsification (where the silicone is broken down and dissolved). ‘Delamination’ was determined to be the point at which the silicone had 100 % adhesive failure (from one or both substrates) where as ‘digestion time’ was determined to be the point at which the silicone was completely dissolved into the silicone digesting solution from both substrates. Each sample substrate panel was weighed before and after silicone was either separated from the substrate or completely dissolved to evaluate if there was a weight gain or weight loss that could be indication of remaining silicone residues or dissolution of substrate itself. Any change in the physical appearance of the substrates before and after immersion was also noted.

**Results**

The results of the study had three significant findings: removal effectiveness of solvent or silicone emulsifier based on visual delamination of silicone and digestion of silicone (Tables 3 and 4), effects of silicone type on rate of removal (Table 5) and change in substrates evaluated.

Table 3. Time intervals where silicone was observed to delaminate from substrates.

![Delamination Time Chart](image1)

Table 4. Time intervals where silicone was observed to be completely digested.

![Digestion Time Chart](image2)
Table 5. Comparison of silicones digestion rate versus substrate in combination with silicone emulsifier

<table>
<thead>
<tr>
<th>Digestion Time Ranking:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(&lt;3hrs), 2(3hr to 8hr), 3(8hr to 24hr), 4(&gt;24hr)</td>
</tr>
</tbody>
</table>

As hypothesized, the solvents did not dissolve or breakdown the siloxane bonds. IPA did not produce delamination between the silicone and substrate within 24 hours. Xylene showed slightly better performance on aluminum. Note that electronic grade IPA is typically recommended for use as a final wipe to remove residues left from cleaning solutions and residual water.

The silicone emulsifiers evaluated ranked in the following order from most to least effective in dissolving silicone within the shortest time: D3 > D2 > D1. The commercially available silicone emulsifier, D2, completely dissolved most silicones within 24 hours (4). The prepared silicone emulsifier solution, D3, dissolved most silicones within 8 hours (3) and in some cases, within 3 hours (1).

It was noted that the silicone formulation may have a significant affect on how easily the silicone can be removed, with less influence from the substrates on removal. For example, in all cases the Die Attach (DA) and Resin Filled Adhesive (RFA) silicones were not dissolved within 24 hours in all but one test condition. The commercially available silicone emulsifier, D2, was the only silicone emulsifier able to dissolve RFA when adhered to copper. On the other hand, the Silica Filled Adhesive (SFA) and the Thermal Interface Material (TIM) where dissolved within 8 hours in all but two test conditions. The TIM and DA formulations each contain ~80% (w/w) of dense fillers (therefore having low overall concentrations of silicone). Each reacted with the silicone digesters differently--the DA was difficult to dissolve on all substrates and the TIM was digested relatively quickly (the rate varied slightly based on the substrate).

The effects on substrates from the solvents and silicone emulsifiers were inconclusive based on weight loss. Only the final weights of the samples where the silicone was completely removed through delamination and/or digestion within 24 hours were measured. Any weight loss or weight gain was less than 0.05% and was considered insignificant. All the silicone digesters changed the color/appearance of the aluminum to some degree. There were also visual changes seen in the color of copper substrates exposed to D1 after 1 hour at 40°C. What may have caused the appearance change (and what affect it may have on substrate) is unclear. Further substrate exposure experiments will be conducted to determine if there are any significant surface effects from the silicone emulsifiers. In practice, depending on the substrate, observed surface effects may or may not alter the device performance.
Summary

In general, solvents were not as efficient in removing cured silicone as the silicone digesters. With the exception of the Die Attach, each of the silicone digesting solutions evaluated dissolved the silicone within 24 hours. Commercially available silicone emulsifiers evaluated in this study may not have dissolved the cured silicone as quickly as the 1 % TBAF solution but they demonstrated a reasonable effectiveness in removing various types of silicone and were easy to use. A general-purpose silicone emulsifier solution appears to be an effective means to remove silicone when taking into account the substrate material compatibility and the cleaning solution’s ideal performance conditions. Research is recommended to determine material compatibility and ensure elevated temperatures will not degrade temperature sensitive chemicals in silicone emulsifier solution.

We have seen that there are many variables that may affect the rate of known silicone and substrates. The difficulty of removing silicone from within a microelectronic device itself is much more complex since the device is composed of various substrates, the type of silicone(s) is sometimes unknown and there is a minimal amount of exposed surface area.

Many aspects can influence the rate of removal/emulsification of the cured silicone, such as removal conditions (time/temperature), solubility of silicone in cleaning solution and adhesion. Further studies will be performed to determine the significance that each of these factors may have on the removal of silicone.

Special Acknowledgment
Aurelie Dubout, NuSil Technology LLC

References:
2. Digesil® NC Technical Data Sheet
3. PolyGone™ 535 Technical Bulletin
Versatility and Flexibility from Low Outgassing Silicones

Bill Riegler and Michelle Velderrain, NuSil Technology LLC
T.Y.Lim, Sim Yee Engineering Resources
33 Lorong Markisah 12A, Taman Markisah, Bukit, Mertajam, 14000 Penang, Malaysia

Presented as a Poster at the 11th Electronics Packaging Technology Conference,
An IEEE Event
9th-11th December 2009, Singapore
Abstract
Silicone materials have unique characteristics allowing use in a broad range of applications and preservation of mechanical properties when exposed to extreme conditions. These mechanical properties absorb stresses incurred during thermal cycling as well as remain stable at temperatures up to 300°C for short intervals. The aerospace industry has utilized silicone adhesives and coatings for over fifty years because of these unique properties.

Miniaturization of electronic packages has led to using thinner and more fragile materials. This, in combination with the use of lead-free solder with solder reflow temperatures up to 260°C, can cause high shear stress during heating and cooling that can damage a device. Subsequently, there is growing interest in silicone adhesives and encapsulants for terrestrial electronic packaging applications.

A major concern surrounding use of silicones is the volatile component observed to outgas when silicones are exposed to high temperatures and low pressures (vacuum) for extended periods of time. These volatile components may contaminate sensitive surrounding surfaces and equipment making adhesion or soldering difficult in an upstream process. In extreme cases, such as in Micro Electro Mechanical Systems (MEMS) devices, volatiles can cause catastrophic failures with the device operation itself.

Introduction
New silicone materials designed to reduce the potential for contamination while maintaining essential physical and chemical characteristics have begun to emerge. These materials are ideal for use in specialized electronics applications such as Surface Acoustic Wave (SAW) Guides, hermetically sealed packages, MEMS, and optoelectronic applications. Several agencies, including NASA, historically recommend < 1.0 % Total Mass Loss (TML) and < 0.1% Collected Volatile Condensable Material (CVCM) as a screening level for the acceptance or rejection of a material for space applications, as tested per ASTM E-595. ASTM E-1559 is an additional method used to characterize materials by monitoring the outgassing kinetics and identifying the volatile components of the material. In this paper, we examine silicones with different levels of outgassing, comparing cured physical properties, out gassing profiles, and cost of each material.

Silicone Chemistry
The basis of virtually all silicone systems, including fluids, gels, elastomers, and adhesives, is the silicone polymer. The proper name for silicone polymers is actually polyorganosiloxanes, and the diagram in Fig 1 shows their typical structure.

![Structure of polyorganosiloxane](image)

Fig. 1. Structure of polyorganosiloxane; Typically R is equal to CH₃, phenyl, CF₃CH₂CH₂-

Ring Opening Polymerization (ROP) is commonly used for commercial production of silicone polymers. The process begins with polyorganosiloxane cyclic units to provide the body of the chain and end blocker units to control chain length and participate in the crosslinking reaction. The reaction occurs in the presence of reactive acid or base initiators. Figure 2 shows the reaction components for the most widely used polymer, polydimethylsiloxane (PDMS). Here, octamethylcyclotetrasiloxane (D₄) is reacting with a vinyl functional chain terminating species, Divinyltetramethylsiloxane, also known as “end blockers.”

![Basic Ring Opening Polymerization (ROP) reaction](image)

Fig. 2. Basic Ring Opening Polymerization (ROP) reaction for a vinyl terminated polydimethylsiloxane.

The ROP reaction is thermodynamically controlled and allowed to reach equilibrium. When a polymerization is allowed to reach equilibrium conditions, the concentration of total cyclics and linear polymers in the reaction mixture remain constant over time. When ROP is complete, the divinyltetramethylsiloxane end blockers are ultimately responsible for controlling the molecular weight distribution of the polymer, also known as Degree of Polymerization (DP).

