

Silicon chemistry and silicone breast implants

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Abstract Breast implants are applied to correct the size, form, and feel of a woman's breasts in post-mastectomy breast reconstruction, for correcting congenital defects and deformities of the chest wall, for aesthetic breast augmentation, and for creating breasts in the male-to-female transsexual patient. The most widely applied silicone implants have an elastomer silicone shell filled with viscous silicone gel. It has become increasingly clear that it is important for plastic surgeons to know and to provide patients with the latest information on silicone breast implants. This article was therefore written to provide more insight into the composition of silicone breast implants and their characteristics. After describing the chemical properties of silicones and silicone implants, gel bleeding and the consequences of aging of silicone implants will be discussed. The information provided can also give a hint as to why silicone implants have been consistently implicated in health issues ever since the late 1960s.

Level of Evidence: Not ratable.

Keywords Silicon · Silicone · Silica · Breast implant · PDMS · Gel bleed

Introduction

Silicone gel implants have been widely used for breast augmentation and reconstruction since the 1960s. Although their design has been altered over the years, including changes to the cohesiveness of the silicone filler gel and texturing of the shell, the basic device design remains a silicone elastomer shell surrounding a viscous silicone gel. The biocompatibility and safety of silicone implants have been a source of long-standing controversy. In this respect, it is not only important to consider effects of the elastomer shell but also of the filler gel, because over the years the majority of the silicone implants will be ruptured, i.e., tears may occur in the implant shell, which often remains undetected, and because virtually all silicone implants will *bleed* components from the filler gel. In response to many claims of implant-related systemic disease, the US Food and Drug Administration (FDA) imposed a moratorium in 1992 on silicone gel breast implants for cosmetic purposes, which ended in 2006, when silicone breast implants were re-approved by the FDA, due to failures to link systemic disease with silicone breast implants. However, it is important to note that research to elucidate this phenomenon has yet to be conducted.

To gain deeper insight into health problems that might be related to silicone breast implants, which may become manifest in only a certain subset of women, it is essential to understand the chemistry of silicone polymers, the major components of silicone breast implants. For medical professionals interested in this subject, the relevant information is scattered, too technical or too superficial, so that it becomes very difficult to grasp the chemical dynamics involved in women with these types of breast implants. It is with the aim to provide coherent information on the chemical composition

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and behavior of silicone breast implants that this overview was written.

Silicon

Various aspects of silicon-containing compounds, including silicones, have been described in a series of excellent review articles [1–6], which served as a basis for this section of our article. Silicon is the second most abundant element on earth (28 %), the first being oxygen (47 %). Elemental silicon is unknown on earth due to its high reactivity toward oxygen. It readily forms silicon dioxide, SiO₂ (silica), which occurs in a variety of morphologic forms such as sand, quartz, minerals, and glasses. In the periodic table of elements, silicon is found in group 14, immediately below carbon. Like carbon, it is normally tetravalent and preferentially forms four bonds in a tetrahedral configuration; however, being a period 3 element, it is also able to form compounds with five or six bonds. Whereas carbon, which is considerably less abundant than silicon, is the basis for terrestrial life, silicon is generally only present in minor quantities in living organisms. The main reason for this difference is of electronic nature. The silicon atom is electronically much more complex than the carbon atom, and this prevents the formation of stable complex molecular structures common to carbon. Long silicon–silicon chain structures and multiple bonds which are common structural elements in carbon chemistry and which are essential in bioorganic molecules are hardly seen in silicon chemistry. Moreover, in contrast to carbon, stable combinations of silicon with elements other than oxygen are rare. Silicon compounds with carbon, nitrogen, phosphorous, and hydrogen, do generally not occur in nature, because thermodynamically the synthesis of these compounds in biosystems is simply prevented. Silicon dioxide, silica, which is the most abounding source of silica on earth, is thermodynamically far too stable to allow such conversions. In addition, silica forms extremely stable high melting and insoluble crystal lattices which obviously also minimized the possibility of chemical changes during the evolution of life. Silicon in combination with oxygen is ubiquitous and together the silicas make up 75 % of the earth's crust. Most naturally occurring silicas are crystalline. The principal health-hazard associated with them is silicosis, which is associated with prolonged inhalation of silica dust. Amorphous silica is believed to be much less pathogenic than crystalline forms, and although it has the same basic structure, it lacks the highly ordered geometry of the crystalline forms [2].

