Beyond rheology modification: Hydrophilically modified silicone elastomers provide new benefits

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Synopsis

The development of silicone elastomers with hydrophilic functionality in the form of PEG substituents provides benefits beyond the rheology modification (thickening) that can be achieved with silicone elastomers that lack functional substituents. We have shown that PEG-modified dimethicone crosspolymer (PEG-DCP) is an effective emulsifier for water-in-silicone (w/s) emulsions where the continuous phase is cyclopentasiloxane. The utility of PEG-DCP for producing simple antiperspirant gels and also multiple emulsions (w/s/w) was demonstrated. Additional benefits for PEG-DCP such as improved compatibility with polar organic oils and reduced syneresis in anhydrous antiperspirants were also shown to be associated with the addition of hydrophilic groups to the silicone elastomer.

The performance and physical properties of a series of PEG-DCP samples from a two-level factorial design were evaluated. The variables studied were the level of PEG substitution, the length of the PEG chains, and crosslink density. All of the PEG-DCP samples were synthesized and tested in the form of dispersions in cyclopentasiloxane. Variations in the composition of PEG-DCP such as the level of PEG substitution and the length of the PEG chain were shown to have a significant effect on the viscosity of the PEG-DCP and its emulsification performance in a simple w/s emulsion. Variation of a process parameter that affects the crosslink density of the elastomer also changed the emulsification properties of the PEG-DCP.

INTRODUCTION

The introduction of silicone elastomers to the personal care industry has provided formulators with new tools for modifying the rheology and aesthetic properties of silicone-based formulations. These silicone elastomers are based on crosslinked dimethicone and are typically supplied in the form of swollen gels that contain various silicone oils. Cyclopentasiloxane in particular is the silicone fluid most often used as the swelling solvent, although other silicone fluids such as dimethicone are also used. One such elastomer with the INCI name dimethicone crosspolymer (DCP) has been shown to be useful for thickening various types of formulations, particularly anhydrous antiperspirant formulations, where cyclopentasiloxane is the vehicle (1). This silicone elastomer

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also provides novel sensory properties that are unlike anything attainable with silicone fluids.

The unique properties of the DCP/cyclopentasiloxane blend have been attributed to the extended structure of the elastomer that has the ability to absorb large amounts of silicone fluid. When the elastomer is synthesized in cyclopentasiloxane, the elastomer and cyclopentasiloxane form what is essentially one large gel in the reaction vessel. This gel is then sheared to produce gel particles that thicken silicone oils in much the same way that carbomer gel particles thicken aqueous formulations. These soft gel particles are what provide the unique aesthetic properties in many formulations.

The addition of hydrophilic polyethylene glycol (PEG) functional groups to DCP affects both the chemical and rheological properties of the silicone elastomer. This new class of materials, hereinafter referred to as PEG-modified DCP (PEG-DCP), encompasses a wide variety of different materials that range from liquids to elastomeric solids. The PEG-DCPs have very different properties from the unmodified silicone elastomer. The hydrophilic PEG substituents change the wetting properties of the elastomer and dramatically improve compatibility with polar ingredients (2). The PEG-DCPs are a new class of polymeric emulsifiers that are useful for preparing water-in-silicone (w/s) emulsions where the continuous phase consists primarily of low-viscosity silicone oils such as cyclopentasiloxane. We have also shown that PEG-DCP can be used to prepare multiple emulsions.

SILICONE ELASTOMER CHEMISTRY

All of the silicone elastomers that are made for use as ingredients in personal care formulations are based on the hydrosilylation reaction. This reaction is used to form the crosslinks between the silicone polymer chains and also to attach functional substituents such as PEG. The hydrosilylation reaction involves the addition of a vinyl group (CH$_2$=CH-R) to a silicon hydride (SiH), using a platinum catalyst. This reaction proceeds very rapidly and produces a chemically stable linkage between the silicone and the organic group. Since the silicon hydride in effect adds across the vinyl group, there are no by-products. To make a silicone precursor polymer for the hydrosilylation reaction, the silicon hydride groups are introduced randomly along the silicone chain, typically by copolymerization of methylhydrogen siloxane and dimethyl siloxane units. These precursor polymers can then be crosslinked with an α,ω-diene or a vinyl-terminated silicone polymer (e.g. vinyldimethicone). The PEG substituents are incorporated in the form of allyloxy-terminated PEGs that are added to the precursor polymer using the same hydrosilylation reaction.

