Comparative Studies of Deposition and Formation of Complex Coacervates in Conditioning Shampoos

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Abstract

This work aims to evaluate the performance of shampoos regarding the formation of complex coacervates in formulations containing the quaternary polymers Quaternized Gum Guar and Polyquaternium-10, combined with Dimethiconol (and) TEA-Dodecylbenzenesulfonate, an anionic emulsion of a high molecular weight hydroxyl-terminated siloxane.

Formulations were successively diluted in distilled water up to 1:32 and analyzed by Dynamic Light Scattering (DLS) to monitor particle size distribution. Large particles are attributed to the formation of complex coacervates with very good correlation with precipitates in the dilutions.

Slightly bleached Caucasian hair tresses were washed with shampoos and analyzed by means of coefficient of friction (COF) and ease of combing. Deposition on hair fibers was determined by scanning electron microscopy. It was observed a significant increase in silicone deposition when Dimethiconol (and) TEA-dodecylbenezene sulfonate is associated with both Quaternized Guar Gum and Polyquaternium-10. As a result, dry combing work has significantly decreased when compared to the placebo and control shampoos. However, no significant differences were identified in the coefficient of friction.

The results obtained in this study show that the presence of cationic polymers alters the conditioning behavior of shampoos containing anionically emulsified silicones. Dilution and DLS studies showed the formation of poorly soluble complexes in the medium, which are associated with an increase in the deposition of silicones on hair tresses, resulting in the improvement of conditioning performance such as ease of combing. Experimental data reinforces the importance of choosing and associating ingredients that form complex coacervates from shampoos.

Keywords: (Coacervate; Hair; Deposition; Shampoo; Silicone; Cationic Polymer).

Introduction. Hair is a diverse substrate, with different shapes, colors and textures. Its properties vary in many ways and new hair care products are increasingly sought after. The change in appearance, shape, hair color, so common nowadays, causes damage that needs to be mitigated and repaired. In this regard, cationic polymers are widely used as conditioning and damage repair agents for hair. Polyquaternium-10 and Quaternized Guar Gum (Figure 1) are two highly used components in the conditioning product development market. In shampoo and liquid soap formulations, the cationic polymer and the surfactant exist together in a single phase. With the dilution of the formulation during washing and rinsing, that is, at low concentrations of surfactants, the cationic polymers become poorly soluble in the medium, generating a liquid-liquid phase separation due to the formation of a gel-polycation-surfactant complex, or coacervate. During the coacervation process, the polymer and surfactant undergo a series of association and microstructure changes: from a condensed network to globular aggregation (coacervation) to interconnection and association with micelles. The coacervate is then a phase that contains a high level of cationic charge and its main function is to deposit the polymer on negatively charged substrates, forming a film. In addition, coacervates help in the deposition of insoluble actives, such as silicones. Some very relevant and desirable characteristics for the hair, such as shine, softness and combability, are directly related to the conditioning of the hair and, consequently, to the deposition of cationic polymers and/or silicones on the surface of the hair.

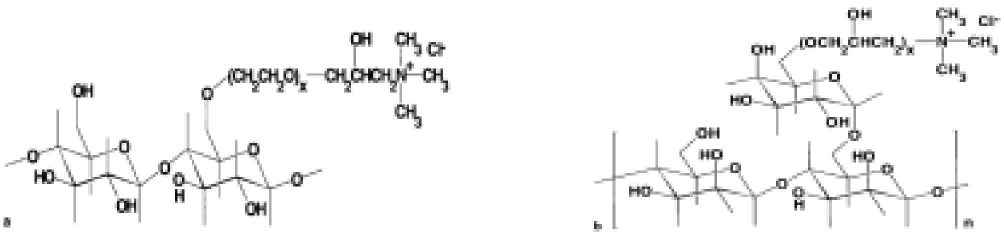


Figure 1. Generic structures of a. Polyquaternium-10 and b. Quaternized Guar Gum

Materials and Methods.

