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Sylgard® Cure Inhibition Characterization

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Goal *Develop new characterization techniques, especially those that can be integrated into production scenarios, to quantify and characterize the cure inhibition of silicone elastomers.*

Background

Silicone elastomers are among the most versatile polymer materials due to their desirable properties, including good thermal and chemical stability, low electrical conductivity, biocompatibility, and good aging characteristics. The properties of silicone elastomers can be tuned giving rise to materials for a variety of applications, such as encapsulants, coatings, medical devices, microfluidic devices, and lithography. Sylgard® is a two-part, liquid silicone-based polymer manufactured by Dow Corning®.[1] Sylgard® can be modified by added cure accelerator and/or filler.[2-5] Modified formulations of Sylgard® are currently used potting materials at LANL and Pantex. One composition of Accelerated Sylgard® 184 that is used is as follow:

Resin (100 PBW total)

Sylgard® 184 elastomer (“base”) 90 PBW

Resin Accelerator 3-6559 10 PBW

Curing Agent (10 PBW total)

Sylgard® 184 curing agent 10 PBW

where PBW corresponds to “part by weight”. The compositions of each of the components in Accelerated Sylgard® 184 are outlined in Tables 1-3.[2, 6-8]

Table 1. Resin Component: Sylgard® 184 elastomer (“base”).

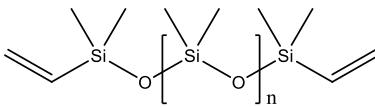
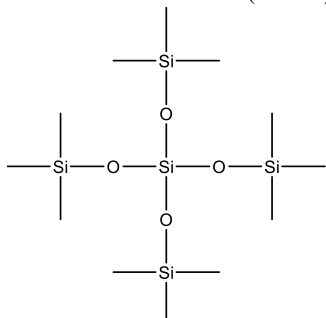
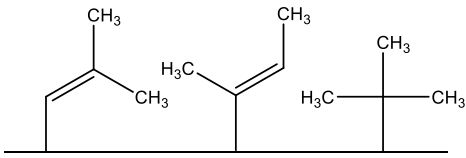
CAS #	Wt. %	Component
68083-19-2	>60.0	Dimethylsiloxane, dimethylvinyl-terminated 
3555-47-3	1.0-5.0	Tetra(trimethylsiloxy)silane  Branched volatile siloxane (VMS)
68988-89-6	30.0-60.0	Dimethylvinylated and trimethylated Silica  SiO ₂ Surface modifier Silica filler

Table 2. Resin Component: Accelerator 3-6559.

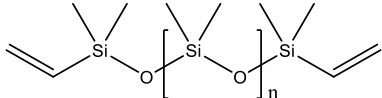
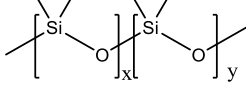
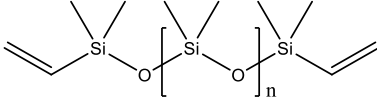
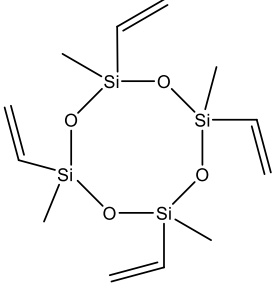
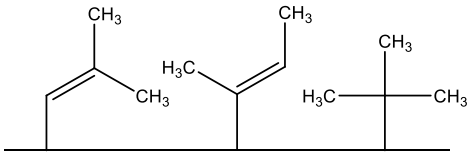
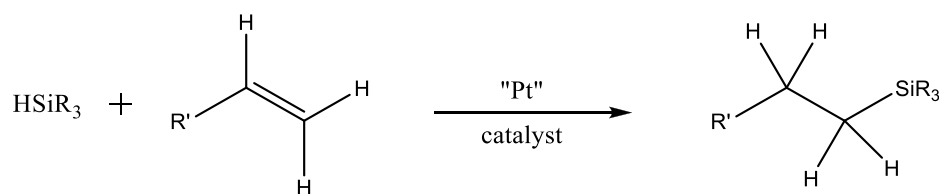
CAS #	Wt%	Component
68083-19-2	>60	Dimethylsiloxane, dimethylvinyl-terminated 

