

The Influence of Various Silicones on the Rheological Parameters of AZG Containing Silicone-Based Gels

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Abstract

Aluminium zirconium tetrachlorohydrate glycine (AZG) is a popular antiperspirant/deodorant agent, formulated in various forms including the clear gels. Silicones are used for the preparation of these gels, giving them desirable characteristics. The aim of this study was to investigate the influence of various silicones, when used in combination, on the rheological properties of the resulting AZG gels prepared. Based on preliminary studies, various AZG containing silicone-based gel formulations were prepared. Silicones used (as ternary mixtures) included ABIL[®] EM 97, ABIL[®] 8839 and ABIL[®] 8852. Formulations prepared were then examined rheologically and their plastic viscosity and yield values determined. Results showed that the amount of ABIL[®] EM 97 (used as an emulsifier) present within the gel formulation is critical. An increase in the amount of this silicone, corresponding to a small decrease in the amount of the hydrophobic structure building (gelling agent) ABIL[®] B8839, increased the plastic viscosity and yield values of the gel. On the other hand, an excess amount of ABIL[®] B8852, as a hydrophilic co-surfactant, reduced the viscosity and yield values of the resulting gel. Eventually, among the formulations prepared, formulation F5 with suitable aesthetic and skin feel properties, spreadability and rheological behaviors, was selected for further studies. By constructing the up-curve and down-curve of this formulation, presence of a plastic thixotropic behavior was confirmed. Inclusion of various amounts of the hydrophobic silicone-based agent, dimethicone, within formulation F5 showed that by increasing the amount of dimethicone present, the plastic viscosity and yield values of the gel would be reduced. This reduction was significant at dimethicone concentrations above 0.5%. Furthermore, by increasing the amount of dimethicone present, the calculated "*percentage of reduction in plastic viscosity*" also increased. This means that the extent of thixotropy of the gel formulation increases by the addition of dimethicone. This finding was also backed up by the resulting rheograms constructed. Overall, addition of 0.75% dimethicone produced the most acceptable product in terms of an appropriate viscosity, yield value and extent of thixotropy. In conclusion, this study shows that in-depth rheological assessment of AZG gels prepared from silicones could be used as an important tool during their formulation and characterization in order to obtain an effective formulation with desirable properties.

Keywords: AZG; Antiperspirant; Deodorant; Silicone-based gels; Rheology, Plastic viscosity; Yield value; Thixotropic behavior.

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Introduction

Personal health and hygiene is of great importance in today's life. Among the various hygienic products are antiperspirants and deodorants. Perspiration is a natural bodily process in human being and is responsible for regulation of temperature and elimination of some waste compounds (1). Excessive perspiration and/or unpleasant odor of sweat, created as a result of being acted upon by the existing bacterial flora of the skin, could be socially and personally undesirable and troublesome. For this purpose various agents, especially the aluminium and zirconium complexes stabilized through glycine (such as aluminium zirconium tetrachlorohydrate glycine or AZG), have been of interest with respect to their good antiperspirant and deodorant properties. These complexes are being formulated and available in global commercial market in various forms, including the clear gels. Clear gels have the distinguished ability not to leave any white physical residue on the skin surface and clothing, as well as good spreadability, substantivity and consumer acceptance (2). The use of silicones for the purpose of preparing these gels has attracted a great deal of attention, particularly in the past decade. Various silicones are used in combination for this purpose, in an attempt to prepare a product which does not feel oily, greasy or tacky (sticky) on application and provides a feeling of softness, smoothness, dryness and coolness on the skin (3-5).

Assessment of the rheological behavior of topical products, and in particular semisolids, is important in obtaining an acceptable formulation with desirable viscosity, spreadability, stability and good substantivity on the skin surface. Furthermore, the overall skin feel and consumer acceptance is influenced by the rheological characteristics of the product (1).

Unfortunately, very few studies have been conducted on the use of rheological parameters for the assessment of antiperspirant/deodorant silicone-based clear gels. In all these rather limited studies, the only rheological parameter determined was the viscosity of the product, as a single point determination (i.e. viscosity determined at a specific shear stress and shear

rate). Based on these investigations, a viscosity greater than 50000 cps (50 Pa sec) and up to about 100000 cps (sometimes even up to 200000 cps) has been recommended to be desirable for antiperspirant/deodorant silicone-based clear gels (3, 4, 6, 7). However, despite emphasizing the importance of assessing the rheological characteristics of silicone-based gels in order to obtain a product with good skin feel and applicability, none of these studies have gone beyond the determination of viscosity (as a single point evaluation).