A. Materials: Polyquaternium-10 (PQ-10) and Dimethiconol (and) TEA-Dodecylbenzenesulfonate (SiOH) were obtained from the Dow Chemical Company, Quaternized Guar Gum (GG) was obtained from Solvay and slightly bleached Caucasian hair tresses were purchased from International Hair Importers.

B. Methods: Studies on hair tresses were performed in duplicates, 6 runs per replicate. Averages for each technique are reported. Coefficient of friction (COF) was determined in a Diastron MTT-175 with a UvWin Controller, coupled with a parallelogram. There is a direct correlation between smoothness and COF. Ease of combing was also determined in a Diastron MTT-175 and UvWin Controller by the analysis of the total work needed to pass a comb through a hair tress. Both parameters are strong indications of the level of conditioning from polymers in a shampoo formulation.

Deposition of silicone polymer or coacervates on hair fibers was determined qualitatively by Scanning Electron Microscopy (SEM) in a benchtop Phenom ProX with backscattered electron detector, at an approximation of 1600 times, manual brightness/contrast adjustment, and 5 kV electron beam intensity.

Each shampoo sample was successively diluted in distilled water at 1:3, 1:5, 1:8, 1:16 and 1:32 in order to evaluate the formation of co-phases/complex coacervates. Particle size distribution for each dilution was analyzed by Dynamic Light Scattering (DLS) and visually inspected to identify the formation of such coacervates. DLS was performed in a NanoPlus from Particulate Systems, 70 accumulations, aperture of 20 and incidence angle of 165°.

C. Design of the Experiments: shampoo formulations are identified and quantitatively described in Table 1. Quaternary polymers and silicone emulsion were added to the placebo formulation at 0.25% and 1.20%, respectively. Concentrations are in active levels. A third shampoo with silicone emulsion unassociated with quaternary polymers was also included as an important reference point. Hair tresses were treated with 0.40g of shampoo per gram of hair, rinsed and left to dry overnight.

Table 1. shampoo formulations for this study

Ingredients	Placebo Shampoo	Shampoo with SiOH	Shampoo with PQ-10 + SiOH	Shampoo with GG + SiOH
Potassium chloride	0,7	0,7	0,7	0,7
Aqua (water)	75,6	73,6	73,35	73,35
Lactic acid	qsp	qsp	qsp	qsp
Methylchloroisothiazolinone/methylisothiazolinone	0,1	0,1	0,1	0,1
Disodium EDTA	0,1	0,1	0,1	0,1
Sodium hydroxide	qsp	qsp	qsp	qsp
Parfum (fragrance)	0,5	0,5	0,5	0,5
Dimethiconol; TEA-dodecylbenzenesulfonate (60% active levels)	-	2	2	2
Polyquaternium-10	-	-	0,25	-
Guar hydroxypropyltrimonium chloride	-	-	-	0,25
Sodium laureth sulfate; cocamidopropyl betaine	23	23	23	23
Total	100	100	100	100

Results and discussions

A. Coacervation: it can be defined as a process during which a homogeneous aqueous solution of charged macromolecules undergo liquid-liquid phase separation, generating a dense phase rich in polyelectrolyte.

The dilution process helps to understand the range in which coacervated complexes are formed, also called "coacervation window". The scheme represented in Figure 2 depictures the process of coacervate formation on the surface of the hair. Coacervates are gel-polycation-surfactant complexes that contain water in their structure and are highly used to control the deposition of silicone and other insoluble compounds, being rich in polycations from quaternary polymers. In other words, the silicone is captured in the coacervated complex and "delivered" on the hair, generating high substantivity, deposition and conditioning to the hair (Figure 2).