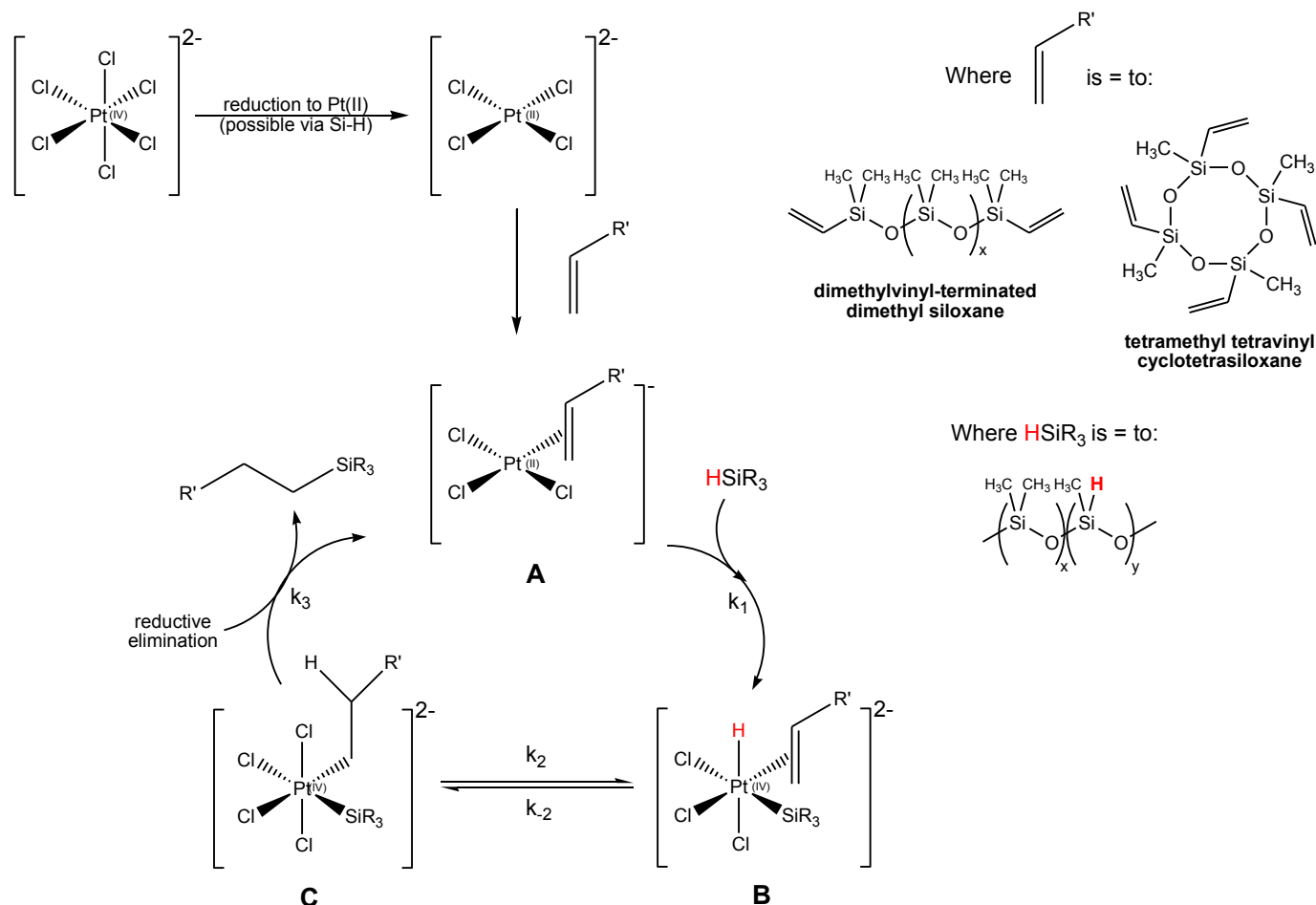
Table 3. Curing Agent Component: Sylgard® 184 curing agent.

CAS#	Wt. %	Component
68037-59-2	40.0-70.0	Dimethyl, methylhydrogen siloxane 
68083-19-2	15.0-40.0	Dimethylsiloxane, dimethylvinyl-terminated 
2554-06-5	1.0-5.0	Tetramethyl tetravinyl cyclotetrasiloxane  Network formation
68988-89-6	10.0-30.0	Dimethylvinylated and trimethylated silica  SiO ₂ Surface modifier Silica filler

Silicone elastomers are formed through the reaction of a “base”, dimethylvinyl-terminated dimethylsiloxane, with a crosslinking agent, such as tetra(trimethylsiloxy)silane, in the presence of a catalyst. The crosslinking process is usually catalyzed using platinum species such as Karstedt’s catalyst or H₂PtCl₆ through a hydrosilylation mechanism, see Scheme 1.