The ROP initiator is deactivated when the polymerization reaches thermodynamic equilibrium. What remains is a stable mixture of various molecular weights of cyclics, short chained linear polymers, and higher molecular...
weight polymers where the concentrations of each species are based on their thermodynamic equilibrium (Fig. 3). The oily substance and fogging associated with silicones are primarily caused by the low molecular weight species; however these species can be eliminated by heat and vacuum in order to prevent contamination.

![EQUILIBRIUM DISTRIBUTION](image)

Fig. 3. Molecular weight distribution of silicone polymer

**Low Outgas Material Choices**

Different electronic applications may require different maximum levels of outgassing based on risk assessment. Therefore, NuSil Technology has developed four different groups of materials based on outgas levels: Standard (R/CF) materials that do not have weight loss requirements; Electronic Packaging Materials (EPM) with low outgassing for typical electronic applications, Controlled Volatility (CV) materials for extreme electronic and space applications; and Ultra Low Outgassing™ (SCV) materials for the most demanding applications.

**Material Cost**

A very important aspect of deciding which material to use in an application is material cost. The four types of materials described above have a defined cost structure to allow this factor to be properly assessed (see Fig. 4).

![Cost vs Risk Diagram](image)

Fig. 4. Assessment of risk versus cost for desired level of processing to reduce contamination.

Table 1 qualifies these four levels of materials and their outgas specifications.

<table>
<thead>
<tr>
<th>Test</th>
<th>R/CF-None</th>
<th>EPM-1hr @ 275°C</th>
<th>CV-1% TML</th>
<th>SCV-&lt;0.1% TML</th>
</tr>
</thead>
</table>

* Total mass Loss
** Controlled Volatility Condensable Materials

**Test Method E-595**

ASTM E 595 is a widely accepted test standard used to screen materials for volatile content that may outgas from a material in a vacuum or space environment. NASA and the European Space Agency (ESA) recommend testing low outgassing materials per ASTM E 595 prior to use in space. A maximum TML of 1% and CVCM of 0.1% are base requirements set out by these agencies.

Each material sample is preconditioned at 50% relative humidity and ambient atmosphere for 24 hours. The sample is weighed and loaded into the test chamber within the ASTM E 595 test stand, as shown in Fig. 6. The sample is then heated to 125°C at less than 5x10⁻⁵ torr for 24 hours. The volatiles that outgas under these conditions escape through an exit port and condense on a collector plate maintained at 25°C. Once the test is complete, the samples are removed from the chamber and the collector plate and weighed.
Fig. 5. E-595 test chamber.

Physical Property Comparison
A common practice used by end users is baking out the volatile substances once the silicone is already cured into its final state. This process is costly because it adds additional processing time and can greatly reduce the mechanical properties of the cured silicone. Tables 2, 3 & 4 compare the four types of materials and their physical properties. Note that removing the volatile species early in the process does not greatly affect the elastomeric properties between the standard and low outgases materials.

Table 2. Physical property comparison of optical materials.

<table>
<thead>
<tr>
<th></th>
<th>R/CF-</th>
<th>EPM-</th>
<th>CV-</th>
<th>SCV-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td>3.800</td>
<td>3.000</td>
<td>3500</td>
<td>3300</td>
</tr>
<tr>
<td>Worktime, hrs</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Cured</td>
<td>15 min @ 150°C</td>
<td>same</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>Durometer, Type A</td>
<td>50</td>
<td>45</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>Tensile,MPa</td>
<td>8.5</td>
<td>5.5</td>
<td>4.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>100</td>
<td>95</td>
<td>110</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3. Physical property comparison of robust silica reinforced adhesive materials.

<table>
<thead>
<tr>
<th></th>
<th>R/CF-</th>
<th>EPM-</th>
<th>CV-</th>
<th>SCV-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td>65000</td>
<td>50000</td>
<td>50000</td>
<td>50000</td>
</tr>
<tr>
<td>Worktime, hrs</td>
<td>3</td>
<td>1/2</td>
<td>1/2</td>
<td>&gt;24</td>
</tr>
<tr>
<td>Cured</td>
<td>15 min @ 150°C</td>
<td>same</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>Durometer, A</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Tensile,MPa</td>
<td>8</td>
<td>4.5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Elongation %</td>
<td>575</td>
<td>350</td>
<td>350</td>
<td>300</td>
</tr>
<tr>
<td>Lap Shear,MPa</td>
<td>N/A</td>
<td>2.75</td>
<td>2.75</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Table 4. Physical property comparison of thermally conductive materials.

<table>
<thead>
<tr>
<th></th>
<th>R/CF-</th>
<th>EPM-</th>
<th>CV-</th>
<th>SCV-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td>paste</td>
<td>36000</td>
<td>paste</td>
<td>paste</td>
</tr>
<tr>
<td>Worktime, hrs</td>
<td>3</td>
<td>6</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Cured</td>
<td>30 min @ 150°C</td>
<td>same</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>Durometer, A</td>
<td>90</td>
<td>55</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Tensile,MPa</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Elongation %</td>
<td>20</td>
<td>50</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Bulk conductivity, W/mK</td>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Test Method E1559
ASTM E 1559 is an additional test method used to characterize materials by monitoring the outgassing kinetics and identifying the volatile components of the material. The isothermal outgassing test apparatus is explained in detail by Garret et al., and will only be discussed here briefly. A schematic of the ASTM E 1559 test stand is shown in Fig. 7. The material sample can range from 0.5 g to 10 g and is placed in a temperature-controlled effusion cell in a vacuum chamber. All samples are preconditioned in accordance with ASTM E 595, unless otherwise specified.

Outgassing flux leaving the effusion cell orifice condenses on four Quartz Crystal Microbalances (QCMs) that are controlled at selected temperatures. The QCMs and effusion cell are surrounded by liquid nitrogen shrouds to ensure the molecular flux impinging on the QCMs is due only to the sample in the effusion cell. The TML and outgassing rate from the sample are determined as functions of time from the mass deposited on an 80 K QCM and normalized with respect to the initial mass of the sample.

The amount of outgassing species that are condensable, VCM, is measured as a function of time from the mass collected on the 298 K QCM. After the outgassing test is complete, the QCMs are then heated to 398 K at a rate of 1 K/min. As the QCM heats, the deposited material evaporates. The species that evaporate can be analyzed by a mass spectrometer to quantitatively determine the species observed.
**Fig. 6. Schematic of A1559 test stand.**

**E1559 Comparison Results**

To better characterize the two best low outgas materials, CV- and SCV-, both materials were tested via E1559. Fig. 7 shows TML levels using E1559.

![Graph showing TML levels using E1559](image)

**Figure 7. TML using E1559**

**Fig. 8. Total Mass Loss of CV- & SCV- as a function of time.**

Fig. 9 shows the total outgassing rate data as a function of test time for CV- and SCV-. These outgassing rates are for species condensable at 80 K and thus would not include certain gases such as nitrogen and oxygen.

![Graph showing total outgassing rate](image)

**Fig. 9. Total Outgassing Rate for CV- & SCV- as a Function of Test Time**

(Species Condensable on 80 K QCM).
Fig. 10 shows the mass collected on the 80K QCM as a function of time and temperature. This clearly demonstrates that there can be a profound difference in the mass that outgasses when optimized to be Ultralow Outgassing™.

Conclusion
As devices and processes become more advanced and sensitive to molecular contamination, more characterization of the construction materials must be obtained. Ultra low outgassing specification requirements of ≤ 0.1% TML and ≤ 0.01% CVCM can be useful in the overall management of outgassing species. The results from kinetic outgassing data allow engineers to better predict the levels of contamination, migration, and deposition of the material. Achieving these lower levels does not show to compromise physical properties and thus a broad range of silicone materials with unique and specific properties and cost are available.

REFERENCES

Biography
Bill Riegler is the General Manager Asia for NuSil Technology LLC. NuSil, established in 1979, is a 400 employee, private silicone manufacturer, headquartered in the United States. Bill has a BS in Chemistry and a Masters in Business and has been in the silicone industry for almost twenty five years.

Michelle Velderrain is Technical Specialist for NuSil’s Electronics/Optoelectronics materials. She has a BS in Biochemistry and has spent 13 years at NuSil in various technical positions.

