

Chapter 11

Silicone Elastomeric Particles in Skin Care Applications

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Silicone elastomeric particles are spherical particles of vulcanized silicone rubber based on polydimethylsiloxane (PDMS). These particles have a mean particle size distribution of 2-10 μ m and they are produced commercially via an aqueous emulsion process. Silicone elastomeric particles are used in industrial and personal care applications, the latter include both skin care and hair care. When applied to skin, silicone elastomer particles impart a pleasant sensation and they are also capable of absorbing various liquids such as emollients and sebum. Thus silicone elastomeric particles can be used in skin care applications to deliver certain substances to skin or to control sebum deposition on skin. Described are preparation and properties of silicone elastomeric particles and their uses in some skin care applications.

Introduction

Silicone elastomeric particles, referred to as silicone elastomer powders, E-Powders, or silicone particles, are spherical particles of vulcanized silicone elastomer based on polydimethylsiloxane (PDMS) that have a mean particle size distribution on the order of 2-10 μ m. Figure 1 depicts the structure for PDMS. A micrograph of silicone elastomer particles is shown in Figure 2. Silicone elastomeric particles were invented in Japan over 20 years ago and have found commercial utility in both industrial and personal care applications (1-5). Industrial applications of silicone elastomeric particles include modifying

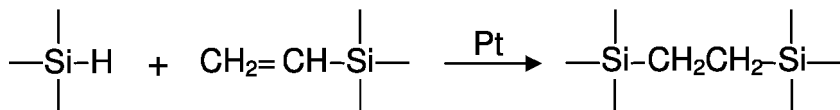
thermosetting resins for electronics, providing slip to polymeric surfaces and also producing light-diffusing plastic components for electronic video displays.

Silicone elastomeric particles also enjoy a substantial business in the field of personal care. In these applications, silicone powders are used in both skin care and hair care compositions. Silicone elastomer particles provide an extremely pleasant and likable sensation when applied to skin. They also provide conditioning effects when applied to hair. Silicone elastomer particles can absorb significant quantities of liquids such as oils or emollients and still retain a non-wet appearance and consistency. They can also absorb sebum from the skin. Thus silicone elastomer particles are useful in skin care applications where sebum control or addition of certain substances to skin is desired (6). This paper describes preparation and properties of silicone elastomer particles. Absorption of various liquids by silicone elastomer particles is also presented and discussed.

Discussion

Preparation

Silicone elastomer particles are composed of spherically shaped, vulcanized silicone rubber that is formed in an aqueous emulsion process. Although there are numerous methods for vulcanizing or curing silicone polymers to form rubber or elastomer, the platinum (Pt) catalyzed, hydrosilylation addition process has emerged as the method of choice for preparing silicone elastomeric powders for personal care applications (6). The cure chemistry of this process is depicted by the following equation:



A chief benefit of hydrosilylation is its rapid reaction rate and its absence of significant byproducts. The fact that Pt catalyzed hydrosilylation is unaffected by water coupled with these features makes it an ideal route for preparing silicone elastomeric particles. The relatively fast reaction kinetics lead to process cycle times that are fairly short thus providing a practical and efficient manufacturing process. Although the reaction will occur at ambient temperature, heat can be applied to increase reaction rate and shorten cycle times if desired.

To carry out the hydrosilylation process and form the silicone elastomeric particles, a vinyl functional siloxane polymer is mixed with a silicon hydride functional siloxane (crosslinker) and the mixture is emulsified in water in the presence of one or more surfactants using high shear. In this process an oil-in-water (o/w) emulsion is formed. In the presence of a Pt catalyst, the composition reacts to form a crosslinked network. Since the particles are dispersed in water, the networks are confined to each individual particle; therefore each particle becomes an elastomer. The emulsion process also leads to spherical particles as emulsion particles typically assume a spherical shape in order to minimize free energy of the dispersed system. It is also possible to control

