 SCIENCE FOR FORMULATORS

Selecting PEG/PPG Dimethicone Silicone Surfactants The Agony and the Ecstasy

KEYWORDS: PEG/PPG Dimethicone, formulation, testing, minimally disruptive technology, structure / function, silicone, aesthetics, science for the formulator, D/D* ratio.

Abstract

Personal care formulations are like fine gourmet meals in which proper choice for the silicone polymers is to function as the spice of the meal, not the meat or potatoes. This means that small amounts of silicone polymers added to formulation (less than 5%) can make a tremendous difference on consumer perception. We have called this type of formulation minimally disruptive technology (MDT). These versatile polymers need to be used at low concentrations to provide formulations that cannot achieve the overall effect without them. The task of selecting the proper PEG/PPG dimethicone polymers is a complicated but necessary one.

Silicone polyethers, also known as PEG/PPG dimethicone in the personal care industry, contain one or more of a silicone-soluble (siliphillic) group and a water-soluble PEG/PPG (hydrophilic) pendant groups. The ratio of the two groups, the molecular weight of the polymer and ratio of the PEG/PPG portion in the molecule in great part determine the solubility and specific properties of polymers from this diverse class of compounds. For purposes of this article we refer to these materials as PEG/PPG dimethicone, although they have many other more trivial names.

PEG/PPG dimethicone polymers are chosen for formulation to fulfill a basic need that cannot be achieved using other chemistries. PEG/PPG dimethicone polymers have a handful of salient properties that make them valuable in formulation. It is the job of the formulator to optimize the polymer to a specific application and even to a specific formulation. The job of the silicone chemist to make the optimized polymer. The desirable properties are outlined in Table 1.

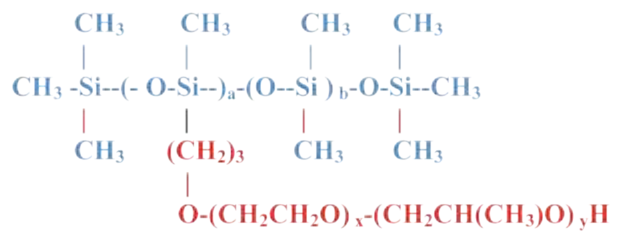
A properly chosen the PEG/PPG dimethicone polymer can provide the following attributes to formulations;

1. Lowering surface tension to around 25 dynes/cm
2. Providing unique skin feel.
3. Provide altered foam.
4. Increase wetting / spreading of formulation on hair and skin.

Table 1. PEG/PPG Dimethicone Desirable Properties.

The formulator must first decide which of these properties is required in each formulation then evaluate the proper type of silicone. We suggest the minimally disruptive formulation technique to evaluate several silicone polymers in formulation. This powerful approach makes changes to formulations in which the silicone is present in low concentrations with other silicone polymers to evaluate each in an established chassis, allowing for fine tuning of the silicone polymer for the effect desired by the formulator.

The silicone polymers we examine are referred to as PEG / PPG Dimethicone compounds. Formerly, these materials were referred to as dimethicone copolyols. Regardless of the INCI designation these materials conform to the structure shown in Figure 1 (1). It is also impossible to determine the exact structure of the polymer, which is critical to the functionality, merely by INCI name.



Water Soluble Group is depicted in blue
Silicone soluble group is depicted in red

Figure 1. PEG/PPG Dimethicone.

One of the recommended salient tests for PEG/PPG dimethicone polymers is the ability of the polymer to lower surface tension. If the product fails to lower surface tension in the formula, the effectiveness will be significantly lowered. One of the issues that can cause this is a polymer with too high a molecular weight.

FORMULATION TIP

Just because a "PEG/PPG dimethicone polymer" has been added to a formulation does not necessarily mean there will be any benefit to the formulation. If a water-soluble silicone polymer is being added to effect wetting, spreading or aesthetics, if the surface tension of the formulation is not lowered, there is likely no benefit to these attributes. Attributes like emulsification are an exception in that the emulsion may be stable with no decrease in surface tension.

Molecular Weight

To demonstrate the effect of molecular weight a series of homologous polymers were made in which the a:b ratio is 1:2. The difference in the series is that the molecular weight is increased with the a:b ratio being kept the same.

Designation	MW	Surface Tension 0.2% wt in DW	CMC
A	633	20.87	0.07
B	781	21.96	0.07
C	1,400	23.49	0.07
D	2,019	26.00	0.07
E	2,638	26.81	0.10
F	6,356	29.80	0.11
G	12,541	31.77	0.14

Figure 2. PEG 8 Dimethicone Series.

As can be readily seen the surface tension is clearly directly related to the molecular weight of the polymer. The product selected should have a surface tension in formulation of around 25 dynes/cm. Keeping in mind that cocamidopropyl betaine has a 0.2% wt surface tension of 32, the "G" polymer has fatty surfactant surface tension. From the table above in deionized water (DW) the use of polymers above a molecular weight of 2,000 is not suggested, in fact 1500 is the recommended as a starting point.