Scheme 1. General hydrosilylation reaction scheme.

A more detailed illustration of the hydrosilylation mechanism of platinum-catalyzed silicone elastomers is represented in Scheme 2. This mechanism was initially proposed by Chalk and Harrod in 1965.[9] A Pt(IV) species is first reduced to a Pt(II), the active catalyst. The Pt(II) species coordinates to the alkene groups. For Sylgard®, alkene groups are present in the dimethylvinyl-terminated dimethyl siloxane or tetramethyl tetravinyl cyclosiloxane based on the proposed formulation outlined in Tables 1-3. Then, an oxidative addition of HSiR_3 occurs to form species **B** that is in equilibrium with species **C**. Then, the SiR_3 is added to the alkane/alkene species and the product is released after a reductive elimination process. .



Scheme 2. General mechanism of platinum-catalyzed hydrosilylation proposed by Chalk and Harrod.

An important aspect of the mechanism in Scheme 2 is that the platinum catalyst can be poisoned or inhibited by competing reagents affecting the overall properties of the final product. These competing reagents or impurities can bind to the platinum catalyst and do not allow $\text{C}=\text{C}$ alkene species to coordinate to the catalyst thus inhibiting effective crosslinking process of the material.[1, 10] Known platinum catalyst inhibitors and poisons are:[1, 10, 11] organometallic compounds, sulfur-containing compounds, amine-containing compounds, phosphines, unsaturated hydrocarbons, and solder flux residues. Also, undesired side reactions with other functional groups can occur during the curing process. Cyclic ethers, water, alcohols, and amines (N-H) can compete for the Si-H bond forming polyethers, alkoxysilane, and silazanes, respectively.[12]

Silicone polymers, like Sylgard® are typically cured in contact with different substrates. The substrates most commonly used are polymethyl methacrylate (PMMA), polystyrene (PS), and silica although a tremendous variety of substrates are possible since silicone elastomers, especially Sylgard®, are widely used. Effective curing of silicone elastomers on a substrate strongly depends on the interfacial interactions, composition of the substrate, and potential impurities present in the reaction mixture or on the substrate surface. It is very important to understand what is occurring at the interface between the silicone elastomer and the substrate during the curing process. Network formation, formation of low molecular weight volatiles, side reactions, and inhibition could be occurring during the curing of silicone elastomers. The formation of any of the aforementioned species directly contributes to the bulk properties, more importantly mechanical properties.

Currently, qualitative observations between silicone and the contacting substrate are the only source for determining cure inhibition of platinum-catalyzed silicone elastomers. The procedure used at Pantex is based on a recommended approach from Dow Corning. The qualitative method for analyzing the curing process and determining cure inhibition is simply to examine whether the final product is tacky or not. If the final product is tacky, it means that the curing process was unsuccessful and the substrate or other impurities act as an inhibitor or a poison for curing. Currently, Pantex and Dow Corning do not use any analytical techniques to characterize and quantify cure inhibition of platinum-catalyzed silicone elastomers on a variety of substrates.

Problem

Los Alamos National Laboratory and Pantex have occasionally encountered problems during the curing process of Sylgard® materials. The composition of certain substrates or the presence of impurities resulted in failure or inhibition of Sylgard® while in contact with other materials or substrates. Specific substrates that have resulted in cure inhibition of Sylgard® at Pantex are certain glove materials, powder in gloves, and certain tapes and adhesives. It is not well understood what is taking place at the interface of Sylgard® and specific substrates. However, it is known that curing inhibition is happening because the final product is tacky to touch. Very little has been done to quantify and characterize these materials.

Overall Goal and Project Plan

In this work we will explore potential characterization techniques, especially those that can be integrated into production scenarios, capable of probing the cure inhibition of silicone elastomers. In the course of our investigation, we plan to develop methods that improve our understanding of curing and interfacial behavior of silicone elastomers, with specific focus on Sylgard® materials used in weapon systems. These studies will allow us to optimize the application process and materials used for weapon systems and also support potential surveillance activities. In addition, these studies are relevant for characterization and development of new materials for electronic potting, microfluidic devices, and coatings. Our plan is to study different techniques such as ellipsometry, FTIR microscopy, contact angle measurements to study surface energy, and mechanical testing to explore interfacial adhesion. Details on each technique are discussed below. Other techniques may also be possible.