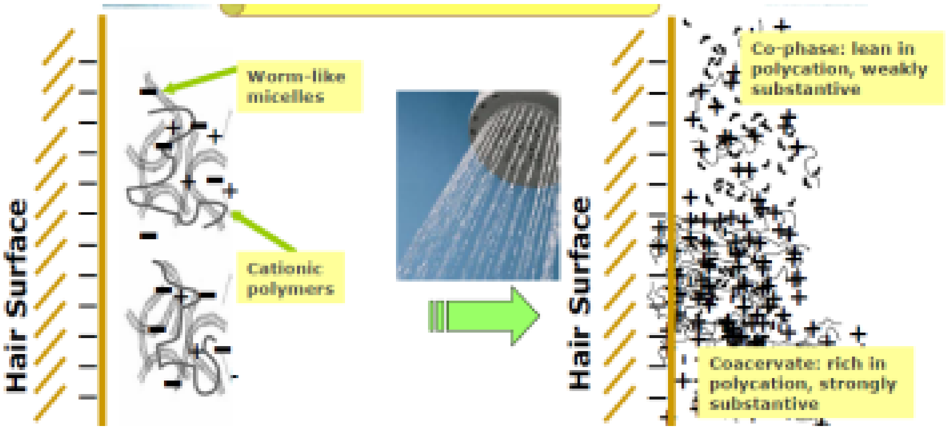
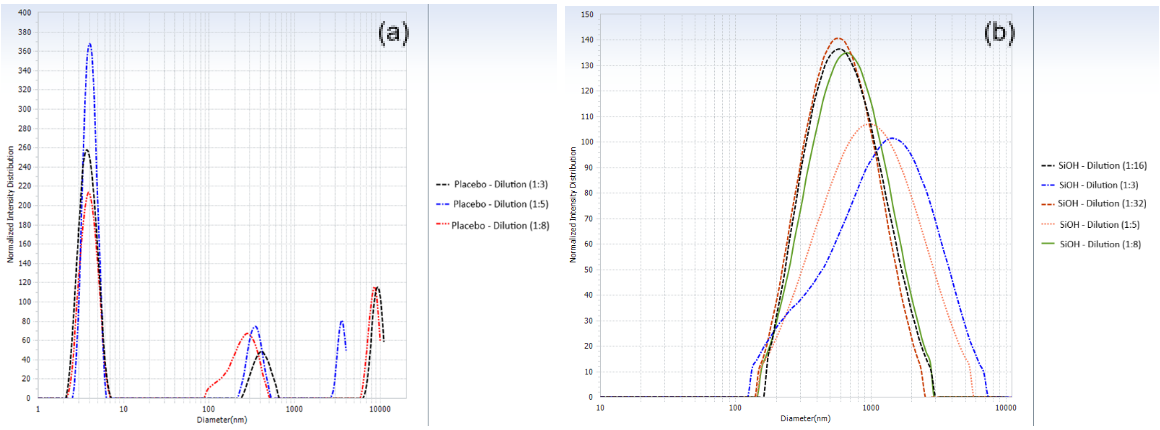


Figure 2. Scheme of the coacervation process on hair, with co-phase formation and coacervate complex, rich in polycations and with high substantivity to the hair.