T.Y. Lim of Sim Yee Engineering Resources is the exclusive representative for NuSil in S. East Asia. He has spent over a decade in the electronics industry in various technical roles.
**HARDNESS TESTING OF PLASTICS – SHORE DUROMETER**

The hardness of plastics is most commonly measured by the Shore® (Durometer) test or Rockwell Hardness Test. Both methods measure the resistance of plastics toward indentation and provide an empirical hardness value that doesn't necessarily correlate well to other properties or fundamental characteristics. Shore Hardness, using either the Shore A or Shore D scale, is the preferred method for rubbers/elastomers and is also commonly used for 'softer' plastics such as polyolefins, fluoropolymers, and vinyls. The Shore A scale is used for 'softer' rubbers while the Shore D scale is used for 'harder' ones. Many other Shore hardness scales, such as Shore O and Shore H hardness, exist but are only rarely encountered by most plastics engineers.

The Shore hardness is measured with an apparatus known as a Durometer and consequently is also known as 'Durometer hardness'. The hardness value is determined by the penetration of the Durometer indenter foot into the sample. Because of the resilience of rubbers and plastics, the indentation reading may change over time - so the indentation time is sometimes reported along with the hardness number. The ASTM test method designation is ASTM D2240 00 and is generally used in North America. Related methods include ISO 7619 and ISO 868; DIN 53505; and JIS K 6301, which was discontinued and superceded by JIS K 6253.

As seen in the charts below, the correlation between the two Shore Durometer hardness scales is weak; attempts at conversion between the scales are therefore discouraged. The correlation is higher for materials with similar resiliency properties, but is still too low for reliable conversions. Likewise, conversion between Shore Hardness and Rockwell hardness is discouraged.

**Comparison of Shore Hardness Scales**

![Graph comparing Shore A vs. Shore D hardness](Data from matweb.com)
PART DESIGN

Wall Thickness

The wall thickness does not have to be uniform because the material does not sink like thermoplastic. Very thin walls are possible with silicone molding even down to 0.005 in / 0.127mm.

Tolerances and Molded Part Shrinkage

Tolerances for molded parts are directly related to part shrinkage. The best practice is to build a test shrinkage mold of the part and use data to build prototype or production mold. The variations between lots of Liquid Silicone is little compared to thermoplastics therefore tolerances can be a lot closer. Tolerances of +/- .002 in / .050 mm are attainable.

If a fit tolerance is required it is best to fit the silicone molded part to the fitted part, since measurement of a silicone molded part requires no contact measurement and measurements under .002 in / .05 mm are very difficult.

Tolerances:

"A2" Precision Drawing Designation

Dimensional Tolerance Table for Molded Rubber Products

<table>
<thead>
<tr>
<th>Size (Millimeters)</th>
<th>Above – Included</th>
<th>Fixed</th>
<th>Closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 10</td>
<td>+/- .16</td>
<td>+/- .20</td>
<td></td>
</tr>
<tr>
<td>10 – 16</td>
<td>.20</td>
<td>.25</td>
<td></td>
</tr>
<tr>
<td>16 – 25</td>
<td>.25</td>
<td>.32</td>
<td></td>
</tr>
<tr>
<td>25 – 40</td>
<td>.32</td>
<td>.40</td>
<td></td>
</tr>
<tr>
<td>40 – 63</td>
<td>.40</td>
<td>.50</td>
<td></td>
</tr>
<tr>
<td>63 – 100</td>
<td>.50</td>
<td>.63</td>
<td></td>
</tr>
<tr>
<td>100 – 160</td>
<td>.63</td>
<td>.80</td>
<td></td>
</tr>
<tr>
<td>160 &amp; over</td>
<td>X.004</td>
<td>X.005</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Size (Inches)</th>
<th>Above – Included</th>
<th>Fixed</th>
<th>Closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – .40</td>
<td>+/- .006</td>
<td>+/- .008</td>
<td></td>
</tr>
<tr>
<td>.40 - .63</td>
<td>.008</td>
<td>.010</td>
<td></td>
</tr>
<tr>
<td>.63 – 1.00</td>
<td>.010</td>
<td>.013</td>
<td></td>
</tr>
<tr>
<td>1.00 – 1.60</td>
<td>.013</td>
<td>.016</td>
<td></td>
</tr>
<tr>
<td>1.60 – 2.50</td>
<td>.016</td>
<td>.020</td>
<td></td>
</tr>
<tr>
<td>2.50 – 4.00</td>
<td>.020</td>
<td>.025</td>
<td></td>
</tr>
<tr>
<td>4.00 – 6.30</td>
<td>.025</td>
<td>.032</td>
<td></td>
</tr>
<tr>
<td>6.30 &amp; over</td>
<td>X.004</td>
<td>X.005</td>
<td></td>
</tr>
</tbody>
</table>

Shrinkage

- Occurs during molding and post curing or until fully cross-linked.
- Varies by manufacture and product range from .025 per inch.
- Increased during post baking.
Coefficient of Thermal Expansion

Silicone has a high thermal expansion coefficient and can be used as a temperature activation method or sensor in the design. This expansion is an advantage for sealing applications.

The coefficient of volumetric thermal expansion for all silicone rubber products is in the range of 5.9 to 7.9 $\times 10^{-4}$/°C. The linear coefficient of thermal expansion is roughly one-third of the volumetric coefficient of thermal expansion, and can be used to calculate the total linear thermal expansion of a rubber part over a temperature range.

**Example:**
If the volumetric coefficient of thermal expansion is $5.9 \times 10^{-4}$/°C and the temperature span is 150°C, the total linear expansion of a part one-inch long would be ...

\[
\frac{5.9 \times 10^{-4}}{\text{°C}} \times 150 \text{ °C} \times 1 \text{ in.} = 0.0295 \text{ in.}
\]

Thermal and Electrical Conductivity

Thermal values for any thermal insulating material usually range from 0.330 to 0.515 $\times 10^3$ g-cal/sec/cm²/cm/°C. An electrical value for any electrical insulating material is the value of dielectric strength changes combined with the thickness of the test specimen. For a 10-mil sample silicone rubber, 1000 volts per mil is quite normal.

Silicone is a good insulator and can be compounded to be a good thermal conductor as well by adding certain fillers. A good example of this would be silver.

(See [http://www.siliconesolutions.com/elec_therm_conductive.html](http://www.siliconesolutions.com/elec_therm_conductive.html) for more details)

Optical Properties

Silicone is now being used to replace plastic and glass optical lens. Some Silicone refractive index can equal that of glass (1.53), and are optically clear. It is even possible to have higher surface finishes than typical glass lens at a reduced cost.

The advantages for using Silicone over plastic are UV aging, ability to operate at high temperatures, and the wider spectrum of transmission compared to acrylic and polycarbonate.

**Silicone LED Lens**

(by Albright Technologies, Inc.)

**http://www.Albright1.com/**

Other products that take advantage of Silicone’s Dynamic Properties are:

- Anti-vibration pad
- Spring
- Flexible connection
- Pushbutton (that snaps back)
- Hinges
- Bumper
Radii and Fillets

Radii and fillets improve a product’s appearance and increase its tear strength.

Surface Finish

The surface finish matches the mold texture down to the micron level. Surface finish can be dull, very shiny, or include part identification marks. Surface finish has a direct bearing on the coefficient of friction.

*Note:* Textured surfaces provide better part releases when molding than polished surfaces.

Draft Angles

Draft angles are not required on silicone parts that can be deformed to remove from the mold. Solid parts should have draft angles.

Undercuts

Undercuts on de-formable parts are obtainable. The parts can be stretched to approximately four times their size to remove from cores without deforming the part. Isopropyl Alcohol can be used to assist in expanding the parts to remove from cores or to assemble. The parts will contract once the Isopropyl Alcohol evaporates.

*Note:* Under cuts do not normally require expensive actions (slides) for the mold.

Parts can be rolled off the cores as described in the diagram below.

Parting Lines and Gate Location

Silicone parts are flexible and can be molded over cores allowing the parting lines to be put at the most desirable locations. But as shown in the diagram below most of the parting lines are straight because silicone can flash at .0001 in/. Irregular parting lines are very difficult and should be avoided.
Note: Compression has no gate vestige.

Over-Molding

Silicone rubber can be used to over-mold plastics, metals, electrical connections, electronics and heaters. It has good adhesion, is a good electrical insulator and will keep out moisture.

Bonding of the silicone can be achieved by any of the following methods:

- Mechanical bonding with under cuts on part to be over-molded
- Use of primes on part to be over-molded
- Use of self-bonding silicones

Post curing will assure molded parts are fully cross-linked.
Bonding silicone to metal can be seen in this handle used for medical imaging equipment.