Due to this abundance of silica on earth, living organisms are widely exposed to this material in whatever morphology. It is therefore not surprising to see that some of the material is incorporated. Wannagat [5, 6] discovered that the silicon content of living organisms decreases as the complexity of

the organism rises. The ratio of silicon to carbon is 250:1 in the earth's crust, 15:1 in humus soil, 1:1 in plankton, 1:100 in ferns and 1:5,000 in mammals. In the human body, there is usually only 5 to 10 g of silicon. In mammals and birds, silicon plays a key, but not fully understood role in the growth of hair, nails, bones, and feathers. Interestingly, at the site of a bone fracture, the silicon content increases 50-fold in the collagen web. There are also high silicon levels in unclosed epiphysis. So we may conclude that the human body has a pathway to recognize and deal with *natural* silicon and to apply it for some essential life functions. However, how carbon-based life forms interact with the inorganic world of silicon is largely unknown. In 2002, a carbon–silicon compound has been proposed as an intermediate in the biosilicification in diatoms, a form of algae [7].

Silicon chemistry

Although carbon–carbon bonds are readily formed to give a vast number and diversity of organic (carbon-based) compounds, silicon–silicon bonds are uncommon. Natural silicon–carbon bonds are extremely rare, but can nowadays be created synthetically from silica.

Academic and industrial research in particular in the field of the carbon-silicone or organic silicone chemistry started somewhere at the beginning of the 20th century, after Friedel and Crafts succeeded in synthesizing the first organosilicon compound, tetraethylsilane, in 1863 [8]. Kipping [9], who is considered the father of organosilicon chemistry, defined the term *silicone* as a generic class of materials with polymer chains of alternating silicon and oxygen atoms containing alkyl groups, e.g., methyl groups. Only from 1930 on, large scale processes were developed, which decreased the production costs tremendously [2] and which facilitated the exploration of the potential value of silicones. Depending on the length of the polymer backbone chain and the degree of cross-linking, commercially available silicones may be conveniently divided according to their physical properties. They may be fluid, semifluid (lubricant, gels), rubberlike (elastomers), and solid (resin). Silicones have an unusual array of physical and chemical properties. Key feature is the high chemical inertness of these polymers which is reflected in their thermal and oxidative stability. Important physical properties are the good dielectric strength and low surface tension and the limited dependency of these properties on temperature changes.