The interaction between PEG/PPG dimethicone and other ingredients in the formulation is a key factor to be considered when selecting the optimum product for a formulation. To show this importance of this a solution of 12% sodium lauryl sulfate and sodium Laureth 2 sulfate was prepared. The PEG 8 dimethicone was titrated into the SLE and SLES solutions. Figure 3 shows the results.

PEG 8 Dimethicone	Sulfate Surfactant	% needed to get surface tension 25 dynes/cm
B	SLS	1.2
B	SLES-2	1.2
D	SLS	1.5
D	SLES-2	3.5

Figure 3. % PEG 8 dimethicone needed to get 25 dynes/cm.

The table shows that the higher molecular weight PEG 8 dimethicone (D) and the lower molecular weight (B) interact with SLS in the same way, both needing 1.2% to get to a surface tension of 25 dynes/cm. When SLES-2 is used, with the higher molecular weight PEG 8 dimethicone (D) more than twice the concentration is needed to get to the 25 dynes/cm.

FORMULATION TIP

The example above is given in deionized water, and in two types of sulfated surfactant. We recommend that the test should be run in the formulation. There are a multitude of interactions that occur in formulated products which can alter the ability of a water-soluble silicone polymer to lower surface tension.

D/D* Ratio

Looking at Figure 1, the ratio of water soluble group (a) to silicone soluble group (b) will determine in part the solubility of the PEG/PPG dimethicone. Additionally, the number of moles of EO will determine the solubility as well. Again, the best formulation from a PEG/PPG dimethicone point of view is one that deposits most rapidly. This means a micro emulsion product.

In essentially all rinse off applications, the formulator wants the silicone to end up on the hair or skin, rather than down the drain. This means if the PEG/PPG dimethicone polymer is too water soluble it simply does not remain on the hair. If, however, the silicone polymer is too insoluble, adding it to an aqueous formulation will result in separation and defoaming. The solution is to design the silicone to spontaneously form a micro emulsion. Micro emulsions are very interesting since it is the surfactant that provides a micro emulsion that has the best combination of solubility, deposition and clarity.

Micro emulsions are clear to slightly blue, thermodynamically stable, isotropic liquid mixtures. In contrast to ordinary emulsions, micro emulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions.

The ability to regulate the structure of a silicone polymeric PEG / PPG surfactant to provide a micro emulation in formulation, provides a mechanism that can be used to maximize deposition. Simply put, if PEG / PPG Dimethicone is too water soluble, it will wash down the drain with rinse off and provide little or no additional benefit to the formulation. If you want to add them to efficient PEG / PPG Dimethicone to a formulation for deposition and providing long term effect in a system in which the PEG / PPG Dimethicone is clear and soluble, use a PEG / PPG Dimethicone that provides a micro emulsion in the formula tested.

The best way to do that is to alter the D / D* ratio (the ratio of b:a). In so doing the solubility is altered and a product which is the least soluble without insolubility is added making the lowest free energy on the substrate being deposited on the substrate. This means if you want to get the best delivery on a substrate and still maintain clarity for the formulation, deliver the silicone polymer as a micro emulsion. Figure 4 shows the effect of altering the D / D* ratio in PEG dimethicone.

In fact, it is quite easy to use a formula shown in Figure to effectively determine the number of PEG 8 units in a silicone polymer to make a micro emulsion.

Formula to determine soluble dimethicone copolyol (2)

Minimum needed "b" units = (0.1499)(actual number of "a" units)+1

b is the subscript "b" in the structure above, "a" is the subscript "a" in the above structure. This means that if the number of "b" units is above the value calculated an appreciable concentration of insoluble oligomer will not be present. If the value of "b" in the polymer is lower than the value of "b" requires in the formula for the number of "a" subunits, a soluble product is impossible since there will be an appreciable amount of insoluble polymer present in the oligomer mixture.

Choosing a D : D* ratio that provides a silicone polymer that forms a micro emulsion is the simplest, most cost-effective method to improve the efficiency of a PEG / PPG dimethicone in formulation. The INCI name is even the same!

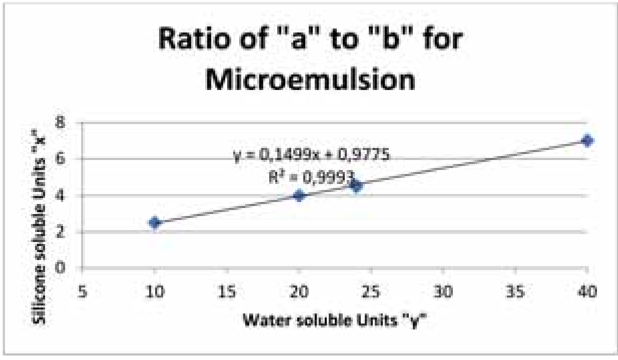


Figure 4. D / D* Ratio.

The above formula was determined by preparing evaluating a variety of PEG 8 dimethicone products. The results are shown in Figure 5.