**Silicone Over Molded Metal Handle**
*By: Albright Technologies, Inc.*

---

**Heat Aging Effects on Silicone’s Mechanical Properties:**
*Source: Dow Corning, [http://www.dowcorning.com/content/rubber/rubberprop/thermal_aging.asp](http://www.dowcorning.com/content/rubber/rubberprop/thermal_aging.asp)*

As silicone rubber is heat aged at temperatures from 150 to 316°C, it gradually hardens and loses its elasticity. However, certain properties may improve. Resistance to compression set normally improves when the sample is heat aged before compression. Tensile strength shows various changes, depending on the rubber being tested. It may decline slowly, remain fairly stable, or may even increase somewhat with continued heat aging. Heat aging performance can be improved with special compounding.

---

**A. Effects on Tensile Strength**
B. Effects on Elongation

Elongation change for heat-stable *Silastic* silicone rubber when aged at 150°, 200° and 250°C (302°, 392° and 482°F)

C. Effects on Hardness

Hardness change for heat-stable *Silastic* silicone rubber when aged at 150°, 200° and 250°C (302°, 392° and 482°F)
**MEDICAL MARKING**

**Laser Marking**

Laser marking provides an ideal permanent marking solution on medical products. Direct part marking eliminates the need for inks, dyes, glues, chemicals, adhesive labels and other high maintenance and or inflexible marking methods.

- Lot Code Tracking
- Product Branding
- Regulatory Marking
- Serialization
- Bar codes / Data Matrix
- Private Labeling

**Inks**

Electronic tags (RFID tags)
SPECIFYING LIQUID SILICONE MEDICAL RUBBER PARTS

The following are some of the specification items. How demanding the specification determines the cost of the tooling and parts.

Material Supplier and Material: Example: Wacker 303060
Durometer – (with value): Example: Shore A 60 Durometer
Color: Typical choices are clear, transparent, color match for tint, solid color. Include color dispersion manufacture product number and percent color.
Part Identification: Laser marking or ink marking.
Dimensional Tolerances: Typical from +/- of .002inch or +/- 0.051 mm to +/- .005 inch or +/- 0.127 mm. Note: in specifying tolerance of a silicone rubber part method of measuring the part tolerances should be considered.
Flash Tolerances: When the two halves of a mold come together there will be flash. It might not be visible without magnification. Typical flash tolerances for parts are projection down to 0.002 inches / 0.127 mm and flash thickness of 0.003 inches to 0.0076 mm and up to what can be tolerated.
Mitre Tolerances: (Mold Miss Match) Alignment of the two mold halves if critical should be specified could affect wall tolerances. Typical mitre could be tolerance of +/- of .002 inch or +/- 0.051 mm.
Air Bubbles: Can effect part performance and vary from no visible to not visible under value of magnification.
Contamination: Surface and part vary from no visible to not visible under value of magnification.
Post Baking: Is important for medical application so that all cross-linking is completed. If cross-linking is not completed possible part will produce volatiles as it completes cross-linking. Post baking time and temperature relates to max part cross-section.
Packaging: Should be double poly bagged and each bag sealed, and labeled.
Validation: Should include material certification and your requirements.

Prototyping Liquid Silicone Medical Rubber Parts:

Strongly recommended to:

✓ Determine the correct silicone material for the properties required.
✓ Choose a durometer and mold parts in that durometer and higher and lower value—note different durometers and manufactures effect the shrink.
✓ Check Fits.
✓ Determine shrink values for part.
✓ Reduce risk in building production tool.
EXAMPLES OF SILICONE PRODUCTS

Delta® Valves
The PS Medical valve is designed to minimize over drainage of cerebrospinal fluid (CSF) and maintain intraventricular pressure (IVP) within a normal physiologic range, regardless of patient position. The normally closed Delta chamber mechanism opens in response to positive ventricular pressure. Working with the membrane valve, this mechanism minimizes over drainage by utilizing the principles of hydrodynamic leverage. All Delta valves incorporate a central reservoir dome, occluders for selective flushing, and a non-metallic design. The valves are fabricated of dissimilar materials -- polypropylene and silicone elastomer -- reducing the chance of valve sticking and deformation. Radiopaque indicators provide an indication of valve-to-catheter approximation.

Silicone for Prosthetics
One good source of information is [http://www.factor2.com/](http://www.factor2.com/). For technical support contact David Trainer.

The incredible story of Mark Tatum found on the factor2 website shows one of the most miraculous uses of silicone rubber in prosthetics. For more on this story see [http://www.factor2.com/Overview_Pages/mark_tatum.asp](http://www.factor2.com/Overview_Pages/mark_tatum.asp).
Glossary of Silicone Terms

An excerpt from The Silicone Elastomer Handbook

Written By: David Brassard

Edited By: Mr. David Crossan, Sr. Editor

**Abhesion** - lack of adhesion, easy release from substrates.

**Abrasion** – surface wear from friction.

**Acetoxy cure system** – a tin catalyzed moisture cure system that liberates an acetic acid/vinegar odor by-product upon curing.

**Adhesion** – the bonding to a substrate by an adhesive or other agent. May be chemical, mechanical, or a combination of both.

**Adhesion promoter** – a silane or zirconate compound which enables a self-priming bonding capability when utilized in adhesives.

**Adhesive** – elastomers, resins or PSA’s that are designed to display self-bonding properties to substrates without primers

**Addition cure system** – a reaction between a two PDMS polymers, where no by-products are generated. Typically referred to as Platinum cure systems, where vinyl terminated PDMS and a methyl hydrogen copolymer PDMS crosslink with a platinum catalyst.

\[
\text{Si-H} + CH_2 = CHSi \rightarrow SI\text{CH}_2\text{CH}_2Si
\]

Can also be a peroxide initiated, free radical cure between two PDMS methyl groups or a methyl and a vinyl group, or two methyl groups resulting in crosslinking of a silicone.

**Agglomerates** - large clusters of aggregates and primary particles. In fumed silica’s, they are attracted by hydrogen bonding of the surface silanols. They can be broken apart through shearing.

**Aggregates** – are clusters of primary particles. In fumed silica’s, they are attracted by hydrogen bonding of the surface silanols. They can be broken apart through shearing.

**Alkoxysilane** – a compound containing a central silicon atom and an Si-OR functionality, where R represents a aliphatic organic group. Upon hydrolysis, generates a alcohol molecule.

**Application time/life** - the usability time of the product after catalyzation is measured here. Often identified as how long until a product will not flow, enable tooling or application into the assembly. Also known as work life, pot life.

**Application rate** – used to measure the flow of RTV sealants from a semco tube. Material is extruded from a semco tube at a stated pressure, usually 60 or 90 PSI through a standard orifice. Reported in grams per minute.
**Antifoam** – a liquid product that when added to a composition retards or inhibits the development of a foam in the composition.

**Arc Resistance** – denotes the resistance of a material to a to an arc produced by an electrical current between two electrodes.

**ASTM** – American Society of Testing Materials, they define standard test methods for industry.

**Base** – a silicone compound that is only partially compounded with fillers. Often un-colorized and un-catalyzed, fabricators of finished rubber parts use bases in formulating their own special compounds.

**BET surface area** - is a method developed by Brunauer, Emmet and Taller in 1931, which is a means of displaying the surface area of powders by measuring the amount of gas absorption under varying pressure conditions. The larger the BET gets, the smaller the primary particle and the larger the surface area of the powder. The BET value relays the square meters of surface area per gram of powder.

**Bladder cure** - a surface only cure condition in a deep section cured product

**Bleeding** – the surface release of a plasticizer or incompatible liquid component from a cured elastomer. Can also identify a oil separation from an uncured product.

**Blow-out resistance** – a green strength – resistance to be displaced while in an uncured state found in some sealants, useful in assembly applications, especially automotive engine assembly.

**Brittle point** – denotes the lowest temperature than an elastomer can be subjected without breaking or shattering upon sudden impact or stress.

**Bulk modulus** – is the elastic/energy absorption capability property of an elastomer when compressed. Silicone rubber will deform approximately only one half of what an organic rubber will when exposed to the same stresses. This is due to the siloxane bond spacing and the high free volume in a crosslinked matrix.

**By-products** – the evolved reaction materials of a condensation cure silicone with moisture. These typically generate the odor found when silicones cure.

**Catalyst** – is a reagent that when added to a compound, initiates a chemical reaction, but is not consumed by the reaction.