Silicones and implants

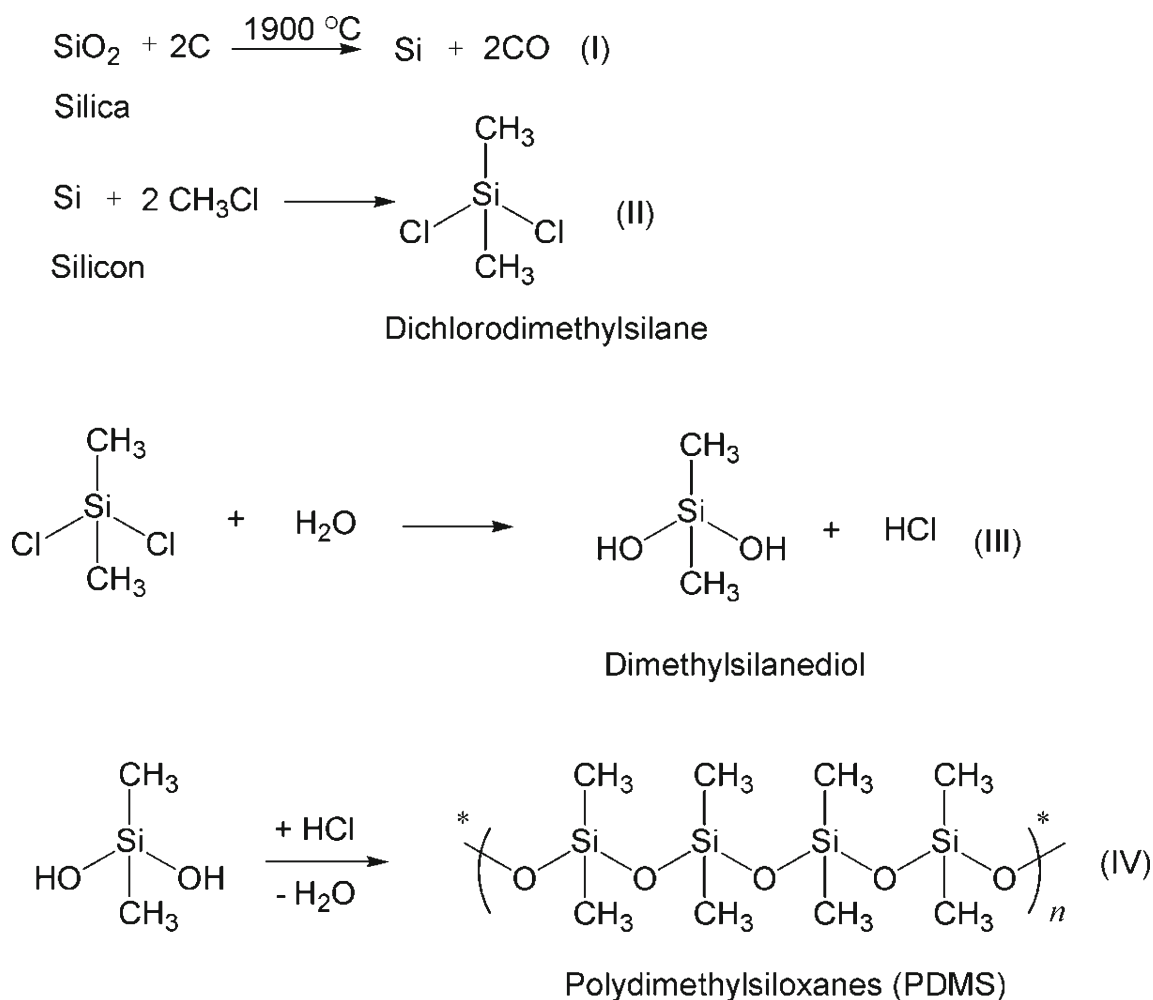
Medical interest in silicones was raised on the observation that silicone-coated glass substantially delayed blood clotting [3].

An extrapolation of this observation to a general inertness toward tissue was rapidly made. The first attempts to apply silicones subdermally were initiated already in the late 1940s. Studies by Rowe and co-workers [10, 11], which suggested that silicones were also physiologically inert and presented no health hazards, caused a boom in research aimed at finding applications for these silicon polymers in medical health care. The production of silicone is possible, because the carbon in many organic compounds can be replaced by silicon, thus combining the families of organic and inorganic chemicals. The aim is that by proper tailoring of the molecules, the tractability and softness of organic rubbers and oils can be combined with some of the chemical inertness inherent in quartz, which is not the same as biological inertness [3].

It is beyond the scope of this paper to explain in detail the chemical production processes of the basic silicone monomers, but an attempt will be made to make an overview (Scheme 1). Basically, the starting point (I) is silica (SiO_2), which is reduced with carbon to produce elemental silicon (Si), which is then reacted with methyl chloride (II) to form

dichlorodimethylsilane. In a subsequent reaction with water (III), it first produces dimethylsilanediol which, due to the presence of the formed HCl, immediately polymerizes to give dimethylsiloxanes, which contains a Si-O-backbone with two methyl groups attached to each silicon atom (IV). Siloxane is an acronym of *silicon, oxide and methane*.