Normalized intensity distribution histograms for shampoo dilutions acquired by DLS are presented in Figure 3. Pictures of the dilutions are presented in Figure 4. Placebo shampoo diluted from 1:3 to 1:8 generates three modes peaking at approximately ~3 nm, ~350 nm and ~9 µm (Figure 3a), possibly corresponding to different micellar aggregates in solution, being spherical micelles the smallest and most dominant one, at 3 nm. There is no significant change in distribution with the progressive dilutions in water. It was not possible to obtain data for dilutions 1:16 and 1:32 due to an excessive level of light transmittance during DLS analysis. Dilutions remained clear with no signs of precipitates, as depictured in Figure 4a. Unexpectedly, particle size distribution becomes monomodal peaking between 0.5 µm - 1 µm with the addition of the silicone emulsion, as seen in Figure 3b, with no significant change when the shampoo was diluted from 1:3 to 1:32, indicating no formation of coacervates. No phase separation was observed, as expected (Figure 4b). When a cationic polymer, either GG or PQ-10, is added to the shampoo SiOH and progressively diluted, four modes are observed. The dominant one at ~3 nm in the placebo shampoo decreases substantially and the peak between 6 µm - 8 µm, which is also observed in the shampoo placebo and SiOH, becomes dominant. The peak between 0.5 µm - 1 µm generated by the silicone emulsion is very pronounced as well. For the shampoo containing PQ-10 (Figure 3c) and diluted at 1:3, another mode is observed peaking at ~200 µm, which can be assigned to the coacervate, confirming the precipitate in Figure 4c. It is not observed at any other dilution, indicating PQ-10 has a narrow “coacervation window”. Meanwhile, the shampoo with GG (Figure 3d) diluted from 1:3 to 1:8 shows a distinctive mode peaking at ~100 µm, which is also attributed to the coacervate, confirming the precipitates observed in Figure 4d. This mode is not present for solutions at 1:16 and 1:32 because phase separation occurred immediately upon dilution and could not be captured by DLS, as shown in Figure 4e.



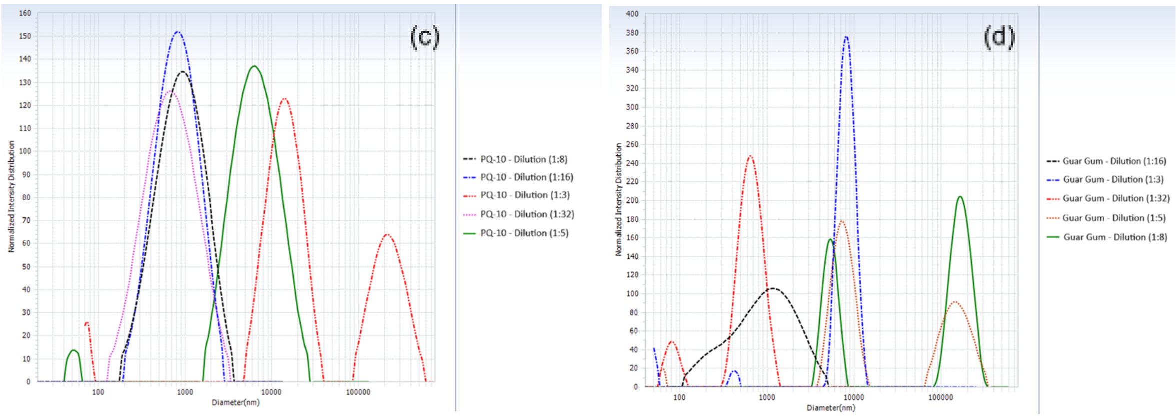
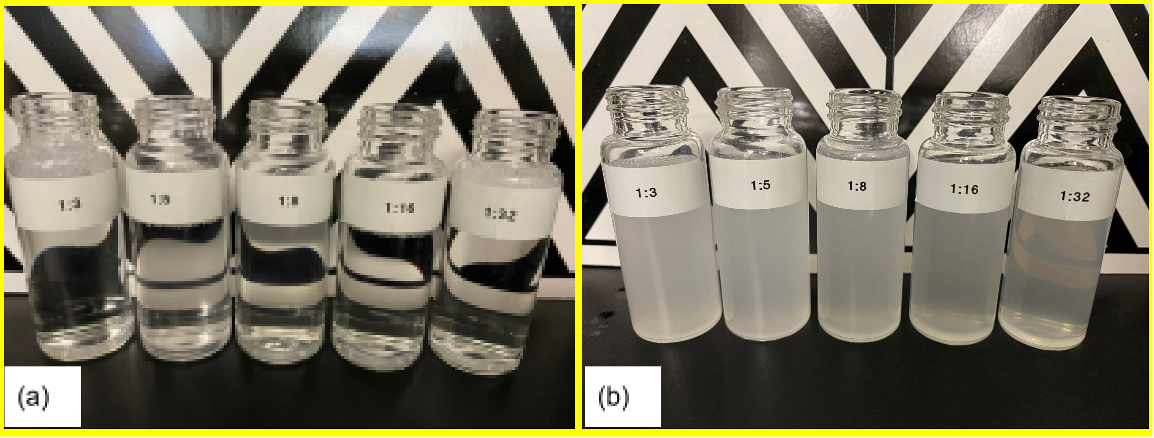


