Silicon, Silicone, and Silica: The Importance of the Right Ending
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Although organic polymers based on carbon have revolutionized the use of commodity materials during the latter half of the twentieth century, polymers based on silicon have also had a remarkable impact in certain specialty areas, especially in medical technology. This article clarifies some of the chemical uncertainties associated with these materials.

The contribution of polymers based on silicon to medical technology has been significant technically, but it has also been controversial. Part of the problem has been a widespread misunderstanding of the characteristics of silicon-based materials, including failure to distinguish between the different derivatives.

Said quickly, silicon, silicone, and silica sound very similar and it is not surprising that many lay people become confused about these words. It is perhaps more surprising that many scientists also display some uncertainty about these substances, an uncertainty that has made the current controversy over the biocompatibility and safety of silicones even more difficult to unravel. In an excellent recent review of the issues surrounding the controversy concerning silicones and connective tissue disease, Gott and Tinkler (Medical Devices Agency, London, UK)[1] referred to the misunderstandings about the various silicon-based products. This article attempts to analyze the misunderstandings in greater detail and provide a basis for the description of the silicones that have such widespread medical use.

Silicon
This should be the easiest to under-stand because silicon is simply an element. It is an abundant element, comprising approximately 28 per cent of the earth's crust; only oxygen is more abundant. It would appear, therefore, that it is an important element and that its structures and properties should be well known. A few features about silicon, however, conspire to make it rather more mysterious. First, it is never found free in nature and although it can, with difficulty, be prepared as a crystalline solid, it was never used as such until recently, and certainly never as a structural material. Second, as a Group IV element, just below carbon in that series, it has some of the characteristics of elements from the left of the Periodical Table and some of those from the right, so that its interactions with other elements are varied. Moreover, it is tetravalent and crystallizes with a diamond structure so that it has many of the characteristics of carbon, but also many differences. As a result, silicon is not usually included in texts of organic chemistry, but equally it is rarely considered as an inorganic chemical. As a profoundly important element, therefore, it often seems to be ignored, a factor that is noticeable in any discussion of classical toxicology, where silicon as an element rarely receives attention. If it were not for the remarkable interest now shown in crystalline silicon as the premier electronic material for integrated circuit technology, where it is made to a purity of 99.99999 per cent in defect-free wafers of 25-micron thicknesses in tonnage amounts, the end of the twentieth century would have little interest in or use for elemental silicon. Yet, it has great affinity for other elements, and this characteristic gives rise to a series of naturally occurring compounds and industrially useful materials. This is where the real medical technology story starts.

Silicone
Although it is tetravalent, just like carbon, silicon does not have the ability to form long chains based on the silicon-silicon bond. These bonds

are possible, but they cannot be oriented to produce long linear molecules. Hence, there is no direct equivalent to the carbon-carbon- based organic polymers. Nor can the silicon easily substitute for carbon in large organic molecules and silicon-carbon bonds are never found naturally. Silicon-carbon bonds can be prepared synthetically, as in silicon carbide, a ceramic-like crystalline material almost as hard as diamond. More importantly, however, silicon has a great affinity for oxygen, and in nature silicon is always bound to oxygen. Thus, both naturally occurring and synthetic silicon-based products involve the silicon-oxygen bond; the four-fold valency of silicon and the two-fold valency of oxygen allows macromolecular structures to be established.

In particular, a repeating silicon-oxygen unit can be formed, which constitutes the backbone of silicone polymers. The silicon- oxygen couplet is known as siloxane and any molecule formed with a siloxane repeating unit is referred to as a polysiloxane or a *silicone.* Thus, a silicone is any macromolecular material based on the repeating unit shown in Figure 1.

Organic groups are frequently attached to the silicon atoms in these structures and the most widely known and extensively used polymer in this family involves the attachment of methyl groups to these atoms, giving polydimethylsiloxane (see Figure 2).

Other organic groups can replace the methyl group and a number of commercially available silicones are copolymers with some segments involving methyl groups and some segments involving other groups, such as phenyl groups.

As with most families of organic polymers, the silicones can exist in a number of configurations, depending on factors such as molecular size and the degree of cross-linking. Linear chains of molecules of polydimethylsiloxane give rise to silicones that are liquid in character. These are usually known as silicone fluids or silicone oils. Within this group there is a range of chain lengths and the liquids display varying viscosities, the parameter that is normally used to characterize silicone fluids. These fluids have widespread industrial uses because they have attractive properties, including the capacity for lubrication under adverse environmental conditions. For example, they are used as a lubricant in a variety of medical products such as syringes.

If these polydimethylsiloxane molecules are cross-linked, that is, if there are some bonds established between adjacent chains via the organic groups, then a three-dimensional molecular network is formed.