Besides linear polymers cyclic oligomers are also being formed. Commercially, hydrolysis of dichlorodimethylsilane is performed either by batch or by a continuous process. The typical yield of cyclic oligomers is between 35 and 50 %. The mixture of cyclic oligomers consists mainly of tetramers and pentamers. Only a small amount of cyclic trimer is formed. The cyclic form of the tetramer is called octamethylcyclotetrasiloxane, also known as D4. Very often this is used by manufacturers in the production of silicone oil. By applying appropriate catalysts, the cyclic oligomers are opened to form linear polymers [12]. The chemical composition of the siloxanes as well as the chain length of the linear polymer is controlled by the ratio of chlorosilane to water, temperature, contact time, and solvents.



Scheme 1 Overview of the chemical production of dimethylsiloxanes

While silicones can be made with different alkyl groups, the dimethyl type is the most common and therefore, these compounds are referred to as polydimethylsiloxanes (PDMS). The physical properties of the polymers are directly related to their polymerization degree. For example, as the number of dimethylsiloxane units in the polymer increases from 2 to 150 to more than 500, the physical form changes from water-like to oil-like to jelly-like material.

Silicone fluids are usually straight chains of PDMS, which are terminated with trimethylsilyl groups. PDMS fluids come in all viscosities from water-like liquids to non-pourable fluids, and all of them are essentially water insoluble (hydrophobic). Silicone gels are lightly cross-linked to give a network type structure [13].

In the fabrication of silicone breast implants such a network can be swollen with PDMS fluid to give a sticky, cohesive mass without form. Its physical appearance is dictated by the amount of cross-linking, and how much fluid is added to the network. The PDMS fluid is not chemically bound to the cross-linked network, but is retained only by physical means. Hence, there is the possibility for leaking or bleeding. In a silicone breast implant, the gel network and the free PDMS fluid are contained within an elastomeric shell.

Silicone elastomers are cross-linked polymers with a three-dimensional structure which is much more intricate than a gel. These rubbers are made through a process generally referred to as curing or vulcanization, which is usually achieved through heating. In order to provide strong, highly elastic materials, the polymer solution is mixed with amorphous high-surface-area fumed silica particles that measure approximately 30 μm in greatest dimensions and have a surface area of approximately 400 m^2/g [3]. Fumed amorphous silica is preferred over crystalline silica as it is assumed to be less pathogenic. In addition to silica, other fillers are added in order to increase the stiffness, electrical conductivity, or radiopacity of the elastomers. These include diatomaceous earths or clays, metal oxide pigments, carbon pigments, conductive metal pigments, calcium carbonate, and barium sulphate. A vulcanized and cured medical-grade silicone rubber of the heat vulcanizing type ultimately and ideally contains only the silicone polymer, silica, and other fillers. The precise composition of these materials, however, remains controversial [3]. The extent to which a fibrous capsule is formed around the implant, as well as the contraction of these capsules, may depend on different surface textures [14]. Further research is required to reveal whether capsular contraction, in addition to gel bleeding, is related to the extent of silicones escaping from the implant.

As the elastomer shell in a silicone breast implant does not completely prevent the bleeding of the PDMS fluid of the gel [12, 15], a bleed retardation layer is added to the inner side of breast implant shells [2]. The elastomers used for this barrier coating are silicone rubbers containing phenyl (C_6H_5) or trifluoropropyl

($\text{CF}_3\text{CH}_2\text{CH}_2$) groups covalently bound to silicon. PDMS is only slightly soluble in this type of silicones, and therefore, migration of PDMS from the core of the implant to the surrounding tissue should be minimal. In this way, a generation of low-bleed implants was born. However, pathological examinations showed later [16–18] that these barrier systems are not able to completely block bleeding, as traces of silicone-containing material were present in capsules surrounding this new generation of silicone breast implants. So far no study unambiguously proved the complete elimination of silicone bleed of the content in these low-bleed implants [12].