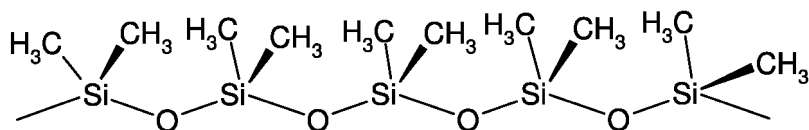


Figure 1. Structure of poly(dimethylsiloxane) (PDMS)

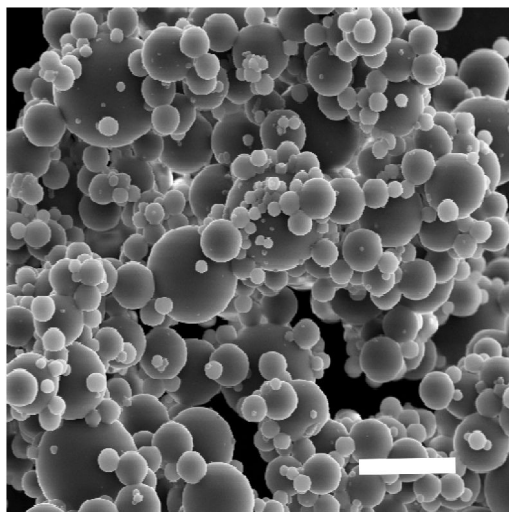


Figure 2. Scanning Electron Micrograph (SEM) image of silicone elastomer particles. White scale bar represents approximately 10 μm .

particle size to some extent by varying certain conditions of the emulsion process. Removal of water leaves silicone elastomeric particles. The process for producing silicone elastomeric particles is shown schematically in Figure 3.

Siloxane Polymers

Modulus, hardness and swelling behavior of cured elastomeric particles are all influenced by crosslink density, which can be controlled to a reasonable extent by choice of the starting siloxane polymer and the crosslinker. Generally higher crosslink densities are preferred over lower crosslink densities. Thus siloxane polymers having somewhat low molecular weights (Mw) are favored over high Mw polymers. Typically viscosities of siloxane polymers under about 1000 cP are preferred for preparing silicone elastomeric powders. This low viscosity also allows for easy preparation of o/w emulsions via high shear. The vinyl functional siloxane polymers actually consist of vinylmethyl/dimethyl siloxane copolymers and are commercially available. Functionality of these siloxane polymers, that is the vinyl groups attached to Si, can be arranged at pendent locations along the polymer chain or at chain ends or both.

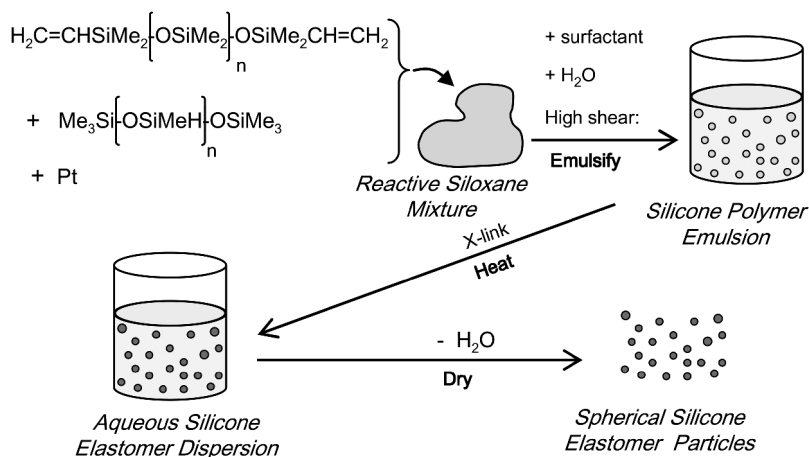


Figure 3. Scheme for preparing silicone elastomeric particles. Vinyl siloxane polymer, SiH crosslinker & Pt catalyst are combined with surfactant & H_2O and emulsified via high shear to produce an emulsion. After x-linking is complete, water is removed leaving spherical silicone elastomeric particles.