To prepare PEG-DCP, the silicone precursor polymer is reacted with allyloxy-terminated PEG and crosslinker (α,ω-diene) in a solvent. For our work, the solvent was cyclopentasiloxane and the samples we evaluated were dispersions of PEG-DCP in this solvent. After completion of the hydrosilylation reaction, the elastomer dispersions were subjected to high shear mixing. When the viscosity of the elastomer dispersion is low (e.g., when the crosslink density is low), the high shear mixing has little effect, but when the hydrosilylation produces a thick elastomer dispersion (gel), the shearing step converts the material to a paste composed of small gel particles.

All of the work we are reporting here was done with PEG-DCP made from the same

precursor polymer so that the number of reactive silicon hydride sites was constant for all of the elastomer samples that were made. In this situation, a trade-off exists between the degree of PEG substitution and the crosslink density since the crosslinker and the allyloxy-terminated PEG both consume the silicon hydride groups on the precursor polymer. So, for a given level of PEG substitution, there is a maximum crosslink density that can be achieved for that PEG-DCP. In practice, however, we have found that various processing parameters affect the extent of the crosslinking reaction so that crosslink density can be varied somewhat independently for a particular level of PEG substitution. The level of PEG substitution is obviously an important factor for determining the properties of a particular PEG-DCP since it will determine the overall hydrophilicity of the elastomer. However, we have found that the crosslink density is also quite important. When the crosslink density is low, the PEG-DCP has a more extended configuration and behaves more like a liquid. When the crosslink density is high, the PEG-DCP has more elastomeric character and behaves more like the unmodified DCP elastomer.

EXPERIMENTAL METHODS

WATER-UPTAKE TEST

The sample of PEG-DCP was diluted with cyclopentasiloxane to produce a dispersion of 9% elastomer in cyclopentasiloxane (emulsions of selected samples were also made with more dilute dispersions). Water was slowly added with a pipette, a drop at a time, to the elastomer dispersion, while mixing at about 300–400 rpm until the emulsion would no longer accept additional drops of water. The endpoint was determined by carefully observing whether or not the drop was incorporated into the emulsion. If there was some doubt, the mixer was stopped and the emulsion was examined to determine if there were droplets of free water in the emulsion. If free water was not observed immediately, then the emulsion was checked again after 24 hours for water separation. If there was water separation, the test was repeated using a fresh sample, and the water addition was stopped short of the previous endpoint and the sample was observed again for water separation. By repeating the test several times, the precise endpoint can be determined. Mixing was accomplished by stirring with a combination of two mixing blades spaced approximately 1.5 inches apart on the same shaft. The mixer was a Lightnin model L1U08. The lower mixing blade was a 1.5-inch-diameter high-shear radial-flow impeller (Lightnin R-100), and the upper blade was a four-lobe pitched impeller (Lightnin A-200). The repeatability of this test was determined to be +/-1%, based on repeated testing of blinded duplicate samples.

ANTIPERSPIRANT GEL FORMULA AND PROCEDURE

	Ingredient	Weight (%)
Silicone phase	PEG-DCP (15% dispersed in cyclopentasiloxane)	6.7*
	Cyclopentasiloxane	10.3
Aqueous phase	ACH-303**	62.5
	Deionized water	8.9
	Propylene glycol	11.6

* Equivalent to 1% PEG-DCP on a 100% solids basis. When dimethicone copolyol was used, 1% of this emulsifier was used and the amount of cyclopentasiloxane was adjusted to keep the amount of silicone phase the same as for the formulas with PEG-DCP.
** 50% aqueous solution of aluminum chlorohydrate (supplied by Summit Research).

Procedure. The aqueous and silicone phases were blended in separate containers until they were homogeneous. The aqueous phase was then added to the silicone phase while mixing with the same Lightnin mixer and stirrer configuration described for the water-uptake test. The mixer speed was set at 1376 rpm, and after all the water phase was added, mixing was continued for ten minutes.

Anhydrous Roll-On Antiperspirant

Ingredient	Weight (%)
DCP (12.5% in cyclopentasiloxane)	Variable
Bentone gel VS 5*	Variable
REZAL 36G powder**	22.0
Cyclopentasiloxane	q.s. to 100%

* A blend of Quaternium-18 Hectorite, cyclomethicone, and SD alcohol 40 (supplied by Elementis Specialties).
** Aluminum-zirconium tetrachlorohydrex-GLY powder (supplied by Reheis, Incorporated).

ANHYDROUS ANTIPERSPIRANT FORMULAS AND PROCEDURE

Procedure. All of the ingredients were weighed into a glass beaker and mixed using a kitchen hand-held mixer (Braun Handblender, model MR 360) for approximately one minute.