**Caulk** – is a compound that is used to fill crevices to enable a moisture or weather-proof seal.

**Centipoise** = a unit of measure for liquid materials. One hundredth of a poise. (centistokes x specific gravity)

**Centistokes** = like centipoises, it is also a method of defining the viscosity of liquids. (centipoises / specific gravity)

**Chain extension** – a process where a high molecular weight linear polymer is fabricated from many lower molecular weight linear components.

**Chain stopper** – an M unit utilized in polymerization reactions, which limits chain growth by having only one hydrolyzable or reactive functional group on the molecule.
**Chlorosilane** – a compound containing at least one Si-Cl bond. Silanes typically being tetrafunctional, have multiple chlorines and/or organic components. These are the building blocks of silicones.

**CIPG** - cure in place gasket. Applying a wet silicone to a part & allowed to dry. Then the part is compressed onto the other substrate compressing the gasket. Compression forces maintain the seal. Adhesion to only the first substrate is required to hold the gasket in-place during assembly.

**Coefficient of thermal expansion or CTE** – the material’s fractional change in dimensions typically measured in length for a given unit change in temperature.

**Cohesion** – the strong attraction of a substance to itself enabling a high resistance to splitting or tearing. Often accomplished through the chemical bonds from crosslinking and reinforcement.

**Condensation cure system** – a composition, which is capable of a reaction between silanol terminated polydimethylsiloxane and multifunctional crosslinker with a catalyst. This reaction creates a water molecule.

\[
\text{Si-OH} + \text{AcOSi} \rightarrow \text{Si-O-Si} + \text{AcOH}
\]

**Compatible** – materials that can be mixed or blended without any chemical reaction or separation taking place.

**Compound** – this has very different meanings:

1. a substance containing two or more elements united in definite proportions by weight.
2. to mix or incorporate finely divided solids into a polymeric material.

**Compression set** – the reduction in thickness of a material caused by the loss of a spring-back capability after being in a compression condition for a period of time. This spring-back capability is key as it creates the sealing forces of a rubber in a compression gasket application.

**Copolymer** – is a compound that contains two different chemical structures within the backbone as the repeating units.

**Creep** – is a cold flow like deformation of a cured elastomer under a load

**Crepe Hardening** – the thickening of an uncured silicone upon ageing caused by hydrogen bonding. Can be offset by softening on a mill or shearing in a mixer.

**Crosslinker** – a silane or methyl hydrogen compound, which when utilized properly in compositions, will enable the formation of chemical bonds.

**Crosslink density** – the concentration of chemical bonds within a cured rubber or elastomer. Measured by durometer and modulus.

**Crosslinking** – a series of reactions that occur as an uncured silicone material cures to form a cured material.

**Cryogenic** – having a very low temperature, in the range of –200°F and lower.

**Crystalline** – is a solid with a very regular, lattice molecular architecture.
**Cure moderator** – cure moderators are added to formulations to function as a timer to delay cure. Very low molecular weight components will preferentially crosslink prior to the higher molecular weight components. Slowly increasing in molecular weight until the viscosity meets the base polymer, then the product would rapidly cure. Through formulation, they enable a very accurate 2 to 30 minute open time prior to a rapid cure.

**Cure speed/time** – The time required to convert the silicone elastomer to cured rubber. Example: 24 hours for 1/8” diameter bead at 77°F and 50% relative humidity or 15 minutes @ 150°C.

**Curing**– a crosslinking reaction which enables silicone liquids, pastes or rubber compounds to harden to a three dimensional matrix.

**Curing agent** – a material which when added to a second material, brings about a chemical reaction, usually causing the hardening of the entire mass.

**Cureometer** – a test device, which measures polymer properties as it cures/crosslinks.

**Cure time** – the time lapsed between the addition of a catalyst and the complete hardening of a material.

**Cyclomethicone** – a low molecular weight cyclic PDMS usually D-3, 4, or 5 and sometimes blends. This is a term utilized by the healthcare industry.

**Cyclics** – a term used to depict the volatile oligomeric components often found in silicone materials as a result of incomplete copolymerization. These can be removed through post baking parts or devolatization of polymers. Cyclics are compounds that are in closed rings as opposed to linear, aliphatic chains.

**D-4** – is industry shorthand to typically depict octamethylcyclotetrasiloxane, a volatile low molecular weight cyclic oligomer. Vinyl D-4 has a vinyl functional group substituted on each silicon atom for a methyl, resulting in a methyl and vinyl group being pendant on each silicon atom.

**Deep section cure** - a silicone product that is formulated to enable cure to any depth or dimension. Most typically found in a 2-part product where all components required for cure are incorporated. Unlike a 1-part moisture cure, which requires atmospheric moisture permeation and cures slowly from the outside in.

**Dehydrogenation** – a chemical reaction where hydrogen is released from a compound.

**Density** – mass per unit volume, as compared to water. Typically reported in grams/cubic centimeter.

**Dielectric strength** – the point when a material loses its insulation capability and enables an electrical current to pass through. Typically measured in volts at a given thickness.

**Dilatant** – a rheological capability to display increasing hardness upon exposure to shear.

**Dimethicone** – another healthcare industry term for Trimethyl terminated PDMS fluid. It is also called simethicone. Found in many consumer products, skin and anti-flatulence preparations just to name a few.

**Dimethylsiloxane** – see PDMS
Dipodal – a silane having twice the level of the typical trimethoxy functionality. This silane molecule will have two functional pendant hydrolysable trialkoxy groups. One is found at each ends of the molecule.

Dispersions- elastomeric or resinous product dissolved in a solvent carrier. Dispersions are applied to substrates and allowed for the solvent to evaporate prior to use. A dispersion allows a very thin film to be applied.

Durometer – resistance to indentation. The measure of the crosslink density of a rubber sample via ASTM D-2240.

Endcapping – The functionalization of a polymer terminus.

Elastomeric – is a rubber-like substance displaying a stretching capability. Some define as the ability to stretch to at least twice its length under light stress and snaps back to its original length upon the release of the stress.

Elongation – (elongation at break) the ability of the test piece to be stretched without breaking. Given in % of original dimension @ maximum elongation. Maximum elongation is determined by attaining the point of breakage. Typically measured via ASTM D-412.

Emulsion – is very small droplets of oil uniformly suspended in water, typically accomplished through the aid of chemical emulsifiers and high speed milling or high pressure homogenization.

EMI/RFI – electromagnetic interference or radio frequency interference are applications that require shielding of cables and apparatus. Electrically conductive silicones are used for shielding.

Encapsulation – the complete surrounding of an electronic component or complex of components with a coating of an insulative material. The purpose is to protect the component from adverse environmental conditions.

Extrusion rate – a measurement of the flow capabilities of a material by dispensing through a narrow orifice under pressure and measuring the grams per minute. Typically tested at 60 or 90 PSI and through a 1/8 orifice.

Fast cure – an order of magnitude faster than typical – Most R.T. cures are slow

Filler – a finely divided powder formulated into a composition to either enhance physical properties or reduce the overall cost of the composition.

FIP – form in place gasketing, RTV’s are applied wet, conforming perfectly to the gap upon mating excess sealants pushed-out. The wet sealant then cures forming a gasket. The gasket seals the two flanges by adhering to each exposed part.

Firm time - an old GE term, the time to obtain 40 Shore A min. in an 2-part tin catalyzed system

Flash point – the temperature that an materials vapors will ignite when it is exposed to an ignition source.

Flowable – a material that is in a liquid state at room temperature and will fill all of the voids in the container into which it is poured.

Fluid – typically defined as a material that will take the shape of any vessel containing it. However, in silicone technology it also refers to a non-functional silicone PDMS polymer of low viscosity
whose terminal groups will be trimethyl. A fluid is the opposite of a resin, which is functional and can be crosslinked. Repeating groups on the polymer backbone can be of a wide variety.

**Fluorosilicone** – a silicone PDMS material with varying levels of trifluoropropyl functionality along the backbone chain. They can be either functional or non-functional.

**Foam** – a silicone rubber containing many gas pockets formed during cure, creating a cellular structure. These voids can be caused from the release of hydrogen gas or a blowing agent, often thermally activated.

**Freshening** - the milling or working of an uncured silicone to break hydrogen bonds and enable better processability.

**Fumed silica** – a very fine silicon dioxide, typically formed through the pyrolysis/flame hydrolysis of silanes.

**Functionalization** – the complexing or chemical reaction of a pendant group with a reactive species, often silanes, which results in a change in activity or potential.

