Polyhedral Oligomericsilsequioxanes: Additives for Unique Cosmetic Properties

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ABSTRACT: *Cosmetics formulators continually search for new raw materials to achieve elevated performance and to distinguish their products in the marketplace. Polyhedral oligomericsilsequioxanes (POSS) can provide an array of unique hybrid inorganic-organic ingredients that span the property spectrum in terms of chemistry, physical form and solubility.*

The cosmetics market is driven by innovation, performance and uniqueness. Formulating chemists have to come up with new products to captivate the imagination of consumers and differentiate products from those of the competition. However, the toolbox of conventional chemicals is becoming exhausted; thus, many formulations tend to contain the same ingredients while savvy consumers look for novel product offerings.

To satisfy this need, in recent years there has been a drive to use more exotic ingredients such as oligopetides, plant extracts and innumerable derivatives of natural products. This article focuses on a new range[a] of synthetic chemicals known as polyhedral oligomericsilsesquioxanes (POSS).

This family of nanostructured[b] molecules offers new performance possibilities. While traditional silicones are well-known, POSS additives provide different properties due to their rigid "silica" core and multi-armed structure.

[a] *POSS is a registered trademark of Hybrid Plastics Inc.; registration number: 2,548,048.*
[b] *Nanostructured is a registered trademark of Hybrid Plastics Inc.; registration number: 2,610,806.*

POSS

POSS are a spin-off technology from the US Air Force Research Laboratories at the Edwards Air Force Base in California and were commercialized in the last decade by Hybrid Plastics Inc. They were first noted for their potential in peak performance plastics (see **Commercialized POSS**).

Beyond the plastics field, POSS have been investigated for lubricants,[1] semi-conductor photoresists,[2, 3] optical applications, coating additives, dental adhesives[4, 5] and more. The unique structure of POSS offers numerous options, as evidenced by thousands of papers and patents in many disparate fields.

Solubility and Miscibility

It is apparent from their structure that POSS have a hybrid composition whereby an inorganic, silica-like core—i.e., a core reminiscent of silica but not identical to it—has been fused to organic side arms. One of the simplest forms of POSS is one in which only hydrogens are attached to the cage, or octahydro POSS (see **Figure 1**), but these substances are neither stable nor readily soluble and thus of limited interest for cosmetics. As organic groups become larger, POSS become soluble. So for example, octa-butyl POSS shown in **Figure 2** can be dissolved in nonpolar organic solvents and oils.

Even longer side groups such as iso-octyl form liquid POSS types. If the formulation is more polar, alternative pendant arms would be chosen to achieve the desired compatibility. For instance, PEG POSS is soluble in polar media such as acetone or ethyl acetate. These POSS with eight equivalent functionalities are known collectively as molecular silicas. They are inert and do not normally react, even under harsh conditions. Their acid stability is exceptional, remaining unaltered under prolonged exposure to bases. This stability is a prerequisite for creating viable cosmetic formulations.

COMMERCIALIZED POSS

POSS have been found to be effective in most polymers. Commercial application of the material includes nylons, polyimide, epoxy resins, COC, PEEK and fluoropolymers. In each case, a specific POSS is chosen to deliver a particular effect. For example, POSS in PP1 and nylon leads to significatn reductions in friction, approaching the low friction of PTFE.

POSS added to nylon improves the flow of the melt to provide better processability. The material is also effective as a flow aid in polymers that are processed at temperatures high enough to break down other additives. For example, COC and PPO/PPE2 have proven themselves in this area, leading to commercializations in areas as diverse as dental adhesives, packaging and military applications, to name a few.

The most polar POSS variants are readily soluble in water. Examples include octatetra-methyl ammonium POSS and octaammonium POSS. The latter is polycationic and has been reported to have biocidal properties.[6] One new POSS type is N-phenylaminopropyl POSS, a liquid that is water soluble at acidic pH values and shows metal complexing activity.

Octaepoxy POSS are a sort of cross-linker for durable coatings and adhesives that are VOC-free.

Perhaps the most interesting new POSS for cosmetics is PEG POSS (INCI naming is in progress as of press). Polyethylene glycols (PEG) are well-known and versatile ingredients for cosmetics.[7] PEG is safe and exhibits an unusual property in that it can dissolve in both water and in organic liquids. Additionally, PEG can bind water and metal cations (Li+, Na+ and K+) the way that crown ethers do. This ability to bind water makes it an ideal humectant.