The extent of the cross-linking and the content of the spaces within the network crucially controls the properties of the resulting material. If the cross links are small in number and the spaces are occupied by molecules of polydimethylsiloxane fluid, then a gel results, not surprisingly known as a silicone gel. It is this gel that has been at the center of the controversy over certain types of breast implant that were filled with this gel. These gels have similar properties to many of their organic counterparts such as the hydrogels used in ophthalmology, which generally consist of a water-insoluble organic network that contains water within the spaces.[2] As the cross- linking increases, so the gel is able to retain its physical form and although the fluid may not be covalently attached to the network, it can be totally retained within it.

If the molecules are more heavily cross-linked, so that there are no spaces to be occupied within the network, then a solid polymer is produced. Specifically, if the degree of cross-linking is arranged appropriately, then an elastomeric polymer can be produced, that is, one that behaves in a rubbery manner with extensive elasticity. These are the silicone elastomers. The degree and character of the cross links will control molecular flexibility under load so that high strains can be produced. Silicone elastomers constitute one of the most versatile of all elastomeric materials, operating under adverse conditions such as elevated temperatures and hostile chemicals. They have been widely used for medical devices for the same general reasons that they have been used for many industries, and are often the materials of choice for catheters and soft tissue reconstruction prostheses. It should be noted that the optimal cross-linking for elasticity renders silicones permeable to some molecules, in particular those elastomers that allow extensive oxygen diffusion, a feature made use of in contact lenses and oxygenator membranes.
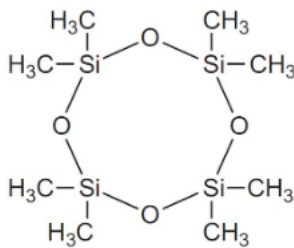
Figure 1: Siloxane repeating unit.
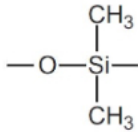
Figure 2: Formula for polydimethylsiloxane
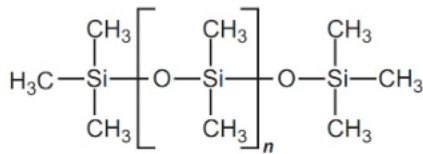
Figure 3: Structure of the cyclic tetramer (D4)

As with all polymers, silicone elastomers exhibit varying molecular size. This has again led to some controversy. This article is not intended to address the issues of biological safety of silicones, but it should be pointed out that all commercial products will contain some low-molecular-mass species as well as the cross-linked macromolecules and that some of the smaller molecules have been considered by some to be more reactive biologically than the larger molecules. It has to be said that it is extremely difficult to remove all small molecules and that in many formulations, traces of some cyclic siloxane molecules may be found. This is not surprising because these cyclic molecules are intermediate products in the manufacture of the polymer. One particular molecule has been cited in this respect in the cyclic tetramer usually referred to as D4, which has the structure shown in Figure 3. Attempts are made to remove these cyclic compounds from the final product.

Silica

Finally there is silica. This is silicon dioxide, SiO_2. In this there are the same silicon-oxygen bonds, but these are arranged tetrahedrally with four oxygen atoms arranged around each silicon atom in the form of a tetrahedron. Each oxygen atom is linked to two tetrahedra, giving a three-dimensional network that involves these, and only these two atomic species. Silica can exist in a crystalline form in which each of these tetrahedra are arranged regularly, for example, in the form known as quartz. Silica can also exist in an amorphous form, in which there is no such regularity. Silica, with all of its different forms, is ubiquitous, a rather obvious statement because it is made of the two most abundant elements in the earth's crust and because sand, of which many deserts are made, is nothing but silica. It is a useful material, as the mention of both quartz and sand implies. Medically it has few uses by itself, although there is one significant application. The silicone elastomers mentioned above do suffer from a relatively poor tear resistance and almost all commercial formulations of the elastomer require some filler to be present to increase this strength.

Silica is among the best fillers, primarily because there is better chemical compatibility between filler and matrix. The controversy over silicones does, however, extend to this particular part of the picture because the toxicology of silica is not a simple matter. It has been known for a long time that prolonged exposure to silica dust can lead to pulmonary diseases, not surprisingly referred to as silicosis. Questions have been raised about the possibility of the silica reinforcement of medical elastomers having similar effects, although it is clear that amorphous silica is far less pathogenic than crystalline silica and it is the former that is employed as the filler in the elastomers.

The above discussion has sought to clarify a few of the terminological and chemical uncertainties associated with this ubiquitous, but somewhat mysterious element. The last syllable in words starting with sili- is sometimes difficult to grasp, as many a lawyer, court reporter, and jury member must have found to their cost. It is to be hoped that some of the problems arising from this will together with the words themselves, have the right ending.

References

1. D.M. Gott and J.J.B. Tinkler, "Silicone Implants and Connective Tissue Disease" (Medical Devices Agency, London, UK, 1994).
2. D.F. Williams, "Hydrogels: Are They Keeping Their Heads Above Water?" *Medical Device Technology* 6(7), 8-11(1995).