Crosslinker

Crosslinking agents for hydrosilylation reactions that form silicone elastomeric powders can be practically any multifunctional silicon hydride (SiH) functional siloxane or silane that is soluble in the vinyl functional-dimethylsiloxane polymer. The most common SiH crosslinkers are methylhydrogen polysiloxanes or methylhydrogen/methyl siloxane copolymers. These copolymers can be either linear or branched. Such siloxanes are readily soluble in the vinyl siloxane polymers and they are also available commercially. Normally a 1:1 stoichiometric ratio of SiH to Si-vinyl is used; however, as SiH is capable of reacting with water in the presence of catalysts, in some cases a slight excess of SiH is used to compensate for some SiH to be consumed by water.

Catalyst

As previously stated, a platinum catalyst is used to prepare silicone elastomeric powders used in personal care applications. Pt catalysts effect cure by hydrosilylation in which an SiH adds to a carbon-carbon multiple bond forming an ethylene linkage. The hydrosilylation reaction is used extensively for vulcanizing neat silicone elastomers; numerous attributes including its fast reaction kinetics and absence of significant byproducts make it ideal for forming such elastomers. Although the high cost of Pt is not trivial, it is manageable in silicone elastomer compositions including silicone elastomeric particles since the level of Pt used is on the order of about 2-3ppm to 20ppm based on polymer weight.

The Pt catalyst used to prepare silicone elastomeric particles as well as neat silicone elastomers is in a form that is soluble in the vinyl siloxane polymer.

H_2PtCl_6 dissolved in isopropanol can be used as well as Pt complexes of divinylsiloxanes dissolved in vinylmethylsiloxane/dimethylsiloxane copolymer, the latter of which is preferred and it is commercially available.

With certain vinylsiloxane polymers, cure will begin as soon as all three components of the elastomeric composition have been mixed (catalyst, SiH crosslinker and vinylsiloxane polymer). Since silicone elastomeric particles require additional ingredients (water and surfactant) and another process step (emulsification), a short delay in the cure reaction is desired. If significant cure of the polymer system takes place prior to emulsification, this step may become difficult or impossible to accomplish or emulsion quality may be compromised as well. Thus it is preferred to have cure take place after emulsification of the polymer composition.

In order to accomplish this, less reactive vinylsiloxane polymers can be chosen or a catalyst inhibitor can be used or both. Pt catalyst inhibitors for silicone cure are well known in the industry and they consist of molecules that complex with the Pt compound in a reversible manner such that heat reverses the complex formation and releases an active Pt catalyst. Examples of Pt catalyst inhibitors include acetylenic diols such as 3-methyl-2-butyn-2-ol or 3,5-dimethyl-1-hexyn-3-ol (Surfynol®61) and esters of dibasic carboxylic acids such as diethylfumarate.

Process

The basic concept behind preparing silicone elastomeric particles is to first prepare an aqueous emulsion of polymer particles followed by crosslinking this polymer to form a dispersion of elastomeric particles (7). The emulsion process is carried out using standard high shear equipment designed for emulsifying liquids. Such equipment includes homogenizers, Cowles® blade, colloid mills, Sonolators®, or Microfluidizers®. A typical process may consist of preparing a mixture of siloxanes, water and surfactant in one vessel by stirring followed by passing the mixture through a high shear device and into another vessel. The second vessel would also be equipped with a stirrer and perhaps a heater such that the emulsion could be heated if desired. As previously mentioned heat can be optionally applied to the emulsion to speed up cure. This heat would be considered to be moderate heat; emulsions are rarely heated to above 80°C as many emulsions are prone to becoming unstable at or near this temperature. The same is true for silicone elastomer emulsions.

The emulsions formed when preparing silicone elastomeric particles are of the oil-in-water type. Particle size of the emulsion is governed by many factors; some of these include viscosity of the oil phase, type of high shear device, pressure of high shear device (if using a pumping-type high shear device), rotor speed (if using a Cowles® blade or other rotary mixer), and type and level of surfactant. Silicone elastomeric powders appear to have an optimum particle size for best sensory effects, which is approximately 2-10µm. Hence the emulsification process is designed to produce emulsion particles within this range.

