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Silicone crosspolymers: customising sensory feel

Silicone crosspolymers (also known as silicone elastomers) are relatively novel products that have provided silicone formulators with new tools to modify rheology and sensory attributes of personal care formulations. These silicone elastomers are based on crosslinked dimethicone and are typically supplied in the form of swollen gels that contain various silicones like cyclopentasiloxane or dimethicones. Silicone crosspolymers provide unique sensory properties that are unlike anything else available in the market.

Silicone crosspolymers for personal care applications were first developed in Japan and continuously enjoyed a successful development ever since; they are now available from several suppliers. Crosspolymers do not only exist in the form of elastomer gels composed of silicone elastomers swollen by silicone fluids but also in the form of powders, emulsions or surfactants. In this article, we will explore the most common form of crosspolymers, namely elastomer gels. Silicones often function as a performance additive in personal care formulations and are crucial for future personal care innovations.

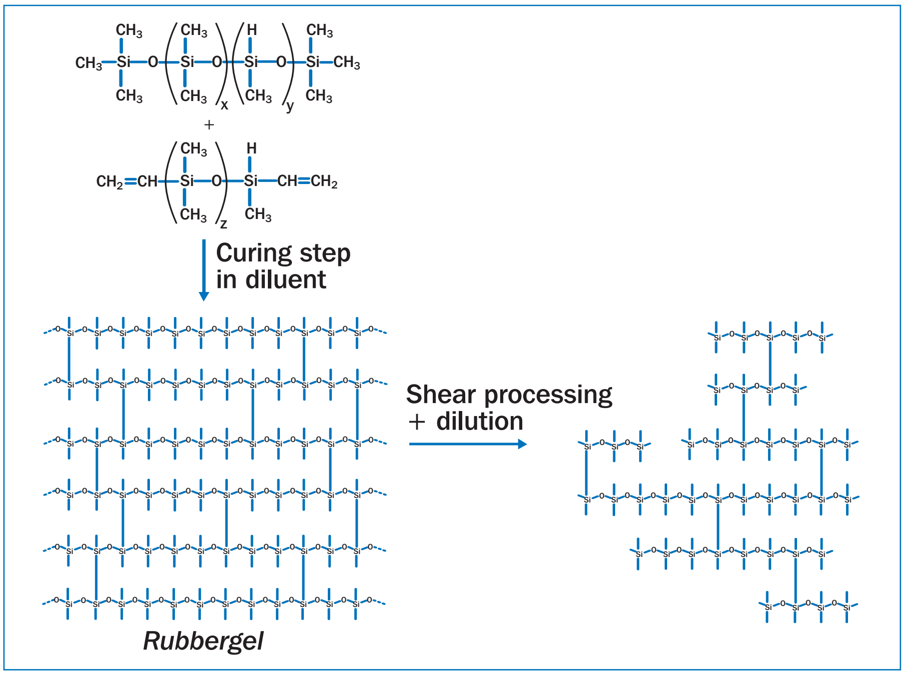


Figure 1: *Silicone crosspolymer production method.*

Applications

Commonly known thickening agents have never been well compatible with silicone formulations, or did not give the right sensory profile. Silicone crosspolymers are materials which have been developed to overcome these problems.

They are used as thickening agents in silicone-based systems (W/Si and W/O formulations and silicone fluids). Additionally they are compatible with various lipophilic active ingredients such as fragrances, sunscreens and vitamins and as such act as stabilising agents. They provide a non-greasy and light silky skin feel and they reduce tackiness of formulations.

As such, they are used in a wide range of personal care applications including but not only limited to skin care, hair care,