**Gel** – a soft, compliant, lightly crosslinked silicone elastomer. Some display a semi solid-form.

**Gel time** – The period of time from initial mixing of flowable reactants in which the material becomes too viscous to flow or be tooled caused by crosslinking to a pre-cure elastomeric state.

**Glass transition temperature, Tg** – the temperature where a brittle solid will soften to a liquid, gel, or if an elastomer, start to display elastomeric behavior.

**Grease** – lubricating products made by thickening fluids with suitable fillers.

**Green strength** – a resistance to be displaced while in an uncured state found in some sealants, useful in assembly applications.

**Gum** – a very viscous polymer sometimes filled with silicas used as a base for rubber compounding. Viscosity is often > 1,000,000 cps.

**Hardness** – Shore A – a scale of measurement used to define the relative hardness of materials.

**HAV** – hot air vulcanization, typically refers to either the curing technique or the actual ovens used to cure elastomers. The ovens can be vertical or horizontal.

**HCE** – stands for high consistency elastomer, or heat cure elastomer. An older term, which is less utilized today.

**HCR** – heat cured rubber or high consistency (silicone) rubber. Crosslinkable with heat, HCR is typically molded with very high pressures. Often highly filled, the very thixotropic silicone rubber appears to be a solid in an uncured state. Also called a HCE, heat cured elastomer.

**HDPE** – stands for high density polyethylene.

**Headspace** – the unfilled portion of a container that is occupied by a gas.
Heat cured – 1 or 2 part product that typically crosslinks into a hard, cured product upon exposure to heat.

Heavy-bodied – an uncured polymer exhibiting a very high green strength or blow-out resistance in an assembly test condition.

Heat cure – a reaction where external heat is applied to either accelerate or initiate a chemical crosslinking to result in a desired end product.

Heat sink – the ability to rapidly transmit heat from a generating component.

Hidden silanols – silanols that are hidden inside of the particle not deactivated in a treatment process.

HMDZ – is an industry shorthand term for hexamethyldisilazane, a very hygroscopic water scavenger and treatment agent.

Humidity – the amount of water vapor present in the air at a given time and place.

Hydrolysis – the reaction of a reactive species like a silane with water generating a by-product.

Hydrolyzable – a reactive species like a silane that will rapidly react with a water or a silanol functionality.

Hydrosilation – a chemical reaction in which a vinyl functional polymer will crosslink with a hydrofunctional polymer.

Hydrolytic stability – the degree of relative resistance to attack of a material by water or water vapor.

Hydrophillic / Hydrophillicity – is a high affinity or attraction to water.

Hydrophobic / Hydrophobicity – is a repulsion of a material to water.

Hygroscopic – is the capacity in which a material will absorb or retain water.

Inhibitor / Inhibition – a volatile reagent intentionally added to a batch, used to delay curing and control open time or work time. Typically evaporated during heat curing.

Instant cure – a rapid room temperature or heat accelerated room temperature cure, usually within 1 minute.

Insulate – to prevent the passage of an electrical current by imposing a barrier substance in the path of the current.

Joint movement – is the movement of two rigid structures within an assembly. It can be caused from differential thermal expansion rates, vibration, shock or other means. Also defined as the ability of a sealant to conform to these movements through high flexibility and maintain a bond.

Killed polymerization – the cessation of a polymerization due to deactivation of the catalyst and/or introduction of a chain stopper.
Lamination – is fully enclosing an adhesive between two sheets, disallowing exposure of the surface, preventing off gas and surface cure. Condensation cured silicones require exposure to air for full cure and cannot be used in a lamination application.

LDPE – low density polyethylene, can allow moisture to permeate in the gas phase.

Ligand – is a pendant organic component of a molecule.

LMW – low molecular weight

LSR – liquid silicone rubber. Actually it’s a misnomer, the products are mostly of a thick paste consistency. It’s a pumpable, moldable and heat curable silicone composition. Also called LIM, liquid injection molding (grade).

Masterbatch – various additives or pigments are pre-dispersed into PDMS liquids to allow ease of addition to batches in production.

Mechanical adhesion – the interlocking of an uncured elastomer with the surface irregularities, which upon curing results in a secure bond.

MeH – industry shorthand term for a methyl hydrogen copolymer. The crosslinker utilized in addition cured platinum catalyzed reactions. The hydrogen functionality can be pendent interchain, on the chain terminus, or both.

Methyl – a central carbon surrounded by three hydrogens, a typical non-functional pendant group on a PDMS molecule, typically written as CH₃.

Micron – 1 x 10⁻⁶ meter

Modulus - see Youngs and Bulk Modulus – the amount of force or energy that can be absorbed by a rubber specimen.

Monomer – an elementary molecule capable of being polymerized into a polymer.

MQ resin – a silicone macromolecule if functionalized, it will have a multitude of crosslink sites. When used properly in silicone elastomers, provides regions of high crosslink density.

Mudcracking – is the surface cracking of a sealant or coating during cure. Caused from poor formulation, weak surface, or high joint movement during cure.

Nanometer – one millionth of a meter

Neutral cure – a condensation cure system that liberates no corrosive (to metals) by-products upon curing. Alkoxy/Alcohol cure systems are neutral cure.

Oil resistance the ability of an elastomer to survive and display minimal changes in a long-term oil immersion condition.

One-part – is a ready-to-use silicone material that does not require mixing with a catalyst or other additive to form a durable rubber or adhesive.

Open time – typically defined as the time that a compound takes to double in viscosity after catalyzation. Some define it as how long a product will flow, enable tooling or application into the assembly.
**Outgassing** – the release of gaseous components from a product often accompanying a curing product by-product release or evaporation of low molecular weight components.

**Oxime cure system** – a tin catalyzed moisture cure system, which liberates an alcohol methyl ethyl ketoxime byproduct upon curing. This byproduct smells like latex paint.

**Parts** – (per hundred) is a rubber industry term depicting formulation components utilization in a formula in a amount relative to the resin (base polymer) depicted as 100 parts

**PDMS** – polydimethyl siloxanes (see siloxane)

**Peel strength** – an adhesion test measuring both the adhesion to the substrate, and the cohesive forces found within a cured rubber. It is measured in pounds per linear inch, PLI, and percent cohesive and adhesive failure. The test is characterized in ASTM D-794.

**Peelable** – displaying no adhesion for easy removal

**Peroxide** – a thermally decomposing agent added to silicone products to result in a free radical addition cure. These free radicals create reactive species from non-reactive groups. These reactive groups then form crosslinks during the curing of the compound. Both vinyl specific and general-purpose peroxides are used. Following this crosslinking route, by-products are generated which must be removed, via post-baking.

**Peroxide cure** - an addition reaction in which free radicals create reactive sites and form crosslinks.

**Phenyl** – a pendant fully conjugated benzene ring functionality on a PDMS molecule, typically written as C₆H₅.

**Plasticizers** – is typically non-functional diluents enabling a lower viscosity, or a more desired plasticity. In methyl silicones typically trimethyl terminated PDMS.

**Platinum cure** – an addition reaction between a hydride functional PDMS with a vinyl functional PDMS, which is catalyzed by a platinum salt, typically chloroplatinic acid.

**Poisons/poisoning** – an industry term that identifies a list of materials (non-toxic) that can complex and or deactivate a platinum catalyst. ie. sulfur, amines, etc.

**Polydispersity** – a characteristic of polymer where it is composed of multiple polymer molecular weight/chain lengths. It is contrary to a unimodal polymer.

**Polymerization** – a series of chemical reactions with oligomers, which result in long chains of repeated units being formed.

**Porosity** – the presence of void or air pockets in a cured composition.

**Post baking / post cure** – the exposure of a crosslinked material component after the initial heated cure to elevated temperatures in an effort to improve the mechanical properties or evaporate undesirable volatile components.

**Pot life** – the amount of time available between the moment that a catalyst is stirred into a base material and the approximate moment that it becomes too thick to apply in the recommended manner.
**Potting material** – an electrically insulative, moisture resistant material, supplied in a liquid or putty-like form and used as a protective coating on sensitive areas of electrical and electronic equipment.

**Pourable** – is a self-leveling composition that can be easily dispensed from a package as a liquid.

**Precipitated silica** – is wet process silica formed through the reaction of sodium silicate and sulfuric acid. Typically can contain up to 7% water.

**Primer** – a organo-functional silane in a multi-solvent solution. Upon application to a substrate, a silanol rich surface remains, rendering the surface highly prone to adhesion reactions.