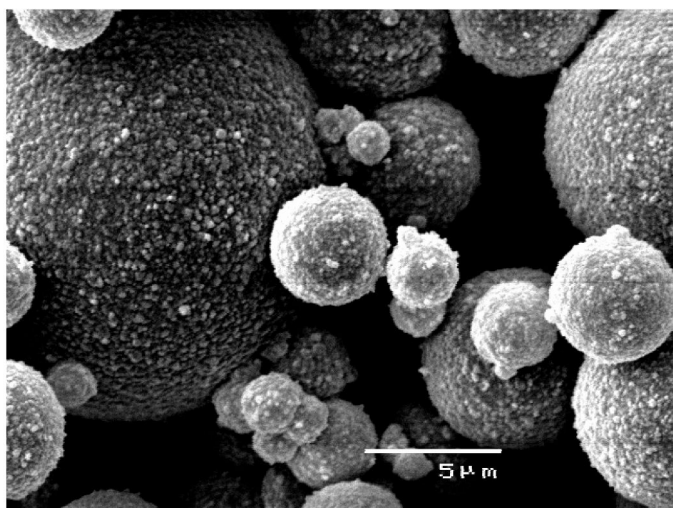


Figure 4. Scanning electron micrograph (SEM) of silicone elastomeric particles treated with Al_2O_3 nanoparticles. Scale bar represents 5 μm . Silicone elastomeric particles treated with inorganic oxides have different sensory and optical properties from untreated particles.

A silicone content or percent solid of the silicone emulsion is not extremely important, but it is typically on the order of 50 percent silicone. Higher solids emulsions would offer the benefit of having less water to remove, but along with higher solids comes higher emulsion viscosity. Difficulties in handling higher viscosity emulsions can outweigh the benefits of having less water to remove.

Since numerous factors affect particle sizes of emulsions, manufacturers of silicone elastomeric particles usually rely on their experience to produce emulsions of the curable elastomeric compositions having desirable particle sizes. It should be noted that particles made by these emulsification procedures described produce a distribution of particle sizes. In other words, they are not unimodal particles. A particle size distribution of a typical sample of silicone elastomeric particles made by conventional emulsification methods is shown in Figure 5.

Microfluidic techniques are used to produce truly unimodal emulsions (8). It should be possible to produce unimodal particles of silicone elastomer particles by using such techniques. Such a process would be envisioned to consist of pumping a curable silicone composition through a capillary or orifice into a flowing mixture of water and surfactant under controlled flow conditions. As the silicone emerges from the orifice, it would form spheres of uniform size and cure. In this manner silicone elastomer particles or silicone resins having a spherical shape and a monomodal particle size distribution might be produced.

Once crosslinking is complete, particles are harvested by removal of water. This can be accomplished by filtration, vacuum drying or spray drying. Although filtration would appear to be straightforward, it still requires a drying step (heat) and problems with filter plugging can be significant. Spray drying has become the preferred method for harvesting silicone elastomeric particles.