In another study by Dederen and coworkers, it was stated that a silicone-based gel should be formulated in such a way to show a non-Newtonian rheological behavior, with viscosity being reduced by shearing the product (8).

Finally, in a study by Starch et al, it was found that the use of polyethylene glycol as a hydrophilic moiety in modified dimethicone cross-polymers (as emulsifiers), could be found useful in the preparation of water in silicone emulsions and helps to increase the viscosity of the product (9).

As mentioned above, to the best of our knowledge, construction of rheograms and determination of the rheological parameters and behavior of AZG containing silicone-based clear gels, as a useful mean to characterize these products has not been extensively investigated. Hence, the present study was undertaken to examine the influence of various silicones, when used in combination, on the rheological properties of the resulting AZG containing gels prepared.

Experimental

Materials

Aluminium zirconium tetrachlorohydrate glycine was purchased from Reheis Co., USA. ABIL[®] EM 97, ABIL[®] 8839 and ABIL[®] 8852 were all kindly donated by Goldschmidt Co., Germany. Dimethicone 200 Fluid was obtained from the Dow Corning Co., USA. Propylene glycol was purchased from the Merck Chemical Co., Germany.

Methods

Based on preliminary studies conducted, the

formation of silicone-based gels was only found to be feasible when three different silicones were compounded as a ternary mixture. For this purpose three different silicones (silicone phase, overall accounting for 17.25% of the final formulation), which were ABIL[®] EM97 (EM97), ABIL[®] 8839 (B8839) and ABIL[®] 8852 (B8852) used in this study. Table 1 shows the amount of each silicone used in the formulations prepared. Each formulation contained a fixed amount of 20% aluminium zirconium tetrachlorohydrate glycine (AZG) as the antiperspirant/deodorant agent, along with 28% propylene glycol, and made up to volume with distilled water (aqueous phase). The aqueous phase was then slowly added to the silicone phase under a constant stirring rate of 200rpm at room temperature. Following complete addition of the aqueous phase, the stirring rate was increased to 2000rpm and maintained at this speed for around 10min, in order to allow gel formation.

The influence of the presence of various amounts (0.5-1.5% in the final formulation) of dimethicone (Dow Corning[®] 200 Fluid) added to the silicone phase as an aesthetic and feeling agent (to improve skin feel), was also investigated in formulation F5. Gels prepared were then individually examined at room temperature, using a Brookfield DV-III+ rheometer equipped with spindle number 3 geometry. By the application of various shear rates (SR) and shear stresses (SS), relevant rheograms were constructed and used for the determination of plastic viscosity (η_{plastic}) and the yield value (Y_{plastic}). η_{plastic} values were calculated by determining the slope of the linear region of the rheograms constructed (in all the rheograms at SR values between 115.2 – 384 sec⁻¹). Y_{plastic} values were determined by initially finding the non-linear region of the rheograms (in all the rheograms at SR values below 115.2 sec⁻¹). Next, in order to make this non-linear region as linear as possible, in order to determine the y-intercept (yield value) more accurately, the log₁₀ values of SS were plotted against the log₁₀ values of SR. In this way, a linear equation ($y = mx + c$) for this region (SR values below 115.2 sec⁻¹) was obtained, and by calculating the antilog of the y-intercepts (c in the equation), Y_{plastic} values were determined.

Furthermore, the thixotropic behavior of dimethicone containing AZG silicone-based gels were also examined by constructing the appropriate up-curves and down-curves, followed by calculation of the "percentage of reduction in plastic viscosity" (%RPV) using the following equation: %RPV = [(up-curve η_{plastic} – down-curve η_{plastic}) / up-curve η_{plastic}] x 100. For this purpose the slopes of the linear region of both the up-curve (at SR values between 115.2 – 384 sec⁻¹) and down-curve (at SR values between 115.2 – 230.4 sec⁻¹) of each rheogram was determined and placed into the equation to calculate %RPV, as an index for the extent of thixotropy of the gel.