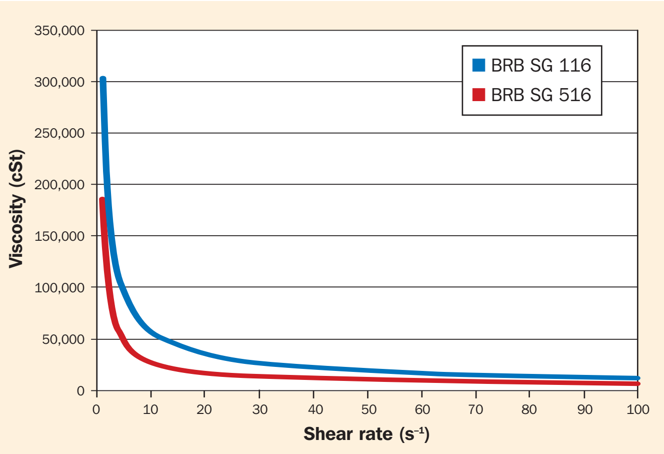


Figure 2: *Viscosity of vinyldimethicone/dimethicone crosspolymer.*

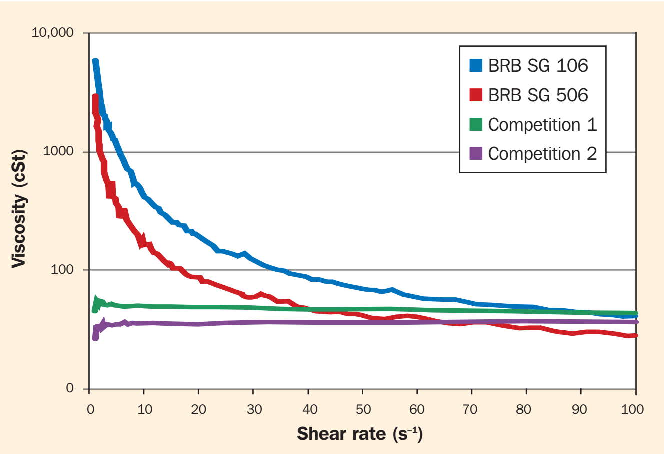
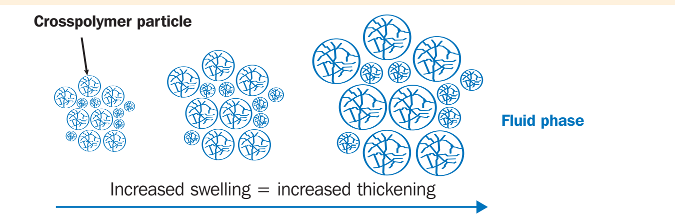
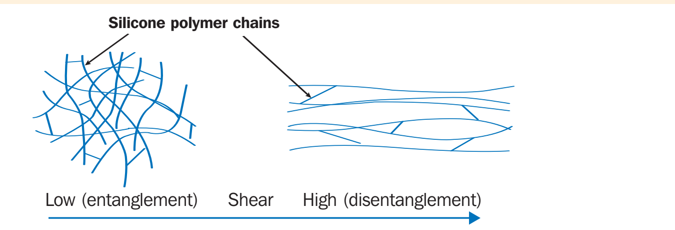
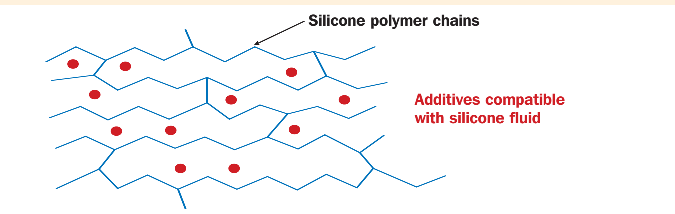


Figure 3: *Rheology of BRB crosspolymers dilutions compared to competitor products.*

Table 1: Formulations for eyeshadow and liquid foundation.	
Eyeshadow formulation	
Ingredient	**%**
Vinyldimethicone/dimethicone crosspolymer (and) cyclopentasiloxane	67.5
Phenyltrimethicone	22.5
Copper mica	5.0
Silver mica	5.0
Liquid foundation formulation (quick drying, light feel, low cost)	
Ingredient	**%**
Cyclopentasiloxane and PEG/PPG-18/18 dimethicone	12.0
Vinyldimethicone/dimethicone crosspolymer (and) cyclopentasiloxane	3.0
Dimethicone	10.0
Isotrideceth-5	1.0
Water	60.4
Cyclopentasiloxane and dimethiconol	0.5
Sodium chloride	2.0
Glycerin	3.0
Preservative	0.1
Titanium dioxide	6.0
Iron oxides Yellow	1.2
Iron oxides Black	0.3
Iron oxides Red	0.5

Table 2: Silicone crosspolymer properties in relation to their chemical composition.