Figure 3. Normalized intensity distribution histograms for successively dilutions of shampoos (a) Placebo; (b) SiOH; (c) PQ-10+SiOH; (d) GG+SiOH

As expected, images and particle size data proves that, upon dilution of the shampoo in water, there is phase separation in presence of both cationic polymers (PQ-10 and GG) associated with the anionic emulsion of the hydroxyl-terminated siloxane (SiOH). Phase separation can be visually identified and assigned to the coacervate. "Coacervation window" for GG is significantly wider compared to PQ-10, as coacervates are observed from 1:3 to 1:32, even though its size is half the one obtained with PQ-10.



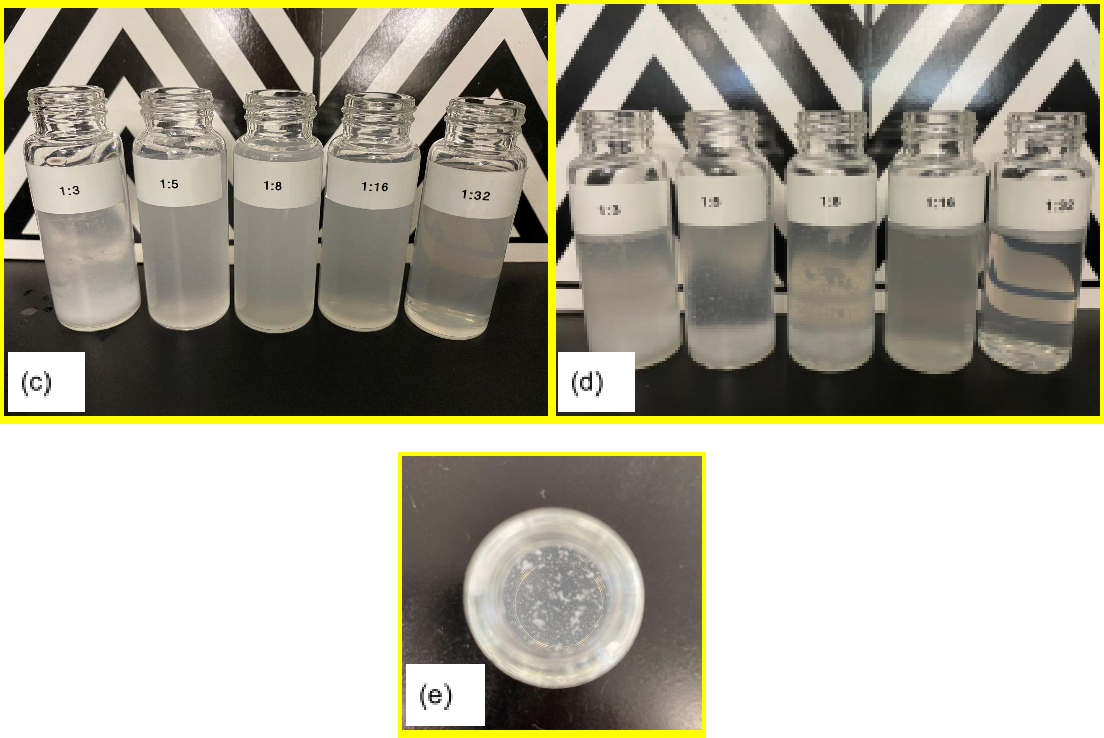


Figure 4. Dilutions from 1:3 to 1:32 for shampoos (a) Placebo; (b) SiOH; (c) PQ-10+ SiOH; (d) GG+SiOH; (e) view from the top of the flask for GG+SiOH diluted at 1:32

B. Silicone Deposition on Hair: SEM images of fibers treated with shampoos containing SiOH, associated or not with quaternary polymers, are presented in Figure 5.