Results and discussion

The use of antiperspirants and deodorants has been considered as a rather important commodity for personal hygiene worldwide. As mentioned earlier, AZG is a relatively new complex of aluminium and zirconium stabilized by glycine and is capable of providing both antiperspirant and deodorant properties (1, 2). In recent years clear gels and sticks have been introduced as highly efficient and popular forms of antiperspirant/deodorant products, leaving no white physical residue on the skin surface and clothing. For the purpose of preparing clear gels, silicones have been proposed as a good candidate for gelation and structure building within the system (3-5).

Table 1. Various AZG containing silicone-based gel formulations investigated in this study. The overall amount of the silicone phase, consisting of a ternary mixture of silicones EM97, B8839 and B8852, in all formulations was 17.25%.

| Formulation | Silicone phase (amount in %) | | |
|-------------|------------------------------|-------|-------|
| | EM97 | B8839 | B8852 |
| F1 | 8.0 | 87.5 | 4.5 |
| F2 | 9.0 | 86.5 | 4.5 |
| F3 | 10.0 | 85.5 | 4.5 |
| F4 | 11.0 | 84.5 | 4.5 |
| F5 | 12.0 | 83.5 | 4.5 |
| F6 | 13.0 | 82.5 | 4.5 |
| F7 | 14.0 | 81.5 | 4.5 |
| F8 | 15.0 | 80.5 | 4.5 |
| F9 | 11.0 | 81.0 | 8.0 |
| F10 | 12.0 | 80.0 | 8.0 |
| F11 | 13.0 | 79.0 | 8.0 |
| F12 | 7.5 | 84.5 | 8.0 |
| F13 | 8.5 | 83.5 | 8.0 |
| F14 | 9.5 | 82.5 | 8.0 |

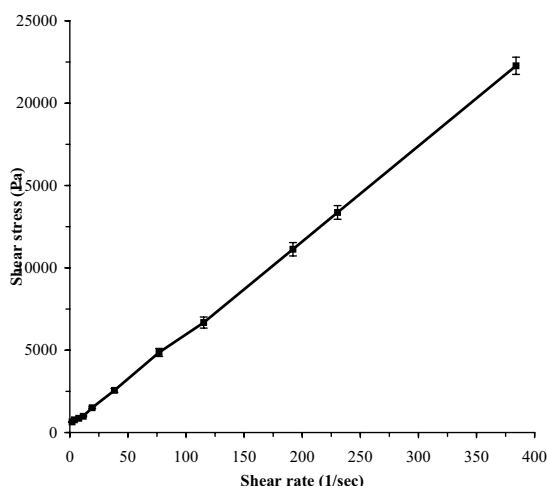


Figure 1. Rheogram of the AZG containing silicone-based gel formulation F5, showing the presence of a plastic rheological behavior ($n = 3$, data points are presented as mean \pm SD).

Viscosity and rheological behavior are among the most important and note-worthy characteristics of any vehicle used for topical application within the hygienic/cosmetic field (1). Spreadability, sensory and aesthetic properties, as well as consumer acceptability of an antiperspirant/deodorant gel could be greatly affected by its' viscosity and rheological behavior. Hence, in this study the influence of the presence of some well-known silicones, as ternary mixtures, on the rheological parameters of the resulting AZG gels was investigated. This type of studies is rather scarce and limited in the

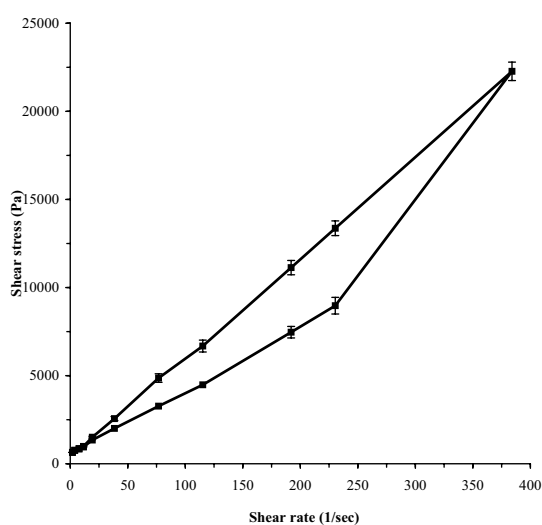


Figure 2. Rheogram of the AZG containing silicone-based gel formulation F5, showing the presence of a plastic thixotropic behavior ($n = 3$, data points are presented as mean \pm SD).

literature and their conductance could provide valuable data for the formulation of a desirable and acceptable product.