Anhydrous Soft Solid Antiperspirant

Ingredient	Weight (%)
Elastomer (DCP or PEG-DCP)	Variable
AZG-370*	25.0
Cyclopentasiloxane	q.s. to 100%

* Aluminum-zirconium tetrachlorohydrex-GLY powder (supplied by Summit Research).

Procedure. All of the ingredients were weighed into a glass beaker and mixed using the same laboratory mixer and stirrer configuration described for the water-uptake test. The mixer was stopped periodically so that the sides of the beaker could be scraped down to ensure that the formula was uniformly mixed.

MULTIPLE EMULSION FORMULA AND PROCEDURE

	Ingredient	Weight (%)
Part A	PEG-DCP (12% in cyclopentasiloxane)	5.7
	Cyclopentasiloxane	12.4
	Tocopherol acetate	1.0
Part B	Deionized water	45.8
	Magnesium sulfate	2.1
Part C	Laureth-7	3.0
Part D	Deionized water	28.7
	Magnesium sulfate	1.3

Procedure. The ingredients in Part A and Part B were mixed in separate containers until uniform. Part B was then added to Part A while mixing with the same Lightnin mixer and stirrer configuration described for the water-uptake test. The mixer speed was set at 1376 rpm, and after all of Part B was added, mixing was continued for ten minutes. Next, Part C was mixed into the emulsion formed by Parts A and B, and this mixture was then dispersed into Part D while mixing with the same mixer, but at a lower speed (500 rpm)

SYNERESIS TEST

To determine syneresis for an anhydrous antiperspirant soft solid formula, 30 g of the formula is weighed into a 50-ml polypropylene (disposable) centrifuge tube (Fisherbrand, cat. # 05-539-9). The sample is then spun at 3000 rpm for 30 minutes using a bench top centrifuge (International Equipment Company, model HN-SII). After centrifuging, the tube with the sample is placed on an electronic balance and tared. The supernatant fluid is carefully pipetted from the top of the sample and the amount of fluid removed is weighed by difference. Syneresis is reported as a percentage of the original sample weight (i.e., [weight of removed fluid]/[sample weight] × 100).

VISCOSTY MEASUREMENTS

Viscosity measurements were made using a Brookfield Model RVDVII+ equipped with a Helipath stand. Various combinations of "T" spindles and speeds were used according to the type of formula tested:

PEG-DCP dispersions: Spindle #93 @ 2.5 rpm
Antiperspirant gel viscosity: Spindle #93 @ 2.5 rpm
Antiperspirant roll-on formula viscosity: Spindle #91 @ 50 rpm (Helipath off)
Antiperspirant soft solid formula viscosity: Spindle #93 @ 2.5 rpm

RESULTS AND DISCUSSION

SYNTHESIS AND EVALUATION OF PEG-DCP VARIANTS

In order to evaluate the effects of various composition and process variables on the properties of PEG-DCP, a two-level factorial experimental design was performed. The variables (factors) studied were the level of PEG substitution, the length of the PEG chain, and a process variable that was thought to have the largest effect on the crosslink density. This process variable is referred to as the "crosslink density process parameter." In a designed experiment, a series of runs are made in which the variables under study are systematically changed in order to determine their effects on the properties of interest. For this study, we evaluated the viscosity of the PEG-DCP samples and their emulsification abilities as measured by the water-uptake test. The water-uptake test provides a measure of the emulsification effectiveness. It is used to determine the maximum amount of water that can be incorporated into a w/s emulsion where the dispersion of PEG-DCP in cyclopentasiloxane is used as the continuous phase.

The viscosity results for the PEG-DCP samples from the experimental design runs are

shown in Figures 1 and 2. Figure 1 shows the results for the set of runs where long-chain PEG was incorporated into the elastomer. All of these PEG-DCP samples had relatively low viscosity, except for the sample where the PEG substitution level and crosslink density were both low. When the PEG-DCP was prepared using short-chain PEG, the results shown in Figure 2 indicate that crosslink density had a larger effect on the viscosity of the dispersion. It should be noted that the central data point shown in Figures 1 and 2 (medium PEG substitution level and medium crosslink density process parameter) corresponds to a PEG-DCP made at the midpoint for all three process variables (including PEG chain length). This is a consequence of the experimental design that calls for multiple runs at the "center point" of the variables being studied.