**PSA** - pressure sensitive adhesive, typically supplied in a dispersion. Upon evaporation of the carrier, a permanently tacky, gel-like adhesive results that sticks to substrates through a light pressure application, like applying a label. The common label and sticker backings are PSA’s.

**Quenching** - is the secondary addition of a crosslinker, often with an adhesion promoter targeted at providing an enhanced shelf-stability potential.

**Reinforcement** – is adding to the strength of an elastomer system. This is typically accomplished by adding reinforcing fillers and resins.

**Rheology** – the study of the deformation and flow of materials, in terms of stress, strain and time.

**Resin** – a polymeric material often of a high molecular weight and flowable, utilized as a base raw material in elastomeric compositions. It is often a crystalline material in a solvent carrier.

**Reversion** – a de-polymerization of a cured silicone rubber into its original polymeric components.

**R.T.** – room temperature cure

**R.T.V.** – room temperature vulcanization (curing without heat)

**RTV-1** – a 1-part RTV system. No mixing, ready to use.

**RTV-2** – a 2-part RTV system. The mixing of the two components is required prior to use.

**Sag resistance** – a test that measures the resistance to flow of a one-inch plug of uncured sealant after being placed on a vertical plane.

**Scavenged /scavenger** – the chemical reactions of silanes or MeH with silica silanols, water or other functionalities rendering them less reactive.

**Scorch** – a cure speed that exceeds the design of the targeted utilization. Curing too fast at a given temperature to fully fill mold cavities.

**Self-leveling** – a high flow, syrup-like condition, unlike thixotropic

**Shawningan black** – a carbon black manufactured from a natural gas stream that is free from sulfur contamination. Typically used in platinum catalyzed addition cure systems.

**Shear** – the introduction of energy into matter via applied displacement force and or restriction of flow.
**Shelf-life** – the period of time that a packaged product is useable.

**Silane** – A highly reactive molecule having a Silicon atom as the central unit. Outside of their main utilization to produce monomers or silica, in silicones they are typically functionalized and used as crosslinkers and adhesion promoters.

**Silbond™ 40** – a 40% hydrolyzed tetraethoxy silane, typically used as a primer, hydrophobizing agent and adhesion promoter.

**Silica** – silicon dioxide in a finely divided powder form. Can be generated from quartz, precipitated from sodium silicate or created via flame hydrolysis of certain silanes.

**Silicate** – a salt of silicic acid

**Silicone plasticizers** – trimethyl terminated siloxane fluid having no functionality that cannot crosslink without the use of peroxides.

**Silicone rubber** – a crosslinked silicone polymer. It maintains its elasticity and electrical properties over a wide range of temperatures and is widely found in sealants, gaskets, insulation, tapes, etc.

**Silanol** - a Si-OH functionality. It can be found in a silica, glass and silicone polymers.

**Siloxane fluids** – polymers having a regular alternating silicon and oxygen central atoms, typically having pendant dimethyl functionality. These polymers can be functionalized interchain and at chain terminus for a wide range of applications.

**Silsequioxane** – a ladder polymer, which can provide reinforcement in compositions.

**Simethicone** – trimethyl terminated siloxane fluid, also called dimethicone by non-silicone industry formulators. Found in skin and anti-flatulence preparations.

**Skin-over** – the formation of an integral skin over the surface of a quantity of sealant.

**Softening** – reducing the viscosity of a compound by shearing which breaks hydrogen bonds. Freshening is required of HCR on 2-roll mills prior to processing.

**Solubility** – the ability of a substance to dissolve in a solvent.

**Solvent** – a material that has the ability to dissolve of other materials.

**Specific gravity** – is the ratio of the weight of any volume of a material to the weight of an equal volume of water.

**Specific heat** - the quantity of heat required to raise the temperature of one gram of a substance to one degree centigrade at 15°C.

**Starved** – a condition where a insufficient level of crosslinker or adhesion promoters exist in the uncured silicone composition. This results in very high product viscosities and or very slow to incomplete curing capabilities.

**Stoichiometry** – is the chemical balance of reactants in a reaction. Ideally one mole of A will fully react with one mole of B.
Substrate – a materials surface in which an adhesive or other agent is in contact with and acted upon.

Surface inhibition of cure – contamination of a platinum cured product by “poisons” found on a substrate, or oxygen inhibition of a peroxide cured system.

Surface tension – is an effect of the forces of attraction existing between molecules of a substance. These forces are only exerted on the surface layers.

Surface wetting – is the full surface contact of a substrate by an adhesive or coating.

Tack-free time – the time it takes for a sealant to cure to a point where none of the applied material will stick to your finger, a spatula or a plastic weighted film.

Tear strength – the resistance to the propagation of a nick or cut in a test piece when tension is applied. Given in pounds per inch (ppi), Newton per millimeter (N/mm) or (kN/m) kilo Newton per meter.

Tg – see glass transition temperature

Tensile strength (tensile at break) – the amount of force required to break a test piece. Given in pounds per square inch (PSI), mega Pascals (MPa), or Newton per square millimeter (N/mm2).

Thermal conductivity – the speed with which a material is capable of transferring a given amount of heat through itself.

Two-part – is a dual component A & B silicone material product, which must be mixed together to enable curing to form a durable rubber.

Thixotrope – an additive that imparts thixotropy to a composition generally enabling hydrogen bonding to occur.

Thixotropic – is a non-slump or sag property, resulting in no flow without pressure. Having high static shear strength and low dynamic shear strength, the material exhibits a highly predictable time-dependant loss of viscosity when exposed to shear. Viscosity decreases under steady shearing then slowly rebuilds. This is caused by Hydrogen bonds breaking and reforming.

Treated – a chemical coating applied to fillers to hydrophobize and enable enhanced processing capabilities.

Ultraviolet (UV) cure – is the process of curing resins and adhesives with high intensity UV light. Through the use of photoinitiators and certain functionalized polymers, this is made possible.

Uncured – a silicone material, which has not yet vulcanized or formed a durable rubber.

Unimodal – a polymer having a uniform molecular weight within a very narrow range.

Untreated silica – is silica filler that has no surface treatment and typically has a high surface silanol content.

Vinyl – is an unsaturated, two-carbon pendant functional group containing a double bond and capable of crosslinking with an adjacent hydride functional PDMS.

Viscosity – a relative measurement, it’s the viscous property of a fluid as measured by shear stress divided by shear rate. Usually considered to be the relative thickness or thinness of a fluid as
compared to the thickness (thinness) of water. Any viscosity value can be changed, by modifying the test conditions of shear stress or shear rate.

VOC’s - volatile organic content, any evaporative component or by-product released from a material. Measured in grams per liter.

Volatile – a liquid that changes rapidly into a vapor when exposed to air, heat, or both.

Volatile – low molecular weight un-reacted silicone materials from polymerization. Found in certain silicone polymers, these materials that can become airborne and create appearance and performance problems.

Volume expansion – a measurement of the increase in bulk or space occupied by a material in relation to an increase in temperature.

Volume swell – the amount of increase in volume of an elastomer after exposure to an aggressive condition. Typically identified in liquid immersion testing. Caused by the polymer dissipating stress via coil chains unwinding and expanding in size three dimensionally.

Youngs modulus – the amount of force per square inch to stretch a test piece to a given elongation. Typically measured @ 50, 100 or 200% elongation. ASTM D-412 test method is typically utilized.

Yield stress – yield point or flow limit is identified as the pressure applied to a sample where plastic flow of a thixotropic material starts.

Vulcanization – the curing/crossliking of a rubber composition.

Weep – is a permeability of a seal or gasket to a sealed media resulting in a wicking behavior.

Weight loss – the loss of volatile materials removed from a substance after being subjected to heat, vacuum or both.

Wettability – the ability of a substrate to attract another substance based on the relative surface tensions between the two materials, or the surface finish.

Wet-out – is to fully impregnate the surface irregularities of a substrate with an adhesive. This is accomplished either with an appropriate low viscosity or surface energy of an adhesive or with adequate application forces.

Work time/life – the usability time of the product after catalyzation is measured here. Often identified as how long up until a product will flow, enable tooling or application into the assembly. Also known as work life, pot life or gel time.