In this study three different silicones; namely EM97, B8839 and B8852; were employed. EM97 is a silicone product consisting of a combination of cyclopentasiloxane (hydrophobic nature) and dimethicone copolyol (hydrophobic nature). Hence, EM97 is expected to have emulsifying ability, and used as an emulsifier in this study. On the other hand, B8839 is a silicone product made up of a mixture of cyclopentasiloxane and cyclohexasiloxane, both having a lipophilic nature and act as the main gelling agent in here. Finally, B8852 is a hydrophilic surfactant and emollient made of dimethicone copolyol (10). Based on preliminary studies and construction of a ternary phase diagram, a combination of all three silicones mentioned above (as a ternary mixture) was found to be critical and essential for gel formation. The pH values of various formulations prepared (Table 1) on this basis were all within the acceptable range of 5.2 - 5.3, suitable for topical application within the armpit region (1, 2, 5). All the AZG containing silicone-based gels prepared showed a typical plastic rheological behavior. An example of such rheogram (for the selected formulation F5) has been shown in figure 1. Based on the non-Newtonian rheogram obtained, it is clear that following the application of shear stress, initially the gel structure resists movement and flow due to the three-dimensional gel network present within the system. This section of the rheogram represents plastic deformation of the gel network, which is then followed by structural breakdown at higher applied stresses, and a resulting flow and plastic deformation. Eventually the system behaves like a Newtonian fluid (at higher shear rates), showing a linear region, the slope of which could be used to determine the plastic viscosity of the gel. The rheological parameters determined for different AZG containing silicone gels prepared in this study are shown in Table 2. The results show that the amount of emulsifier EM97 used in the formulation is rather critical and an increase in the amount of EM97 (up to 15%), corresponding to a decrease in the amount of the hydrophobic structure building silicone B8839, could increase viscosity and strengthen

the gel structure as reflected from the yield values (Y_{plastic}) obtained. This finding shows the important role of EM97 as an emulsifier in these formulations and it is presumed that the hydrophilic chains of the gel-forming silicone B8839 are better stretched, aiding subsequent chain entanglement required for the formation of a strengthened three-dimensional gel network. Hence, an increase in the amount of EM97 helps to increase the viscosity and yield values of the resulting gel, despite a corresponding decrease in the amount of B8839. Nevertheless, the η_{plastic} and Y_{plastic} values of formulation F7 and F8, containing the greatest amount of EM97 were undesirably high, making spreadability and dispelling the product out of the application container rather difficult and cumbersome. Hence, overall, formulations F4, F5 and F6 were found to have desirable viscosity [within the recommended range of above 500000 cps for antiperspirant/deodorant silicone-based gels (3, 4, 6, 7)] and yield values, based on their ease of application and spreadability. Formulations F1 to F3 had lower viscosity and yield values, being significantly ($P < 0.05$, ANOVA with Tukey post Hoc test) lower than formulations F5 and F6. This suggests that the presence of at least 84.5% B8839 in the silicone phase is critical to achieve a gel formulation with suitable rheological characteristics. Furthermore, in formulations F9 to F11 the amount of B8852 was increased, with a corresponding decrease in the amount of B8839 and in formulations F12 to F14 the increase in B8852 corresponded to a decrease in EM97. These attempts all resulted in formulations with significantly ($P < 0.05$, ANOVA with Tukey post Hoc test) lower viscosity and yield values than formulations F4 to F6. These findings suggest that the presence of an excess amount of B8852, as a hydrophilic surfactant, can not match the viscosity increasing and structure-building effects of the emulsifier EM97. In another word, by reducing the amount of EM97 and maintaining the amount of B8839 constant (formulations F12 to F14), the increased B8852 can not provide the same degree of surfactancy as EM97, resulting in an overall reduction in viscosity and yield values of the gel formulation. This is presumably due to the rather hydrophobic nature of B8839, requiring greater surfactancy