The water-uptake results are shown in Figures 3 and 4. All of the PEG-DCP samples made with long-chain PEG were effective emulsifiers, producing water uptake values of greater than 70%. Water uptake for the PEG-DCP runs with short-chain PEG, shown in Figure 4, were somewhat lower. The sample made with the minimum PEG substitution level and high crosslink density had the worst emulsification efficiency, with a water-uptake value of only 25%. Overall, the PEG-DCP runs where the long-chain PEG was used produced the most effective emulsifiers. When PEG-DCP was made with short-chain PEG, the best emulsifiers were made with the high level of PEG substitution.

The water-uptake values were initially measured for PEG-DCP dispersions that contained 9% by weight of the elastomer. The water-uptake test was repeated for dispersions that were diluted (with cyclopentasiloxane) to 7% and 5%. For the PEG-DCP sample made with long-chain PEG, dilution did not have a large effect on water uptake. For two of the PEG-DCP samples made with short-chain PEG, dilution dramatically increased the water uptake, as shown in Figure 5. This dilution effect may be due to the elastomer assuming a more extended configuration at lower concentrations. Emulsions made with the diluted PEG-DCP samples appear to be just as stable as those made with the original PEG-DCP samples (9% elastomer).

EVALUATION OF PEG-DCP IN ANTIPERSPIRANT GEL

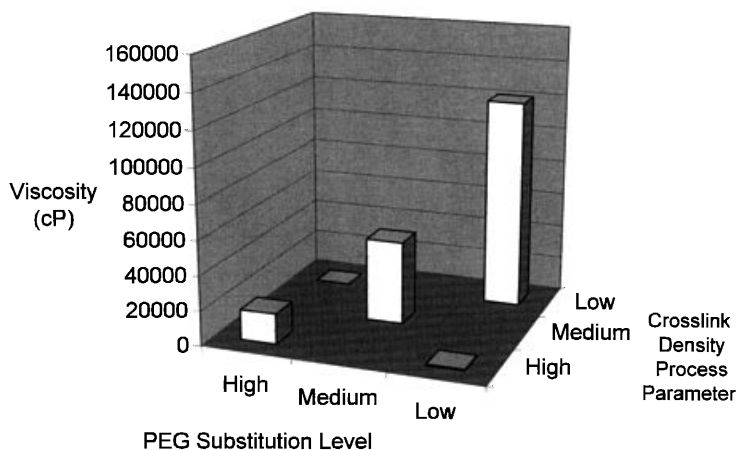One of the largest commercial applications for w/s emulsions where the continuous phase

Figure 1. The effect of PEG substitution level and crosslink density process parameter on the viscosity of PEG-DCP made with long-chain PEG.
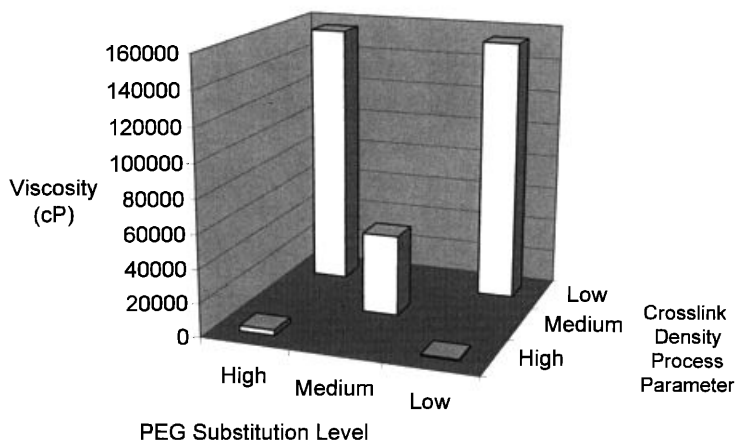
Figure 2. The effect of PEG substitution level and crosslink density process parameter on the viscosity of PEG-DCP made with short-chain PEG.
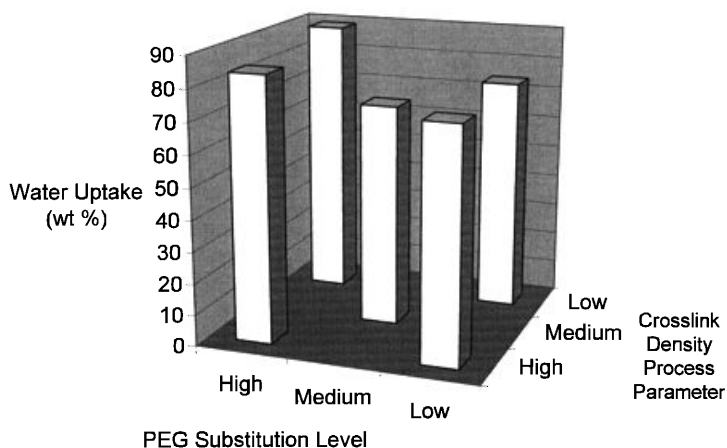