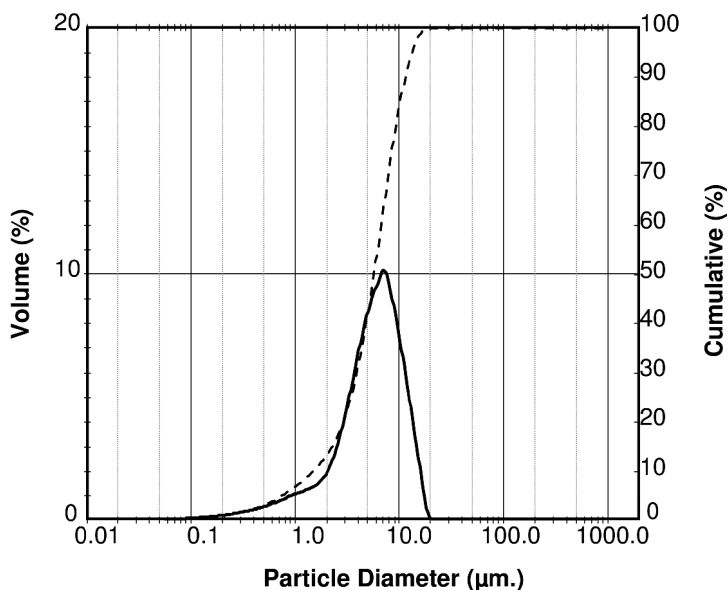


Figure 5. Particle size distribution of a typical silicone elastomeric powder. Volume percent, $(D_{v, 0.5}) = 5.71 \mu\text{m}$. Solid curve is volume % while dashed curve is cumulative %. Results were obtained on a Malvern® Mastersizer S (version 2.81).

Surfactants

One or more surface active agents (surfactants) are used to form a stable aqueous emulsion of the silicone elastomeric composition prior to crosslinking. In most cases, stability of the emulsion is required for relatively short periods of time – 24 hours – so choice of surfactant(s) is not all that critical. As the surfactant remains with the dried silicone elastomeric powder, choice of surfactant is dictated mainly by its compatibility with personal care applications. Namely it should be non-toxic to humans and non-irritating to skin. In addition, the surfactant should also be compatible with Pt catalyzed hydrosilylation reactions. In other words, it should not be a Pt poison.

As a result of these requirements, nonionic surfactants have been selected as surfactants of choice for preparing silicone elastomeric particles. Alcohol ethoxylates (alcohol EO) are the preferred nonionic surfactants and examples of such surfactants include Brij® 35 (lauryl alcohol EO-23) and Genapol® UD-080 (unidecyl alcohol EO-8). It should be realized that numerous other surfactants can be used to prepare silicone elastomeric powders besides these surfactants listed and combinations of surfactants can also be used if desired. The amount of surfactant used to prepare silicone elastomeric powders is also not very critical as the emulsion lifetime is very short. Usually from 0.5 percent by weight to 5 percent by weight of surfactant based on silicone polymer is used.

It also may be desirable to prepare silicone elastomeric powders having ionic surfactants such as anionic or cationic surfactants to achieve certain properties associated with the particles. For example, a cationic surfactant could be used to

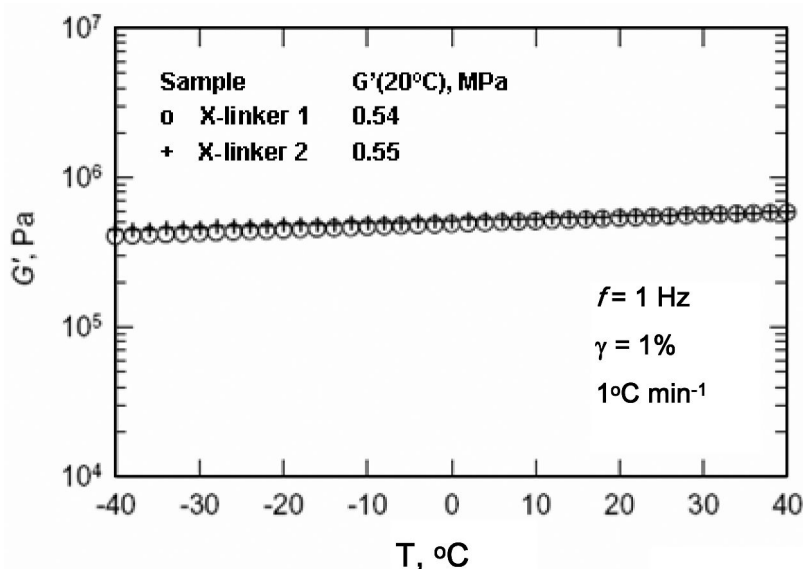


Figure 6. Dynamic shear modulus of two silicone elastomer particle compositions prepared with different crosslinkers. Modulus was determined on elastomeric films cast from the identical elastomer compositions used to prepare silicone elastomer particles. Measurements obtained on an ARES® controlled strain rheometer.

impart a positive charge to silicone elastomeric particles. Examples of anionic or cationic surfactants are Hostapur® SAS-30 (sodium *sec.*-alkane sulfonate) and Arquad® 16-29 (cetyltrimethylammonium chloride), respectively.