The PEG POSS is designed in two versions that differ by the length of the PEG arms. This allows formulation tuning. Normally higher molecular weight PEGs crystallize and become solid. The multi-armed PEG POSS has a high molecular weight but crystallization is prevented by the 3D star structure (see **Figure 3**).

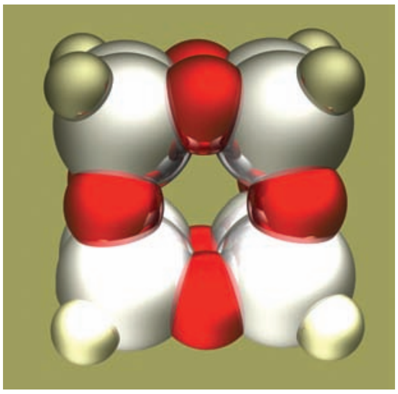


Figure 1. Octahydro POSS are dense and insoluble, like silica. **Note: Here, silicon is depicted in silver, oxygen is red, carbon is green and hydrogen is shown in khaki.**

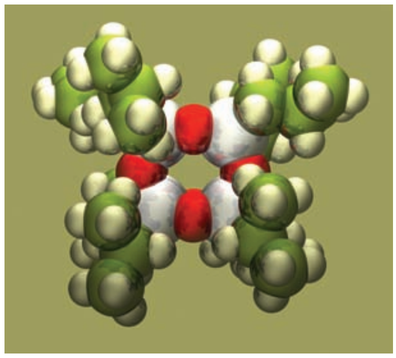


Figure 2. Octaisobutyl POSS are readily soluble in nonpolar media.

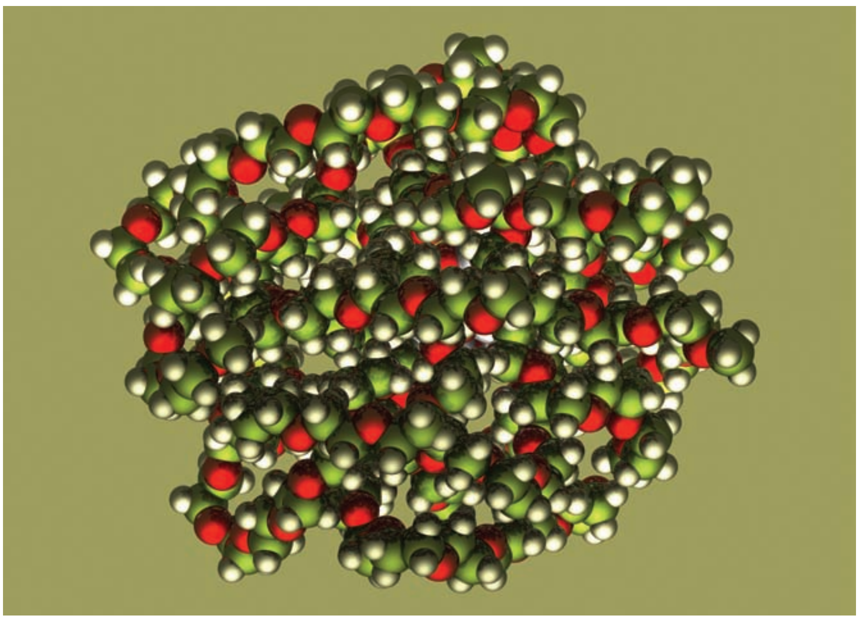


Figure 3. ***PEG POSS humectants are soluble in water and polar solvents alike.***

Thus the PEG POSS provides a PEG type that is a nonvolatile liquid that does not thicken like high molecular weight PEG/PEO does. Example formulations have incorporated PEG POSS to replace glycerol in moisturizers (data not shown). The POSS can be predissolved in either the oil or water phase, depending on the polarity and thus solubility of the POSS, or it may be incorporated into a pre-formed emulsion using a high-speed mixer.