Property	Crosspolymer composition
Thickening agent	Ability to swell in silicone fluid (low viscosity linear, cyclosiloxane) 
Shear thinning	Reduction in viscosity when shear is applied (e.g. mixing or rubbing out)  Low shear ("high viscosity"): • Allowing for easier pick-up • Remains in position after application High shear ("low viscosity"): • Ease of mixing in active ingredients • Ease of product application (e.g. rub-out
Stabilising agent	Compatibility of silicone fluid (which acts as solvent) with various cosmetic ingredients. 

antiperspirants and deodorants and formulations such as sunscreens and colour cosmetics.

As a downside of the success of crosspolymer development, their use in personal care products may be subject to application patents. This has to be taken into account by the reader.

Antiperspirants

Many antiperspirant formulations are based on cyclopentasiloxane or other cyclomethicones. The typical antiperspirant salts which are added to the cyclomethicone tend to settle which causes problems in the aerosol. Crosspolymers are very suitable thickeners, which also provide a thin, dry, non-tacky film to deliver the antiperspirant salts with reduced whitening. The rheological profile of BRB crosspolymers give superior suspension characteristics as the low shear rheology is high.

Also, roll-ons and sticks can be formulated using crosspolymers. In these cases they act as a film former on the skin and can give controlled release of the product. Conventional thickeners, like silica or clays, often lack stability or do not give the right sensory profile. Furthermore, reduced whitening may be obtained by using crosspolymer gels.

Creams and lotions

In today's market, consumers require products that are easy to use and effective in small quantities. Novel sensory profiles are essential, so creams that have a distinctive smooth and silky skin feel, and have a non-tacky feel can really stand out from the competition. This is where creams and lotions based on crosspolymers really can give a competitive edge. Furthermore, the crosspolymer film serves as a layer in which fragrances are contained, and where the films acts as a controlled release, providing a long lasting fragrance.

Silicone crosspolymers can also offer advantages for sun care products, as they can give products a light and smooth feel, are non-tacky, increase water repellency and have a fast skin absorption. In shaving gels they can give the right feel and lubricity. They also can serve to temporarily fill up wrinkles, thus giving a smoother skin appearance.

Colour cosmetics

With the evolution of cosmetic science, colour cosmetics have become increasingly sophisticated. There is a clear need for formulations that offer benefits in addition to colour. Ease of application and longer lasting colour effects have become more important. Furthermore, a non-oily appearance with a pleasant touch, both during and after application, as well as different textures, have made silicone crosspolymers more popular. Silicone elastomers can give unique sensory profiles. They can give a silky touch during application. Also they can provide a non-tacky velvety sensation, improve transfer resistance, durability and modify viscosity profiles of formulations. They can also act as a binder and facilitate spreading. When formulated with a non-volatile carrier, reduced cracking over time of powder cosmetics can be achieved. Crosspolymers may be used in various colour cosmetics like lipsticks and foundations.

Examples of generic formulations can be found in Table 1.

Figure 4: *1% TiO_2 disperions in 33% crosspolymer solutions, showing difference in stability.*

Hair care

Crosspolymers are also used in hair care formulations. Their non-glossy appearance and non-tackiness can be used. They do, however, not have good adhesion to hair, which has to be overcome by using other silicones such as amodimethicones.

Chemistry

Silicone crosspolymer gels are commonly blends of silicone elastomer in silicone fluid, which acts as diluent. The silicone fluid used often is a low viscosity dimethicone (e.g. dimethicone 5 cSt) or cyclopentasiloxane.

The common production method used to produce these materials is depicted in Figure 1.

The production of silicone crosspolymers as shown in Figure 1 consists of two different steps. The first step consists of an additional cured reaction of an SiH functional siloxane with a vinyl functional siloxane. The reaction is carried out in solvent (typically cyclopentasiloxane or dimethicone), and a soft solid, gel-like, 3D crosslinked structure is formed. The creation of connections between linear polymers convert a liquid linear polymer such as a dimethicone into a solid silicone crosspolymer gel.

During a second step, shear processing and additional dilution are used to obtain the typical gel-like structure common for most silicone crosspolymers. This, and the chemical composition determine the properties of the silicone crosspolymer gels.

Crosspolymer properties are completely different compared to linear dimethicones. The crosslinking density determines the properties, the higher the crosslinking density, the higher the hardness of the crosspolymer will be.

Particle size and particle size distribution of the silicone crosspolymer affect appearance, feel and aesthetics of the final formulation. This means proper control of particle size (distribution) is key for many applications, which logically means the importance of using the right method of production.