Figure 3. The effect of PEG substitution level and crosslink density process parameter on water uptake for PEG-DCP based on long-chain PEG.

consists primarily of cyclomethicone (cyclotetrasiloxane and/or cyclopentasiloxane) is in antiperspirant gels. In these products, the water phase consists of an aqueous solution of antiperspirant salt, and often the refractive index of the water and silicone phase are matched to produce a transparent emulsion. For our investigation, we compared a commercial silicone emulsifier, PEG/PPG-18/18 dimethicone (Dow Corning® 5225C Formulation Aid), with two elastomeric emulsifiers. The first was similar to the PEG-DCP samples discussed previously. It was made with a high level of PEG substitution and low crosslink density. For the other elastomeric emulsifier, we used a copolymer of polyethylene glycol and polypropylene glycol (PEG/PPG) as the hydrophilic group in order to make it more similar to the dimethicone copolyol emulsifier. This second type of elastomeric emulsifier is referred to as PEG/PPG-DCP.

Both elastomeric emulsifiers produced stable antiperspirant gels. Figure 6 shows the viscosity for the gels based on the elastomeric emulsifiers and the PEG/PPG-18/18
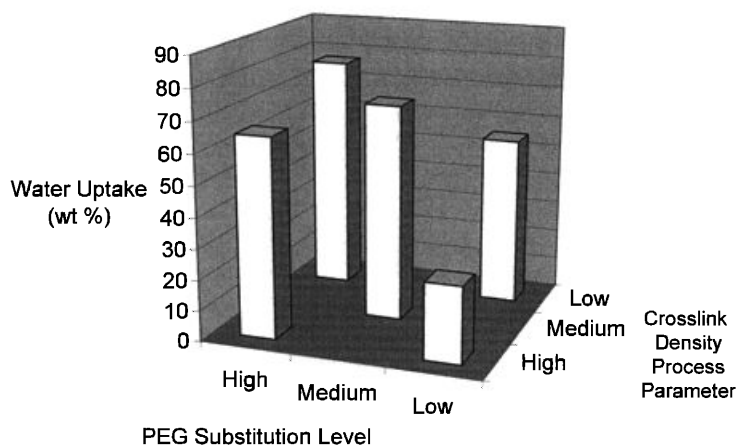
Figure 4. The effect of PEG substitution level and crosslink density process parameter on water uptake for PEG-DCP made with short-chain PEG.
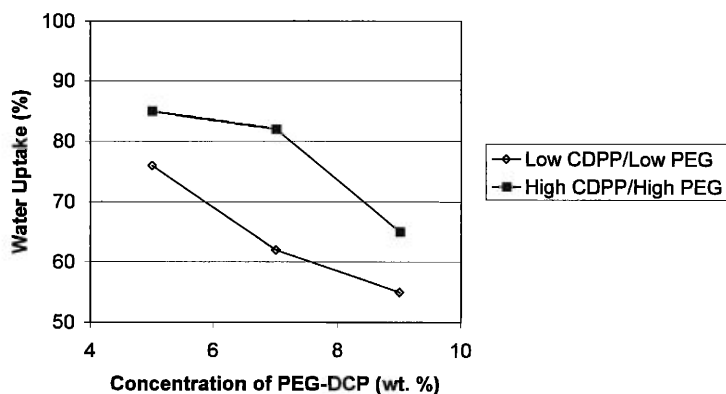

Figure 5. The effect of dilution level on water uptake for two PEG-DCP samples made with short-chain PEG.

dimethicone. The viscosity of the gel made with PEG/PPG-DCP was much lower than that of the gel made with PEG-DCP, and although it appeared to be stable over time, differences were noted when the gels were rubbed on a hard surface. This "rub-out" test is a measure of how stable the gel is when exposed to very high shear, such as when the formula is applied to the skin. An acceptable gel maintains its integrity when rubbed out, but when the emulsion breaks under high shear and releases the aqueous antiperspirant, this is unacceptable because this can produce stickiness and a more noticeable white residue when the formula dries. The gels made with dimethicone copolyol and PEG-DCP passed the "rub-out" test, but the gel made with PEG/PPG-DCP failed.