Yield point – a stress that needs to be applied to a material prior to any plastic deformation or flow to occur. With thixotropic materials, the reduction of thick phase will only be resultant upon a force or stress being applied. The yield point identifies the minimum level of stress or force that is required to apply to attain flow.
**SILICONE RUBBER SUPPLIERS, MOLDERS, MANUFACTURERS AND TESTERS**

**Liquid Silicone Rubber Suppliers:**

- Wacker .......................... [http://www.wacker.com](http://www.wacker.com)
- Dow Corning ................. [http://www.dowcorning.com](http://www.dowcorning.com)
- NuSil ................................ [http://www.nusil.com](http://www.nusil.com)
- Bluestar .......................... [http://www.bluestarsilicones.com](http://www.bluestarsilicones.com)
- GE Silicone ....................... [http://www.momentive.com](http://www.momentive.com)
- Factor 2 ............................ [http://www.factor2.com](http://www.factor2.com)
- Silicone solutions ............. [http://www.siliconesolutions.com](http://www.siliconesolutions.com)
- Smooth on ........................ [http://www.smooth-on.com](http://www.smooth-on.com)

**Medical Silicone Molders:**

- Albright Technologies, Inc  .... [http://albright1.com](http://albright1.com)

Other Silicone Molders can be found at:


**Silicone Equipment Manufactures:**

Can be found at:


**Silicone Medical Product Testers:**

- Dynatek delta........................ [http://www.dynatekdalta.com](http://www.dynatekdalta.com)

**ADDITIONAL SOURCES FOR INFORMATION ON SILICONE RUBBER**

Mfg Focus Micro molded parts June LG

Small Parts Loom Large in Silicone Molding

Molders now make medical parts that are almost invisible to the naked eye.

Written by:
Kevin Franzino
Project Engineer
Albright Technologies Inc.
Leominster, MA
www.albright1.com
www.silicone.pro

Edited by Leslie Gordon
leslie.gordon@penton.com

ARTICLE FOCUS

- Defining types of silicone
- Applying silicone to micro parts
- Why device makers should care

Medical implants are complex components made from ultra-high molecular weight polyethylene and other plastics, which act as cushions to minimize stress on the bone-metal interface. While softer than old-style metallic implants, plastic implants lack the elasticity needed for motile body features. Silicone rubber has stepped in to fit the bill.
Besides being elastic and flexible, the material is also almost entirely bio-inert. It does not corrode or break down over time in the human body. In addition, while the costs of crude oil continue to skyrocket, raising the costs of plastic and rubber elastomers, advances in chemical engineering are actually bringing the costs of silicone down. Large-scale silicone distributors provide a wide selection of specialty materials to meet growing market demands.

Add to this that silicon part tolerances have dropped from 0.010 to 0.0001in., thereby bringing parts into the micro world.

**Types of silicone**

Silicone in general comes in the form of either liquid silicone rubber (LSR) or high consistency rubber (HCR). Both can be used to mold intricate geometries. The earlier HCR form lends itself well to most conventional methods of transfer and compression molding. LSR, on the other hand, suits injection molding and processing similar to thermoplastics. Silicone rubber comes in a two-part solution and must be heated to cure, while thermoplastic comes in a one part resin that must be heated to melt and then cooled to set. The same underlying process is similar for both: Inject raw fluid material into a mold that is under pressure, wait a minute, remove a finished part, and repeat.

Contrary to popular belief, LSR materials can be compression molded with no loss of precision or feature detail. Although cycle times are longer partly because the tool must be either shuttled open and closed, or manually opened and closed by an operator, there is no need to spend time creating mold gates and sprues. Also, no time is lost in setting up the mold in the injection machine or processing in the first shot. Compression molding LSR is not practical in large-scale production, but it works well for short-run rapid prototyping. It might take an extra minute or two per part to manually operate and inject a mold, but spending an extra 20 minutes to make a dozen parts is a lot better than spending two days setting up a machine.

LSR injection molding handles complex geometries with microscopic features (features accurately repeated to the sub-micron level). An 0.03125-in. end mill was once considered a
“micro” tool bit. Compare this to the 0.005-in. ball mill that is often used in the fabrication of today’s micro molds. In fact, 0.001-in. ball mills often cut the finer mold features.

**Cutting and aligning the mold**

Tool bits with microscopic diameters have presented mold makers with a new list of fabrication issues. For example, it takes very little shear force to break a 0.005-in. end mill. To prevent this, CAM programs use low feed rates (5 to 10 in./min) and high rpms (20,000 to 30,000 rev/min) so that the cutter has time to displace any excess material in its path and avoid getting hung up and snapping in two.

Cutting the mold is just the beginning. Aligning the two halves takes extreme skill and patience. Tolerances for mitre (mold alignment) in thermoplastics typically range from ±0.003 to ±0.005 in., depending on the size of the part. However, now that parts are being created as small as 0.010 in., alignment tolerances have tightened to the ±0.0005-in. range. Because of these changes, optical-measurement devices have replaced calipers and micrometers during mold validation. Molders can see and accurately measure parts that are almost invisible to the naked eye.

While it is no easy feat, creating a micro mold for liquid silicone molding is still only half the battle. Processing and running the mold to repeatedly create microscopic parts and features has traded old problems for new problems. There are distinct advantages to producing infinitesimally small parts, the most obvious being the cost of materials is greatly diminished. A high-volume order used to take gallons of raw material, while a high-volume micro part order only takes grams. This opens the door for the use of composite materials that cost thousands of dollars a pound. For example, chemical engineers can embed highly concentrated expensive medications in a LSR matrix. When surgeons implant the fully cured parts, the medicine releases in a controlled manner, providing the patient a steadier and more accurate dose. This can eliminate forgetting pills, periodically changing I.V. bags, and pain associated with hypodermic injection.

In micromolding, shrink is a concern, but not a huge worry. LSR shrinks about 1% to 3% of its original size when it cures. Large parts require higher-level math and advanced design software to
properly calculate shrink. In a worst case scenario, the moldmaker must run multiple tool iterations to find the correctly sized part. A micro silicone part measuring 0.030 in. in length shrinks to about 0.0297 in., typically not enough for the part to go out of tolerance.

While shrink is a relatively minor concern, flash is critical. The largest allowable flash is usually 0.005 in. The simplest solution to removing flash is a secondary process, where the operator manually removes flash using precision tweezers and a microscope. But this approach is time-consuming and cost-prohibitive in long-term runs. Cryogenic tumbling for deflashing is often used as a secondary off-site process, but it becomes a problem when the parts are small enough to be easily lost, or mistaken for debris.

The best answer is to eliminate flash entirely during the molding process. For example, using tooling with features etched and keyed into the mold to provide the flash with a preferred place to flow; increasing the clamping force on the mold; and running the mold under vacuum are a few options. The best method varies with the material durometer and consistency. Ideally, dial-in the shot size precisely to accommodate only the total volume of the sprue and the part itself. Micro injection units today are capable of accurately and repeatedly splitting a milliliter of liquid material.

Silicone comes in commercially available durometers ranging from 1 to 80 Shore A. Lower durometer parts are soft, flexible, and elastic up to roughly 1,000% elongation. Higher durometer parts have a consistency closer to hockey puck rubber. This variability lets medical-device designers more closely match the physical properties of the surrounding tissues of the body with the silicone implant. Historically silicone has been used to create gaskets, valves, o-rings, and other simple components involved in more complex implant assemblies. More recently, the wider durometer choices let the material be used to create entire stand-alone implants intended for both drug delivery applications and mechanical function.

To date, silicone has been used in biocompatible adhesives, shunts, stent delivery systems, tubes, microfluidic blood testing devices, drains, catheters, punctal plugs, intra-ocular devices, cannulas, heart valves, and aesthetic implants (such as breast and testicle). As a biocompatible
elastomer, silicone rubber has doctors and biomedical engineers dreaming up new applications for use in the human body every day. As technologies in imaging, design, machining, and molding continue to advance, expect to see even more micro medical silicone parts.

Although not technically a micro part, the silicone knuckle implant is becoming widely used as a means of replacing knuckles afflicted with arthritis. These one-piece highly flexible implants lack the moving parts associated with metal joint implant assemblies. No mechanical articulations and fewer material interfaces means improved implant longevity and increased comfort. Although there are obvious benefits to the integration of silicone materials in dynamic locations in the body, what is most intriguing is the outside-of-the-box thinking responsible for the design. Silicone by itself won’t revolutionize the medical device industry, but there are still many unexplored applications for its use in the human body.

Micro molded silicone parts are resting on the face of a quarter to show scale.
The image shows common dimensions of micro medical silicone parts.
Examples of medical grade O rings show just how small they can get.

A collection of molded silicone parts feature microscopic features.