A	b	Predicted* (Formula Below)	Observed (Lab Synthesized)
5	1.0	Insoluble	Insoluble
5	2.0	Soluble	Soluble
10	2.0	Insoluble	Insoluble
10	2.5	Micro	Micro
10	3.0	Soluble	Soluble
20	3.5	Insoluble	Insoluble
20	4.0	Micro	Micro
20	4.5	Soluble	Soluble
24	4.0	Insoluble	Insoluble
24	4.5	Micro	Micro
24	5.0	Soluble	Soluble
40	6.0	Insoluble	Insoluble
40	7.0	Micro	Micro
40	8.0	Soluble	Soluble

* using the micro-emulsion formula:
Minimum needed "b" units = (0.1499)
(actual number of "a" units)+1

Figure 5. Solubility (10% Water).

FORMULATION TIP

When selecting a PEG/PPG dimethicone to provide optimum effect, chose one that gives a micro emulsion in the formulation. Adding 1% of the PEG/PPG dimethicone to the formulation should provide an increase in viscosity and a slightly blue tint.

FORMULATION TIP

It must be clearly understood that the PEG/PPG dimethicone that works best in water may not be the one that works best in formulations. Other surfactants for example will co-solubilize the PEG/PPG dimethicone and slow deposition. The best approach is to have several materials of differing D:D* ratio available to test by adding to the formulation. It is also quite effective to replace PEG/PPG dimethicone polymers in formulations that are not near the "micro emulsion range" D:D* ratio. The result is more deposition per unit weight added to formulation.

EO/PO Content
Even though these are silicone surfactants there is some ambiguity in calculating the functional properties, do not be fooled into giving up on using common sense calculations to understand silicone molecules. An example of intuitive evaluation is PEG / PPG 18/18 dimethicone, the structure is shown in Figure 6.

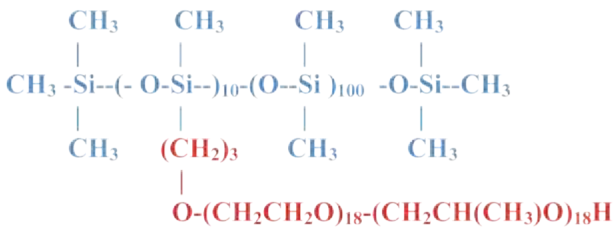


Figure 6. PEG/PPG 18/18 Dimethicone.

Question
Consider that molecule. From the data that was given above consider:

(a) would it be water soluble or insoluble?

(b) what would expect the surface tension to be?

Calculation
Looking at the molecule, there are 100 D units, (or 7,400 daltons). There are 10 units each made up of 18 EO (18 times 44 or 792 daltons) and 18 PO units (18 times 59 or 1,062 daltons) for a total of 18,540 daltons for the EO/PO part. Total of the two parts is (18,540+7,400 = 25,940).

This means that just considering D and D* the molecule is (18,540/25,940 = 71.5 % EO/PO). Simple HLB estimates say the HLB would by 71.5/5 or 14.3. Simple from that calculation one would expect water solubility (and it is). From the high molecular weight, one would a surface tension around 30-33 dynes/cm the actual determined number is 32.0 dynes/cm).

In fact is you look it up you will find:

PEG/ PPG-18/ 18 DIMETHICONE: This ingredient is a synthetic chemical consisting of dimethicone, a silicon-based polymer and polyethylene glycol (PEG)-polypropylene glycol (PPG) poymer.
Function(s): Surfactant – O/W Emulsifying Agent
Synonym(s): PEG/PPG-18/18 DIMETHICONE

Additional Question
How would you make the molecule in Figure 6 silicone wetting agent? All you need to answer this is given in the above.

FORMULATOR TIP

When approaching a molecule that is new, don't forget everything you know that is old. The knowledge you have of the carbon chemistry world has some value in working with silicone chemical. In fact it has a great deal of value. As you test different material and learn of the properties, the ease of future predictions becomes easier and easier.

REFERENCES

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Silicon – Abundant Raw Material

- Silicon: The 14th element in the periodic table.
- Chemical symbol; Si.
- Density = 2.33g/ml.
- Molar mass = 28.09 g/mol.
- Melting point = 1,420°C.
- Boiling point = 3,265°C.
- Electronic configuration [Ne]3s2p2.
- Appearance: metallic-looking.
- Occurrence: does not occur naturally in free form in its combined form, accounts for 27.6% of the Earth's crust.
- 2nd most abundant element on Earth after oxygen and one of the 10 most abundant elements in the solar system.

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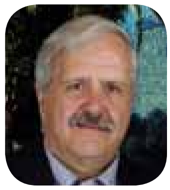

***Tony O'Lenick** is President of Siltech LLC. Tony has published six books, numerous articles and has over 300 patents. He received the 1996 Samuel Rosen Award, the 1997 Innovative Use of Fatty Acids Award and the 1996 Partnership to The Personal Care. Tony was President of the U.S. SCC in 2015 and is currently Education Chair of IFSCC.*