Properties

See Table 2 for an overview of several critical silicone crosspolymers properties and the relation to their chemical composition.

Because of their ability to swell when combined with solvents, silicone crosspolymers are effective oil phase thickeners. Figure 2 depicts the rheological behaviour of typical undiluted crosspolymers. The thickening effect is caused by interactions between swollen gel particles. For more explanation on the rheology of crosspolymers, please see the section about thickening profiles.

Differences between the various crosspolymers types and chemistry

The INCI name or the specification is of little value to determine the equivalency of crosspolymers or the suitability of a crosspolymer in a formulation. Within the INCI name of the active ingredient: Vinyldimethicone/Dimethicone Crosspolymer there is a lot of freedom to influence the properties of a crosspolymer. The degree of crosslinking, elastomer structure, gel content, carrier fluid and shear process used to create the crosspolymer blend all greatly influence the appearance and properties of a product. Therefore it is crucial to test crosspolymers in the formulation and for the application.

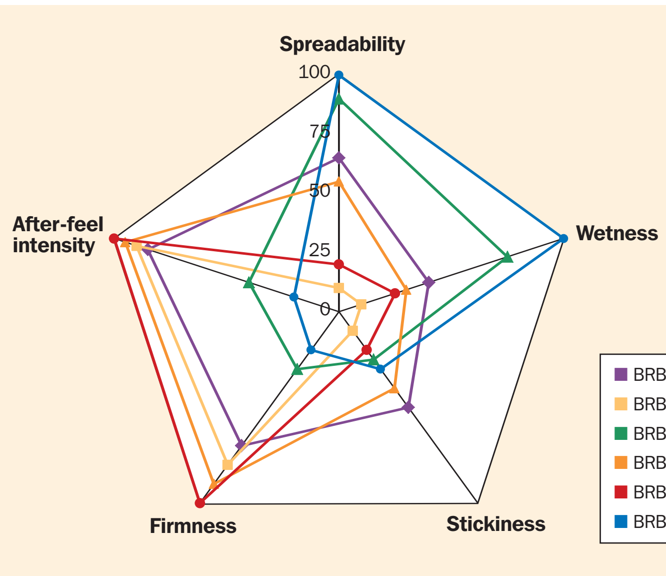


Figure 5: *Radar chart showing a comparison between various sensory attributes of BRB SG crosspolymer series.*

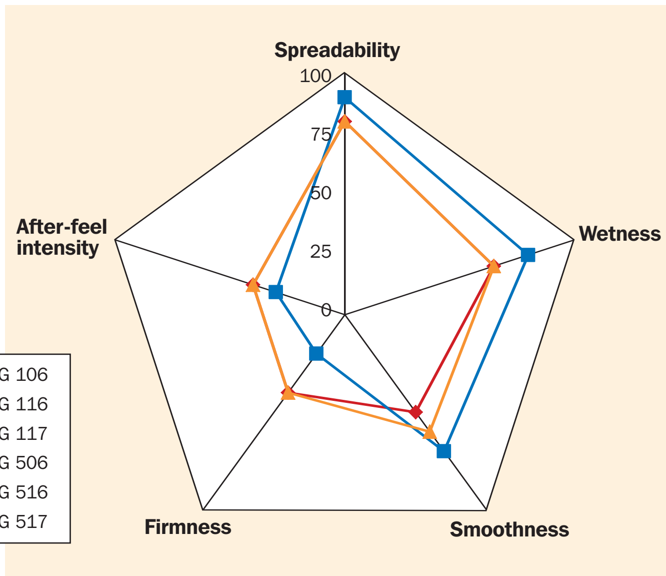


Figure 6: *Sensory characteristics of a body gel formulation containing 20% of three different BRB crosspolymers.*

Table 3: Silicone crosspolymer process and application properties.