It should be mentioned that choice of surfactant and amount can have an impact on particle size of the emulsion and hence the finished silicone elastomeric particles. In addition to varying the emulsification conditions (described above), choice and level of surfactant can be varied to produce an emulsion having a desired particle size.

Silicone Elastomeric Particles with Inorganic Oxides

In the dry state silicone elastomeric particles are usually agglomerated into masses that are much larger than the primary particles. Although these agglomerates can be broken down by shear, it can be difficult in some instances to break down all of the particles into their primary particle state. To overcome this agglomeration phenomenon and also to provide particles with different surface modifications, manufacturers have introduced silicone elastomeric particles treated with various metal oxide particles (9). For example, silicone elastomeric particles having their surfaces treated with SiO₂, Al₂O₃ and TiO₂ are commercially available. These oxide treatments not only confer free flowing and non-agglomerating properties to the particles, but they also provide a different

sensory feel and different optical properties to the particles as well. Optical properties (light scattering) are discussed in more detail in the section titled soft focus. An electron micrograph of silicone elastomeric particles treated with Al_2O_3 is shown in Figure 4.

Aqueous Dispersions of Silicone Elastomeric Particles

In cases where formulators wish to use silicone elastomeric particle in aqueous cosmetics compositions, it may prove advantageous to use preformed aqueous dispersions of silicone elastomeric particles rather than disperse the dried particles in water. In this case, water is not removed from the aqueous dispersion of silicone elastomer particles during manufacture. Also a surfactant system is chosen that can provide stability towards the dispersion for periods up to several years or more. Normally a suitable antimicrobial agent is added to the aqueous suspension to prevent possible microbial growth during transport and storage. Typically aqueous dispersions of silicone elastomeric particles are supplied with 50-60 percent silicone content.

Properties

Silicone elastomeric particles are spherically shaped, fine particles of silicone elastomer that have excellent thermal stability, and have interesting sensory and lubrication effects. The spherical shape and softness of silicone rubber are believed to contribute to the particles' unique sensory properties. Silicone elastomeric particles can be thought of as having the same properties as do conventional Pt cured silicone elastomers; however most conventional silicone elastomers are filled or reinforced with silica while these particles are unfilled.

Silicone elastomeric particles are characterized by their particle size (distribution), by their modulus and by their hardness. Particle size is normally measured on aqueous dispersions of silicone elastomer particles before removal of water using commercial light scattering instruments. Particle size distribution of a typical silicone elastomeric powder is given in Figure 5. Particle size distribution of silicone elastomeric particles is typically 2-10 μm . Modulus and hardness are measured on films or monolithic slabs of cured elastomer prepared from the same composition (excluding surfactant & H_2O) as are the silicone elastomeric particles using a rheometer or durometer, respectively. Hardness of silicone elastomeric particles is in the range of Shore A 30-60. Shear modulus of silicone elastomeric particles is on the order of approximately 50-60MPa @ 20°C/1 Hz. Dynamic shear modulus of two silicone elastomers used to prepare silicone elastomeric particles is given in Figure 6.

Applications in Skin Care

Due to their spherical shape, elastic nature, optical and oil absorption properties, silicone elastomer powders are widely used in skin care for benefits

Table I. Absorption of Various Liquids by Different Silicone Elastomer Powders^a

<i>Liquid</i>	<i>Dow Corning® Brand</i>			
	<i>9506^b</i>	<i>9701^c</i>	<i>EP-9215^d</i>	<i>EP-9293AL^e</i>
Octyl Palmitate	3	1	0.5	0.6
Isopropyl Myristate	5	1.4	0.8	0.6
Mineral Oil	3	1.5	0.6	0.6
Castor Oil	0.5	0.9	0.6	0.4
Sunflower Oil	0.5	0.8	0.5	0.5
Isododecane	2	3	1.5	2
Dow Corning® 245 ^f	4	4.1	1.6	2
Water	1	1.1	0.5	0.6
Ethanol	1.3	1.1	0.4	0.4