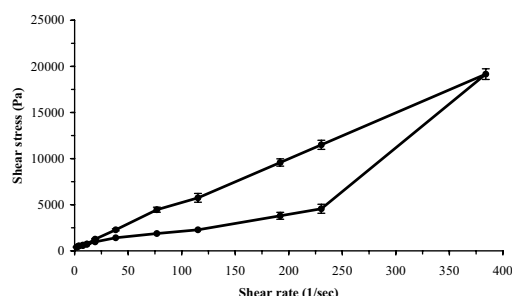


Figure 3. Rheogram of the AZG containing silicone-based gel formulation F5, containing 0.75% dimethicone ($n = 3$, data points presented as mean \pm SD).

for gel formation. Also, these findings show that a reduction in the amount of B8839, in favor of B8852, again significantly ($P < 0.05$, ANOVA with Tukey post Hoc test) reduces the η_{plastic} and Y_{plastic} values of the resulting formulations (F9 to F11). This is possibly because the amount of the gel-forming silicone B8839 has fallen below the sufficient level to produce a strong and desirable gel network. Interestingly, it should also be pointed out that omitting B8852 from the gel formulation, failed to produce an aqueous-based AZG gel formulation, emphasizing the need for B8852 as a hydrophilic co-surfactant for gel formation, besides the main emulsifier EM97.

Among the three desirable formulations (F4 to F6) chosen, formulation F5 which was slightly better than the other two formulations in terms of its' aesthetic and skin feel properties (in particular cooling effect), spreadability and psychorheological behaviors, was selected for further studies. By constructing the up-curve and down-curve of formulation F5 (Figure 2), the resulting rheogram showed the presence of a

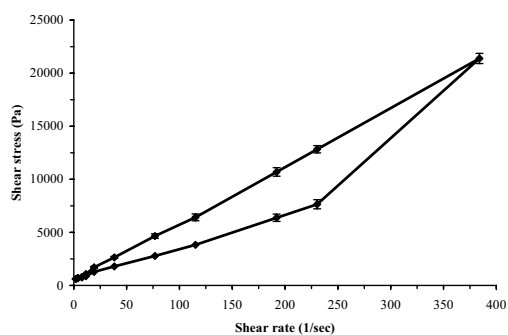


Figure 4. Rheogram of the AZG containing silicone-based gel formulation F5, containing 1.5% dimethicone ($n = 3$, data points presented as mean \pm SD).

Table 2. Rheological parameters (plastic viscosity and yield value) determined for various AZG containing silicone-based gels investigated in this study (n = 3, data expressed as mean \pm SD).

| Formulation | η_{plastic} (Pa sec) | Y_{plastic} (Pa) |
|-------------|----------------------------------|---------------------------|
| F1 | 46.6 \pm 0.8 | 277.1 \pm 3.3 |
| F2 | 48.5 \pm 0.9 | 290.4 \pm 2.6 |
| F3 | 50.9 \pm 0.7 | 314.3 \pm 5.4 |
| F4 | 54.3 \pm 1.1 | 339.4 \pm 5.1 |
| F5 | 58.0 \pm 0.8 | 347.3 \pm 3.9 |
| F6 | 60.4 \pm 0.7 | 359.1 \pm 4.4 |
| F7 | 64.8 \pm 1.8 | 380.7 \pm 7.3 |
| F8 | 67.4 \pm 1.5 | 408.6 \pm 5.3 |
| F9 | 49.7 \pm 1.2 | 328.5 \pm 4.8 |
| F10 | 48.9 \pm 0.4 | 315.2 \pm 3.7 |
| F11 | 48.0 \pm 1.4 | 304.9 \pm 3.9 |
| F12 | 46.1 \pm 2.1 | 275.3 \pm 6.8 |
| F13 | 47.8 \pm 1.2 | 303.4 \pm 5.5 |
| F14 | 49.3 \pm 1.6 | 325.1 \pm 3.7 |

plastic thixotropic behavior. This would suggest that the use of silicones for the preparation of an AZG antiperspirant/deodorant gel could result in a gel network sensitive to shearing, being disrupted reversibly in a time-dependent manner. This is a desirable behavior for a topical gel, since the gel formulation could remain stable following preparation and packaging within the container, and then could break down as a result of shearing stresses applied during exit from the container and spreading on the skin surface. This would in turn result in a reduction in the viscosity of the gel, for a suitable length of time to allow proper and easier spreading of the product on the skin surface.