Another point of interest is the aging of the shell of the silicone breast implants. The tensile strength of the elastomeric shell decreases throughout the years [11] as a result of an ongoing infusion of siloxanes from the silicone oil content of the implant. This is a naturally anticipated phenomenon of many elastomeric materials and can be attributed primarily to swelling effects from components of the gel and oil and not to any chemical degradation of the shell material itself. That is, swelling of the silicone elastomer and not degradation of the elastomer is responsible for loss of tensile strength over the years of implantation. If the integrity of the elastomer shell of silicone breast implants is gradually diminished, this will increase the gel bleed into the surrounding tissues and make the implant prone to rupture.

Safety of silicone gel-filled implants

In spite of the beneficial psychological effects of breast implants, alleged adverse effects of silicone gel-filled implants have been reported ever since these prostheses were used [19, 20]. Most of these effects concern local reactions to silicone exuding from the implants (gel bleed) or released by ruptures, but silicones have also been reported to migrate through the body, which have been proposed to be associated with necrotizing lymphadenitis and with systemic disorders such as autoimmune and connective tissue diseases. Over the years many articles have been published that raise concerns about the exudation of silicones [15, 17, 21, 22], about the dissemination of silicones to lymph nodes [18, 23–26] and other parts of the body [27], and about overall failure of silicone breast implants [28]. Despite the potential drawbacks of silicone gel-filled implants, the FDA is cautiously optimistic about their safety, as stated in the 2011 report [29]. The FDA recognizes that there is a high frequency of reoperations and replacements, and that women should realize that they should constantly examine their breasts. Moreover, according to this report, it is important to note that associations with ill-defined chronic diseases that are very rare or that take many years to become manifest, may not be detected using currently available procedures. A well-designed large prospective study with proper controls is

required to elucidate whether the exposure to (low molecular weight) silicones in some (genetically susceptible) individuals does or does not cause health problems.

For more details on the adverse effects of silicone gel-filled implants and the various pathologies that might be associated with the exposure to compounds of and leaking from these implants we refer to various excellent review articles, in which these topics are extensively discussed [19, 20, 22, 30].

Concluding remarks

In summary, studies have confirmed that gel bleed is present [13, 15–18, 21, 22] and that traces of the raw material, octamethylcyclotetrasiloxane (D4) can be extracted from both the gel and the shell, with the gel yielding a larger amount than the shell [12]. From a chemical point of view bleeding of silicone implants can be expected as the applied silicones contain low molecular constituents due to the manufacturing process and the desired properties. Deterioration of silicones also leads to an increase of low molecular weight material [4]. Infusion of these low molecular siloxanes into the protecting shell affects its integrity as a molecular barrier. In case of rupture of the silicone breast implant, the process of bleeding is accelerated.

To quantify this problem of bleeding in vivo, it is crucial to establish the extent in which this bleeding occurs. However, up until now, the measurement of the Si-CH₃ functionality [2] in the tissues of patients with silicone breast implants is not yet feasible. The next question to be answered is what the effects are of these organosilicone compounds on the female biosystem and how general these effects are. In this respect, it is important to note that although silicone polymers are ubiquitous in our environment, gel bleed stands in a category of its own. With gel bleed of breast implants, the exposure to silicone polymers is through implantation and this is fundamentally different from exposure through the skin (cosmetics) or mucosa (foodstuffs and medications).

We already know that the body needs and can process traces of natural elemental silicon for its health, the question is, can it also process synthetic silicone polymers in excess derived from gel bleed.

Conflict of interest None

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