Functionality

The POSS types known as molecular silicas tend to be inert because in those instances, the core cage is nonreactive and the arms are simple alkyl groups that are recognized as inert to most types of chemistry. However, other POSS types are designed specifically to be functional. Octaacrylate POSS and octamethacrylate POSS are polyfunctional cross-linkers that provide hard coatings with fast cure time, due to the multifunctional nature of the POSS monomer, and high scratch-resistance because of the hardness imparted by the rigid POSS cage.[8]

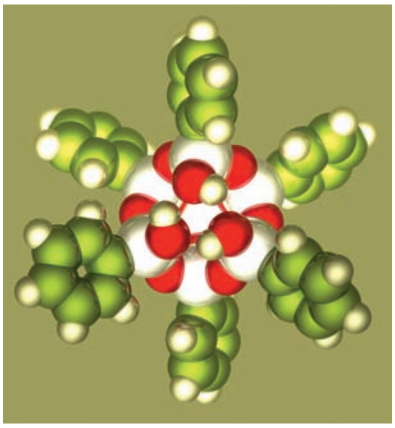
PEG POSS provides a nonvolatile PEG liquid that does not thicken like high molecular weight PEG/PEO does.

As one might imagine, these materials have aroused interest for nail polish products. Octaepoxy POSS are another sort of cross-linker for durable coatings and adhesives that are VOC-free.

The list of functionalities available is wide-ranging, including: carboxylic acids, sulfonic acids, alcohols, amines, thiols, alkyl halides, imides, isocyanates, norbornenyls, olefins and silanes. Custom compounds also can be manufactured. The functional group generally is attached either on each arm or just on one corner of the cage. Of course, other configurations are also possible. Proteins and peptides also can be tethered to POSS.[9]

Fluoroalkyl POSS compounds have been of increasing interest lately because research has shown that they can give ultra hydrophobic and ultraoleophobic surfaces with extreme contact angles.[10] Such surfaces illustrate the Lotus Effect, whereby water beads up and rolls off the surface, taking the dirt with it (self-cleaning); in addition, they repel oily contaminants. The "holy grail" is to create surfaces that stay eternally clean and shiny.

Another aspect of POSS is that they can act as effective dispersants. POSS trisilanols are key ingredients for such purposes[11] because they have one silicon atom removed from the corner of the cage, leaving three reactive Si-OH groups (see **Figure 4**). These trisilanols are the only known well-defined and stable silanol compounds. The so-called organosilanes are well-established dispersants for fillers and pigments, finding use in coatings, plastics and cosmetic products alike.[12, 13]



POSS SNAPSHOT

Density range: 0.9–1.3 gcm-3

Refractive index range: 1.4–1.65

Form: Colorless and odorless solids, waxes, liquids

Polarity: Very low (fluoroalkyl), low (alkyl), phenyl (medium) to polyionic (high)

Chemical stability: Molecular silicas (closed cage) very high, trisilanols good

Safety: All testing was performed on molecular silica and proved POSS to be safe (at the highest possible test dosage with no adverse effects noted).

Purity: Quality control on each batch, standard purity >97%.

Availability: More than 80 types are available and several at multi-ton scale.

***Figure 4.** Trisilanolphenyl POSS are excellent dispersants for pigments such as TiO_2.*

Reactive POSS types also act as adhesion promoters by bonding to both surfaces. For instance, silanols bond to most silicate minerals (silica, mica, wollastonite, kaolin, etc.)[14, 15] so that when a reactive group such as vinyl, epoxy or methacrylate is also attached to the POSS cage, the latter group can bond to the matrix polymer or coating,[16] thereby strengthening the interface. Whereas conventional trialkoxyorganosilanes give off VOCs when they react, usually as methanol or ethanol, POSS trisilanols give off only traces of water instead, making for an odor-free, environmentally sound formulation.

POSS trisilanol treated pigments[17] have been commercialized[c] and this area is expected to expand into printer pigments, light emitting polymers and other related areas. Interestingly other POSS trisilanols have been reported to assist skin healing without scarring; and even regrowth of strong, dense skull bone has been reported.[18, 19]

Conclusion

POSS additives are diverse and unique with a variety of types to fulfill various roles. The rigid silica-like core imparts novel hybrid inorganic-organic properties. Interest in POSS is spreading, as is evident by the more than 2,300 articles and 800 patents[20] generated during the last decade or more. Commercialization has already taken place in the plastics and electronic fields with a steady stream of new applications. Work is ongoing in the optical and medical fields.[18,19]

Most recently, the cosmetics industry has discovered POSS technology.[21–24] Perhaps that is hardly surprising since cosmetics is one of the most dynamic and creative industries and POSS represents a new set of tools for the formulator to craft enhanced products for superior performance.

[c] *The POSS Titania brand is a product of Hybrid Plastics Inc.*

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