^a Values represent g of liquid absorbed per g of powder; composition remains dry to the touch. ^b 9506 is a low hardness particle (Shore A 30). ^c 9701 is a low hardness particle treated with SiO₂. ^d EP-9215 is a higher hardness particle (Shore A 60). ^e EP-9293AL is a low hardness particle coated with Al₂O₃. ^f Dow Corning® 245 is dodecamethylcycllopentasiloxane (D₅).

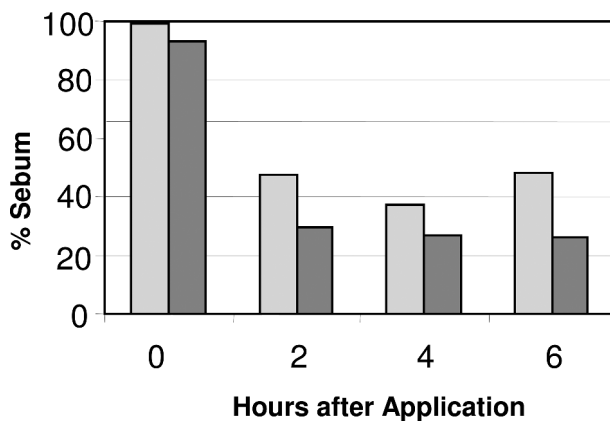
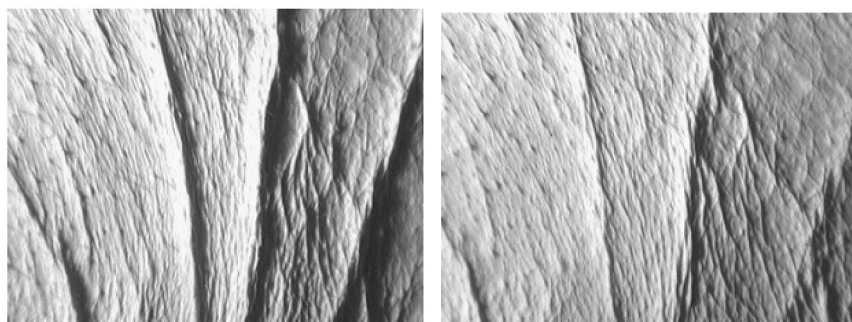


Figure 7. Level of Sebum remaining on human skin after treatment with a formulation containing 23% by weight silicone elastomeric powder. Light bars (left) represent Dow Corning® 9506 and dark bars (right) represent Dow Corning 9701. Both silicone powders are low hardness; 9701 has a surface treatment of SiO₂ particles. Values were obtained using a Courage + Khazaka GmbH. Sebumeter® SM810 and are at a 99% confidence level.

such as silky feel, delivery of actives, sebum absorption, wrinkle masking, matt finish and soft focus.



Before Treatment

1 Hour after Treatment

Figure 8. Before and after treatment of crow's feet wrinkles (facial wrinkles radiating from under or outer corner of eyes) with a water-in silicone composition containing 10% by weight silicone elastomeric powder treated with SiO₂.

Sensory Feel

When silicone elastomeric powders are applied to skin and rubbed, they provide an extremely pleasant and highly agreeable sensation that can be described as soft, silky and velvety. The elastic nature of the particles provides a “cushion” feel while their spherical shape acts as “ball bearings” and roll on the skin surface. These combined effects lead to the extraordinarily pleasant sensation when silicone elastomeric particles are applied to skin. These sensory features are sought after by skin care formulators because of the perception of younger, smoother skin. The threshold level of the perceived benefit for these powders is in the range of 2-5% of a skin care formulation.