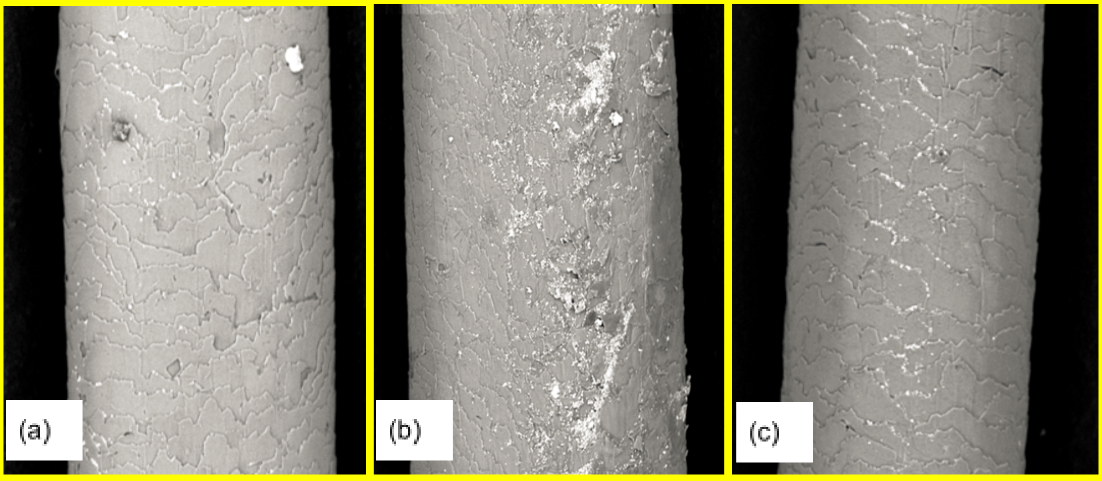


Figure 5. Scanning electron microscopy images fibers treated with shampoo (a) SiOH; (b) PQ-10+SiOH; (c) GG+SiOH

Silicon is a heavy element and, therefore, appears as bright areas during a SEM analysis allowing the visualization of silicone deposition on hair fibers. Clusters, assigned to the coacervate, can be easily observed on fibers washed with the shampoo PQ-10+SiOH (Figure 5b). Deposition is non-uniform and at a significantly higher level compared to fibers washed with shampoo SiOH (Figure 5a). Deposition from shampoo GG+SiOH (Figure 5c) is directed at the edges of the cuticles, to a lesser extent compared to PQ-10+SiOH. It is hypothesized that such differences in deposition between both quaternary polymers are due to a larger particle size PQ-10 coacervates (~200 µm) compared to GG coacervates (~100 µm). It is possible to qualitatively conclude from SEM images that quaternary polymers enhance the deposition of anionically emulsified silicone polymers. The deposition profile is a function of the selected quaternary polymer.

C. Dry Combing: results from the dry combing study are presented in Figure 6. The lower the work required to comb through the hair tress, the higher the conditioning level. It was observed a reduction in combing work for all silicone-containing shampoos compared to placebo. Hair treated with shampoo SiOH showed a 2-fold reduction in combing work, meanwhile PQ-10+SiOH reduced 3-fold and GG+SiOH 2.6-fold. Such differences are statistically significant at 99.9% confidence level. Analyzing the influence of quaternary polymers on the reduction of combing work, the shampoo SiOH was selected as a reference and paired compared to PQ-10+SiOH and GG+SiOH. Only PQ-10 was significantly different at 98.6% confidence level. Significance level for GG was 89.6%, indicating a trend in combing work reduction.