MULTIPLE EMULSIONS

In addition to simple w/s emulsions, PEG-DCP can be used to prepare multiple emulsions, including water-in-silicone-in-water (w/s/w) emulsions (3) and propylene glycol-in-silicone-in-water emulsions (4). In these systems, we believe that the thickening effect
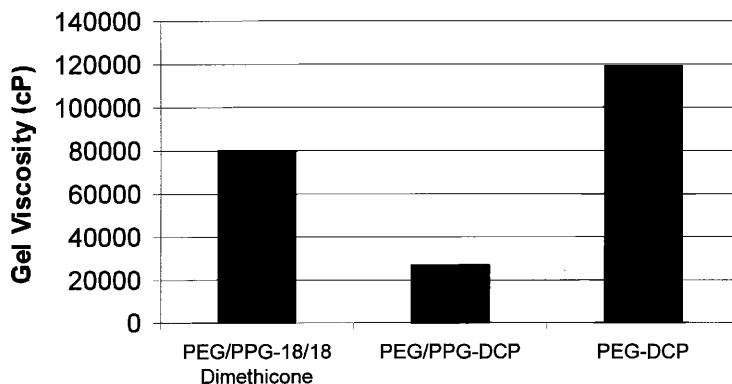
Figure 6. The effect of emulsifier type on the viscosity of w/o antiperspirant gels.

of the silicone elastomer in the silicone phase stabilizes the initial w/s (or pg/s) emulsions and helps protect them against inversion when they are dispersed in water. Multiple emulsions offer the potential to formulate products with ingredients that may not be stable in conventional emulsions. Placing them in the innermost phase of a multiple emulsion could protect such ingredients from degradation and perhaps modulate their release when the product is applied. Figure 7 shows a multiple emulsion that was made by dispersing a primary w/s emulsion into a second water phase (details about the preparation of this sample can be found in the Experimental section).

COMPATIBILITY WITH POLAR INGREDIENTS

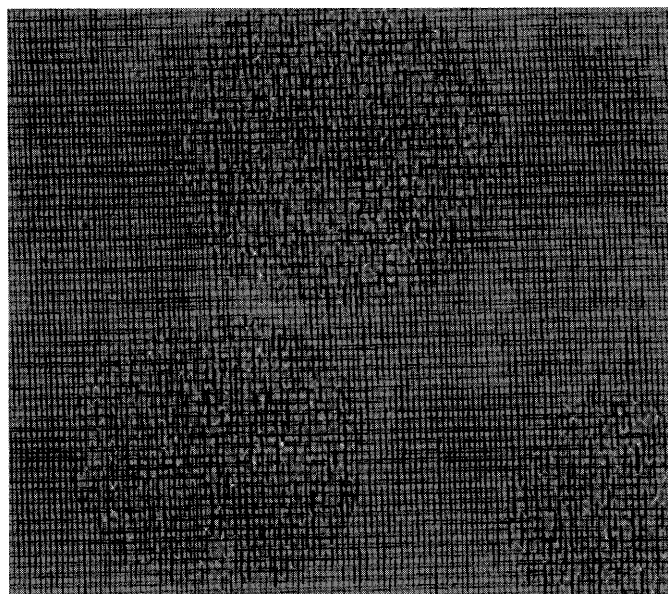We have established that hydrophilically modified silicone elastomers function as w/s

Figure 7. Multiple emulsion photomicrograph (400× magnification).

emulsifiers, but there are other benefits of this modification. One additional benefit is improved compatibility with organic oils compared to DCP. The unmodified silicone elastomer is very sensitive to the presence of polar oils, even oils that are soluble in cyclopentasiloxane. Such oils tend to collapse elastomer gels that are swollen in cyclo- pentasiloxane, leading to a loss of thickening. Common organic oils such as fatty esters will have this effect even at relatively low addition levels. At higher concentrations, fatty esters can precipitate DCP, presumably due to poor solvation of the elastomer. The polar functionality of the PEG-DCP elastomer increases the range of organic oils that are compatible. To illustrate this phenomenon, the PEG-DCP samples from the designed experiment were blended with tocopherol. Tocopherol was chosen partly because it is completely miscible in cyclopentasiloxane and, therefore, any haziness observed in the samples could be attributed to interaction with the elastomer and not the solvent.