Sample Analysis Methods

Ellipsometry

Ellipsometry is a non-destructive method for surface analyses. This technique measures and analyzes the elliptical polarization of light caused by reflection of waves from surfaces and interfaces. It is applied to measure thickness of films and optical constants. When an ellipsometer is coupled with a spectrophotometer more information from the materials can be obtained, such as composition, morphology, crystallinity, and roughness of organic and metal films. Commonly used spectroscopic

ellipsometers cover the ultraviolet (UV), near infrared (NIR) and infrared (IR) region. The two most common instruments are UV-Vis-NIR and Fourier transform infrared (FTIR) ellipsometers. The UV-Vis-NIR ellipsometer analyses samples with wavelengths in the range of 0.2-1.7 μm , and is useful for refractive indexes and morphological characterization of thin films on metals. The FTIR ellipsometer uses wavelengths in the range of 2-30 μm . This method is useful to study electric and dielectric properties and chemical composition of thin films on substrates. FTIR spectroscopic ellipsometry was recently used to study in situ the influence of interfaces on the rate of curing of silicon coatings. At LANL, FTIR spectroscopic ellipsometry was used to study and analyze the time-dependent spectral changes a compressional shock wave would cause in thin films made out of poly(methyl methacrylate) and nitrocellulose. There are two ellipsometers available at LANL, an FTIR ellipsometer currently located at TA-9-32 and an UV-Vis-NIR ellipsometer located in the Center of Integrated Nanotechnology.

FTIR Microscope

Chemical bonds absorb in the IR region at specific wavelengths. Chemical compositions of materials can be determined by their IR absorption. FTIR microscopy is basically a Fourier Transform IR with an integrated microscope. This technique analyzes single points in a material. A specific area of the material to be analyzed is located in the IR beam of the microscope and IR scans are performed on either transmittance or reflectance mode. FTIR microscopy allows analysis from nanogram scale materials with little preparation. This technique is currently applied for the characterization of artistic materials in paintings, organic coatings, inorganic samples, sample identification in forensic laboratories, and to obtain images of surfaces. The C-CDE group at LANL has an FTIR microscope in TA46-24. Specific details on the instrument are as follows:

Spectrophotometer information:

Nicolet Avatar 360:
detector: DTGS KBr
beamsplitter: KBr
velocity: 0.6329

Nicolet Continuum microscope:

detector: MTS, liquid nitrogen cooled
transmission and diffuse reflectance

ATR Accessories:

diamond crystal ATR – single bounce
horizontal attenuated total reflectance accessory diamond crystal with ZnSe interface
spectral region: 4000-525 wavenumber
germanium ATR – single bounce
germanium grazing angle – various angles

Contact angle

The surface energy across an interface, e.g. solid-liquid interface, is a measure of the energy required to form a new interface. One method to calculate surface energy is to measure the angle that a drop of a particular solvent forms at an interface with a solid. The solvents mostly used to study surface energy of silicone elastomers are water and diiodomethane. Once the angle of the drop at the interface is been determined, the surface energy is calculated using Young's equation:

$$\gamma_{\text{SL}} + \gamma_{\text{LV}} \cos\theta_c = \gamma_{\text{SV}}$$

where γ_{SL} , γ_{LV} , and γ_{SV} are the interfacial tensions between the solid and the liquid, the liquid and the vapor, and the solid and the vapor, respectively. θ_c is the equilibrium contact angle that the drop makes with the surface.

This method measures wettability of the surface. If the liquid has a very strong interaction with surface, the surface becomes wet. Wetting occurs at drop angles lower than 90 °C. For penetrant materials, or adhesives, drop angles should be close to 0 °C. On the other hand, if the liquid is not attracted to the surface, the liquid beads-up and wetting does not occur. In this case, the material under study has a low surface energy.

Mechanical properties

In addition to study what is occurring at the interface between the silicone elastomer and the substrate during the curing process, we would like to study the mechanical properties of the final product, more importantly adhesion properties. The study of these interfacial interactions is important to understand the materials general properties and device performance. Several adhesion measurement techniques have been developed, such as atomic force microscopy (AFM), JKR (Jacob, Kendall, and Roberts) measurements, pull-off test, lap-shear test, and screw-driven tensile test. These techniques measure the force applied to a material or the force required by a material until failure. These measurements provide direct indication of the strength between the elastomer and the substrate. Mechanical testing equipment is available in several groups at LANL.

This proposed work will complement current test plans involving Sylgard® materials, include solvent studies and qualitative cure inhibition work at Pantex and LANL MST-7

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