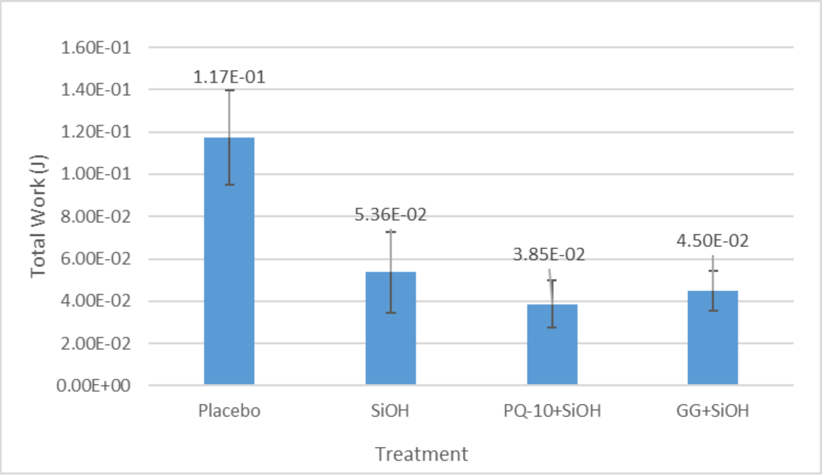


Figure 6. Combing work for hair tresses treated with shampoos

It is possible to conclude that enhancing the deposition of anionically emulsified silicone polymers with PQ-10 significantly decreases the dry combing work compared to placebo and SiOH shampoos.

D. Coefficient of Friction: results from the dry coefficient of friction are presented in Figure 7. COF is directly related with the perception of slip and smoothness on hair fibers. It is calculated from the friction of a rubber probe sliding over a hair tress.

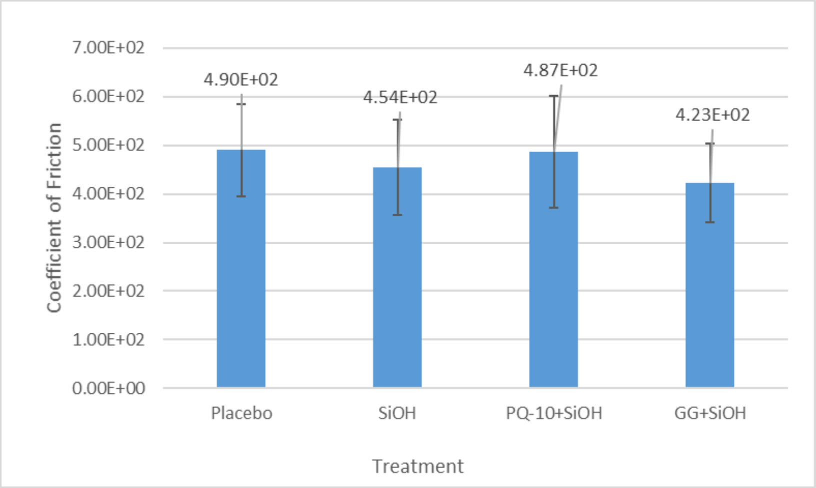


Figure 7. Coefficient of friction for hair tresses treated with shampoos

There are no statistically significant differences among treatments. It is possible to conclude that silicone deposition from the studied shampoos does not decrease COF of hair tresses. Enhanced deposition from shampoos containing quaternary polymers does not have a significant impact on this property.

Conclusions: Dilution studies demonstrated the formation of poorly soluble complexes from shampoos containing quaternary polymers, which are associated with the increase in the deposition of an anionically emulsified silicone polymer on hair tresses. PQ-10 has a narrower coacervate window compared to GG, however, the coacervate is significantly larger, resulting in more deposition and decrease in combing work. No benefits were identified for reducing the coefficient of friction. This study reinforces the importance of choosing and associating ingredients that form complex coacervates to create minimalist and effective shampoos, leading to cost-effective products with superior performance to consumers.

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Conflict of Interest Statement. None

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