The tocopherol was slowly added to the elastomer blends until the mixtures became hazy, indicating incompatibility. The concentration of tocopherol required to produce incompatibility was recorded as the "saturation point" for the particular elastomer blend. When tocopherol is blended with DCP in cyclopentasiloxane, the mixture is hazy even at addition levels of about 1%. The results for the PEG-DCP samples are shown in Figures 8 and 9. When long-chain PEG is used to make the PEG-DCP, the saturation point increases with higher levels of PEG substitution and decreases as the crosslink density increases (Figure 8). Figure 9 shows similar trends for PEG-DCP made with short-chain PEG, but overall the saturation points are lower. Taken together, these data clearly point to the role of PEG substitution in increasing compatibility with polar organic oils. This makes sense because more PEG substitution increases the overall polarity of the elastomer. Prieto and O'Lenick (5) have reported a similar relationship between PEG level and solubility in polar media for the dimethicone copolyols. The effect of crosslink density is also clear, but the explanation of why is not so easy. Perhaps the tighter self-association of more crosslinked elastomer makes it more sensitive to the solvent environment.

USING PEG-DCP TO REDUCE SYNERESIS

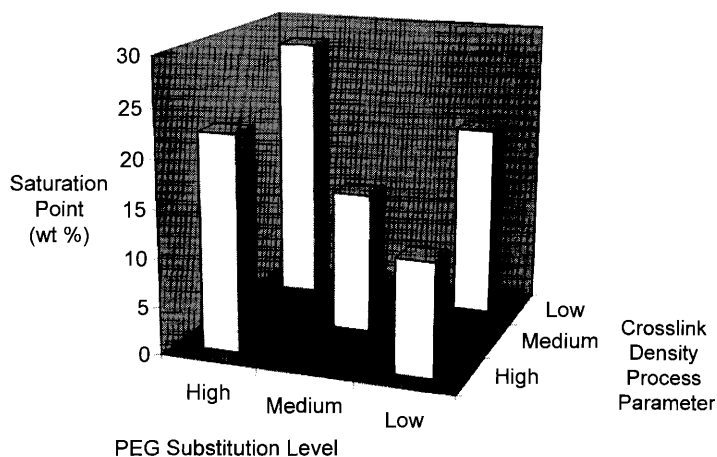One of the applications that was first demonstrated for DCP was its use as a thickener

Figure 8. The effect of PEG substitution level and crosslink density process parameter on the tocopherol saturation point of PEG-DCP made with long-chain PEG.
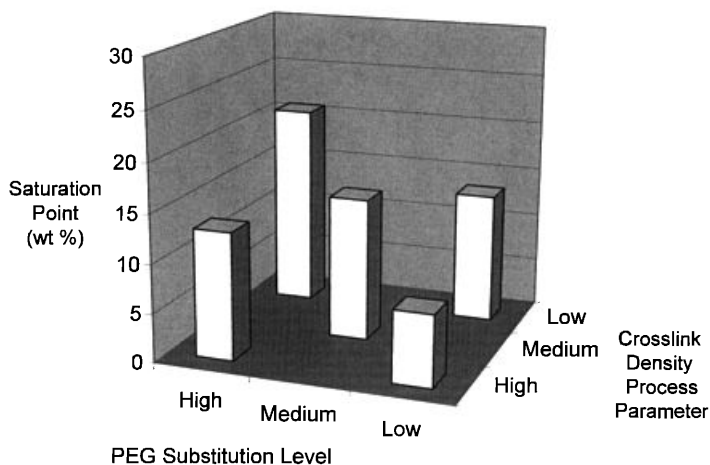
Figure 9. The effect of PEG substitution level and crosslink density process parameter on the tocopherol saturation point of PEG-DCP made with short-chain PEG.

for anhydrous antiperspirants. The utility of DCP for thickening a simple anhydrous roll-on antiperspirant based on cyclopentasiloxane is illustrated in Figure 10. This graph compares the thickening of DCP to that obtained with an organomodified clay (Quaternium-18 Hectorite). Although it is an effective thickener, formulations based on DCP do exhibit syneresis unless the concentration of DCP is quite high (>7% elastomer). Syneresis in this context refers to the separation of cyclopentasiloxane from the formula and is quite undesirable because the silicone fluid tends to leak and coat the outside of the package. Syneresis can appear over time, or when the formula is subjected to shear forces as when it is dispensed from the package. We used a centrifuge test as a measure of the potential for a sample to exhibit syneresis.