Next, it was decided to add small amounts of dimethicone to the selected formulation F5. Dimethicone is a hydrophobic silicone-based compound widely used in hygienic/cosmetic industry. The use of dimethicone in antiperspirant/deodorant products has been recommended due to its' rather varying properties, including emolliency, anti-tackiness effects, improved spreadability and glide, feeling of skin softness and smoothness, and prevention

of white residue build up on the skin surface and clothing (11). The amount of dimethicone added to formulation F5 was within the routinely used range of 0.5 - 1.5% (11, 12). The influence of dimethicone on rheological parameters of formulation F5 is shown in Table 3. It is clear that by increasing the amount of dimethicone present within the formulation, the η_{plastic} and Y_{plastic} values are decreased. This reduction was significant ($P < 0.05$, ANOVA with Tukey post Hoc test) at dimethicone concentrations above 0.5%, compared with gels containing no dimethicone. Furthermore, by increasing the amount of dimethicone present the %RPV is also increased. These findings would mean that dimethicone, being a fluid, could lodge between the silicone chains of B8839, lubricating and assisting the movement of these chains and as a result lowering the extent of chain entanglements and secondary chemical bond formation between them. Hence, the Y_{plastic} value, which is a representative of the extent of elastic components present within the material is reduced and at the same time due to a more prominent viscous nature (characteristic of a Newtonian fluid) of the material, viscosity is reduced. Furthermore, the presence of dimethicone results in the occurrence of a more pronounced thixotropic behavior within the silicone gel structure, and so the extent of structural break down and time required for their re-build would be increased. This could be clearly seen from the rheograms constructed (Figures 3 and 4, corresponding to the presence of 0.75 and 1.5% dimethicone within formulation F5). This property of dimethicone could be useful in terms of an improved stability of the product following packaging and during storage, as well as an improved and easier spreadability and better skin coverage of the product during use. In fact, this characteristic could also increase consumer acceptance of the product.

Table 3. The influence of different amounts of dimethicone added to AZG containing silicone-based gel formulation F5 on various rheological parameters determined (n=3, data expressed as mean \pm SD).

| Amount of dimethicone added (%) | Up-curve η_{plastic} (Pa sec) | Down-curve η_{plastic} (Pa sec) | %RPV | Y_{plastic} value (Pa) |
|---------------------------------|---|---|-------|---------------------------------|
| 0 (control) | 58.0 \pm 0.8 | 38.9 \pm 1.2 | 32.81 | 347.3 \pm 3.9 |
| 0.5 | 56.8 \pm 1.3 | 36.9 \pm 1.3 | 35.03 | 339.6 \pm 8.9 |
| 0.75 | 55.7 \pm 1.0 | 33.2 \pm 0.9 | 40.39 | 321.4 \pm 7.4 |
| 1.0 | 53.9 \pm 1.4 | 29.4 \pm 1.1 | 45.45 | 287.2 \pm 1.9 |
| 1.25 | 52.3 \pm 0.9 | 24.9 \pm 1.4 | 52.39 | 245.4 \pm 5.7 |
| 1.5 | 49.9 \pm 1.2 | 19.8 \pm 0.6 | 60.32 | 207.4 \pm 3.5 |

Overall, presence of 0.75% dimethicone seems to produce the most acceptable product in terms of an appropriate viscosity and yield value. Presence of this amount of dimethicone could help to prevent the formation of a rather runny product (this could increase the chance of product leakage during storage and also insufficient skin substantivity) and produces a desirable thixotropic behavior to improve consumer acceptance, as mentioned above.

In conclusion, this study shows the importance of performing in-depth rheological assessment of a topical hygienic/cosmetic product in order to effectively study the influence of various formulation additives, particularly when considering achievement of desirable spreadability and appropriate skin feel. Furthermore, it seems that the existence of thixotropic behavior within the final formulation could be of importance in this respect.

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