Absorption of Liquids; Delivery of Actives

Being crosslinked networks, the elastomer particles are insoluble in all solvents, but they are swellable by certain solvents. The ability of silicone elastomeric particles to swell in certain solvents is an important property in terms of their utility as therapeutic delivery agents for skin. Due to this swelling behavior and also due to their combined surface area, silicone elastomeric particles can take up moderate quantities of various oils and still remain dry to the touch. Thus silicone elastomeric particles can be used to carry certain oily substances or emollients to skin such as mineral oil, glycerides, fatty esters and sunscreens. Table I lists various liquids that are absorbed by several different silicone elastomeric powders and still provide a dry feel.

Absorption of Sebum

Sebum is an oily substance that accumulates on skin and is secreted by sebaceous glands which are found primarily on the scalp, face and upper chest and shoulders of the human body. Human sebum consists of about 57.5% glycerides and free fatty acids, 26% wax esters, 12% squalene, 3% cholesterol esters and 1.5% cholesterol (10). Sebum accumulates on skin and its presence can make skin appear shiny, which is undesirable, especially on the face. When applied to skin, silicone elastomeric particles are capable of absorbing sebum and hence causing a reduction in the level of sebum on the surface of skin.

It is possible to quantitatively measure the level of sebum on skin to determine how effective silicone powders are at controlling sebum accumulation on skin. Figure 7 shows the relative amounts of sebum remaining on skin after treatment with two kinds of silicone elastomeric particles.

Acne (*Acne vulgaris*) is a chronic disorder of the skin that is prevalent among adolescents and its treatment usually involves controlling bacterial growth and reducing sebum production (10). Although reducing the level of sebum on the surface of skin could be a beneficial strategy for treating acne, it is not known at this time if silicone elastomeric particles offer a therapeutic benefit for treating acne by reducing the level of sebum on the surface of skin.

Optical Properties, Soft Focus and Wrinkle Masking

In an aging population, cosmetic products that hide the effects of aging are highly desirable. Wrinkles and fine lines on skin trap light in crevices and cause the skin tone to look uneven. Pigments from foundations and make-up tend to collect in skin crevices and accentuate fine lines and wrinkles. Simply by covering up the imperfections in some cases creates an unnatural, caked-on appearance. There is a need for materials that can mask the signs of aging, while at the same time project the natural skin tone.

Compositions that coat with transparent materials which give sufficient differences in refractive indices could result in a “soft-focus” effect. The details of the principle and requirements for the soft-focus effect are described by Emmert (11). In a simplified description, the soft-focus effect is apparent when the total reflection is minimal (<20% of total light), total transmission is maximal (>75% of total light) while diffused light reflection is maximal (80%) and diffused light transmission is maximal (>50%). When these criteria are met, the total light transmission makes the natural skin tone show through (like a back light) to give a natural glow, while the diffused transmission would even out the skin tone and hide imperfections. Silicone elastomeric particles coated with either Al_2O_3 or TiO_2 nanoparticles have demonstrated the soft-focus effect (12, 13).

Even without quantification of the soft-focus effect potential, a silicone elastomeric powder treated with SiO_2 particles has shown to give the perception of minimized wrinkles. Figure 8 shows before and after facial skin treatment to reduce the appearance of crow's feet wrinkles (those wrinkles on skin radiating

from under or outer corner of eyes) using a water-in-silicone formulation containing 10% silicone elastomer powder treated with SiO₂.

Summary

Silicone elastomeric particles, their preparation, their properties and their uses in skin care applications have been described. Silicone elastomeric particles are spherical particles of silicone rubber having a mean particle size on the order of 2-10 μm . These particles are prepared by crosslinking aqueous emulsions of silicone polymer compositions followed by removal of water. Silicone elastomeric particles provide a pleasing sensation when applied to skin. They can absorb various emollients and liquids and deliver them to skin. These elastomeric particles are also capable of reducing the level of sebum on skin. Silicone elastomeric particles can also provide desirable optical properties when applied to skin by providing a perceived benefit of soft and natural glowing skin and also wrinkle reduction.

Acknowledgments

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