A series of simple antiperspirant soft solid formulas was prepared using DCP (Dow Corning® 9040 Silicone Elastomer Blend) and PEG-DCP made with long-chain PEG, a high level of PEG substitution, and low crosslink density. Figure 11 shows the
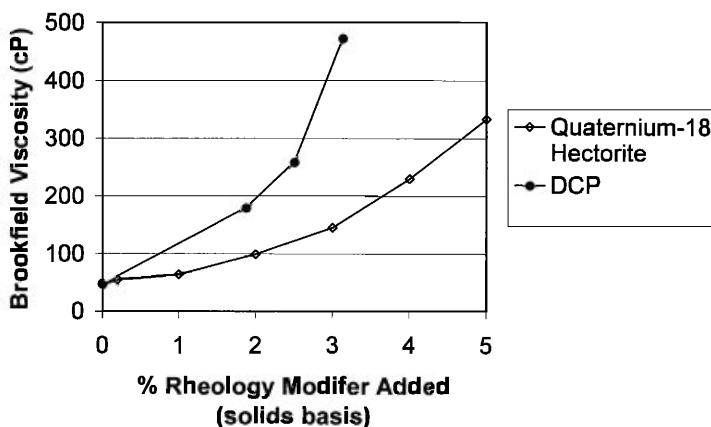

Figure 10. Comparison between DCP and organomodified clay as thickeners for an anhydrous roll-on antiperspirant.
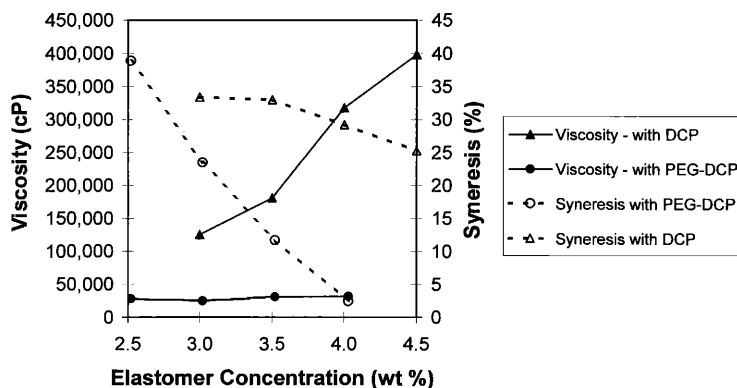
Figure 11. Viscosity and syneresis for anhydrous antiperspirants thickened with DCP versus PEG-DCP.

viscosity and syneresis values for these formulas. Syneresis is reduced as the elastomer concentration increases for both DCP and PEG-DCP, but the effect is much more pronounced for the PEG-DCP. For DCP, the viscosity increase with each increment of elastomer level is such that the viscosity of the formula becomes unmanageable before syneresis is reduced to values close to zero. On the other hand, each increment of added PEG-DCP produced a large reduction in syneresis, while the viscosity was essentially unchanged. It should be noted that the viscosities shown for the formulas made with PEG-DCP are somewhat misleading because these systems are strongly shear thinning. As a result, the measured viscosity is quite variable, depending on the shear rate used. If the sample is subjected to shear—for example, by shaking the container vigorously— the viscosity will be much lower than it was before shaking, but will increase over time. This increase in viscosity over time may be a consequence of chain entanglement be- tween loosely crosslinked elastomer chains, or an association between the PEG substitu- ents. Whatever the cause of the reversible shear thinning effect, we have found PEG- DCP quite useful for making stable low-viscosity antiperspirants such as roll-ons, and we believe this effect would be useful for aerosol antiperspirants as well.

CONCLUSIONS

We have shown that a new class of silicone elastomers, PEG-modified dimethicone crosspolymer (PEG-DCP), can provide benefits that are different from the thickening effects that can be achieved using silicone elastomers without functional substituents. Our work has demonstrated that PEG-DCP has utility as an emulsifier for preparing w/s emulsions and multiple (w/s/w) emulsions where the silicone phase is cyclopentasilox- ane. The addition of the hydrophilic PEG substituents to the silicone elastomer improves compatibility with polar organic oils, and this was illustrated with tocopherol. It was found that PEG-DCP is not as effective as the non-functionalized elastomer (DCP) for thickening anhydrous antiperspirants, but is more effective for reducing syneresis.

In order to evaluate the effects of variations in composition and processing on the performance and physical properties of PEG-DCP, samples from a two-level factorial design were evaluated. The variables studied were the level of PEG substitution, the length of the PEG chains, and crosslink density. In general, PEG-DCP samples made

with longer PEG substituents were more effective emulsifiers, as measured by a water uptake test, and could accommodate more tocopherol. Emulsification effectiveness and compatibility with tocopherol also increased as the level of PEG substitution increased. The crosslink density of the PEG-DCP had the largest effect on the viscosity elastomer dispersion, with lower crosslink density giving the highest viscosities. These findings suggest that PEG-DCP can be tailored for specific applications by selecting the appropriate combination of composition and process.

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(3) Z. Lin, W. J. Schulz, Jr., and S. Zhang, *U.S Patent 5,948,855* (September 9, 1999).
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