Trade name	INCI	Particle size distribution	Crosslinking density*	Carrier fluid	Thickening effect	Sensory characteristics
BRB SG 106	Vinyldimethicone/ dimethicone crosspolymer (and) cyclopentasiloxane	Narrow	High	Volatile	Very high	Firm, intense after-feel and fairly smooth and spreadable
BRB SG 116	Vinyldimethicone/ dimethicone crosspolymer (and) cyclopentasiloxane	Broad	Low	Volatile	High	Firm and intense after-feel
BRB SG 117	Vinyldimethicone/ dimethicone crosspolymer (and) cyclopentasiloxane	Broad	Low	Volatile	Medium	Wet, smooth and spreadable
BRB SG 506	Vinyldimethicone/ dimethicone crosspolymer (and) dimethicone	Narrow	High	Non-volatile	Very High	Firm, intense after-feel and fairly smooth and spreadable
BRB SG 516	Vinyldimethicone/ dimethicone crosspolymer (and) dimethicone	Broad	Low	Non-volatile	High	Firm and intense after-feel
BRB SG 517	Vinyldimethicone/ dimethicone crosspolymer (and) dimethicone	Broad	Low	Non-volatile	Medium	Wet, smooth and spreadable

*Initial crosslinking density before dispersion, subject to further swell depending on solvent

Also viscosity figures are meaningless unless a specific shear rate is quoted at which the viscosity is determined. Viscosities always have to be compared at the same shear rates. Furthermore it is also very likely that crosspolymers with other INCI names such as Dimethicone Crosspolymer or Polysilicone is interchangeable with a crosspolymer with INCI Vinyldimethicone/Dimethicone Crosspolymer. This can only be tested in the end formulation.

Silicone crosspolymers typically exhibit shear thinning behavior which is most apparent when processing the pure crosspolymer. However, once formulated this distinct property becomes less apparent. The diluted crosspolymers often show a more Newtonian rheological profile, as can be seen in the graphs. Also the thickening power of products can differ greatly.

In Figure 3 a dilution of one part crosspolymer with two parts of the base solvent is displayed. The differences are clearly visible in the low shear rate range below $10s^{-1}$. The advantage is that when a crosspolymer is used for thickening, the low shear rheology is crucial for suspending solids. This difference is also observed when stability tests are done. This can be seen in Figure 4, where on the left the diluted SG 106 is displayed. On the right is a competitor product, diluted in the same way. Both mixtures contain 1% TiO_2, which has clearly settled in the sample on the right on this picture. In other words, products with similar INCI/composition can be thickeners exhibiting very different performances.

Sensory profiles

The radar chart is a convenient way to distinguish the effect between the different crosspolymers on the sensory characteristics of the cosmetic formulation in which it will be used. Such evaluation can be used to compare and define the performance of cosmetic formulations to provide direction in product formulation nd research guidance.

Sensory characteristics can be defined by properties such as product pick-up, delivery rub-out and after-feel. There are, however, problems with such sensory evaluation.

- Sensory attributes are very personal so how do you objectively measure them?
- How do you convey results to your audience?

ASTM E1490-03 provides a guideline for qualitatively and quantitatively comparing these various sensory attributes and their intensity (over time). Figure 5 depicts a comparison between the BRB SG crosspolymer series using a “radar chart”.

Although all these products have the same INCI name, they show very different sensory characteristics that can be classified in 3 groups:

- Firm and intense after-feel.
- Wet, smooth and spreadable.
- Firm, intense after-feel and fairly smooth and spreadable.

Each group (SG1 and SG5 series) has a dimethicone and cyclomethicone version. This shows the sensory characteristics can be fine-tuned regardless of these carrier fluids.

Table 3 gives an overview of the process parameters and their application properties. It indicates that a higher crosslinking density tends to give a broader spectrum of sensory attributes. Also there is an optimum crosslinking density for obtaining maximum thickening power.

When formulating products based on crosspolymers, know-how about other formulation and process parameters that influence the application properties is essential.

According to BRB’s experience, cross-polymers which are diluted in formulations behave the same in terms of sensory characteristics in the final formulation. The effects are slightly levelled out though, as you can see in Figure 6. However, the thickening behaviour of a diluted crosspolymer is more difficult to predict based on its undiluted rheological properties (Fig. 5).

Conclusion

The unique benefits of silicone crosspolymer gels are the compatibility with silicones and lipophilic active ingredients, combined with a dry smoothness and a light silky, non-greasy skin feel. The complexity of the crosspolymer chemistry goes far beyond an INCI name and simple physicochemical characteristics. You can find on the market a versatile range in terms of sensory characteristics and rheology. A smart design between crosslinking density, solvent nature, shear process, particle size and distribution allows endless formula customisation of the sensory benefits and the thickening profile. Being rich of an long customising experience, BRB is offering an extremely versatile range of silicone crosspolymers. PC