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**"Interfacial Behavior and Deposition Performance of Nanometric Polymer-surfactant Complexes for Sustainable Conditioning"**

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## 1. Introduction

Increasing concerns about fossil fuel depletion, greenhouse gas emissions, and water scarcity have driven the search for more eco-friendly ingredients in consumer goods over the past two decades. Biopolymers, such as polysaccharides, are promising substitutes for synthetic ingredients due to their biodegradability and diverse chemical structures, which allow flexibility in developing functional materials. However, many applications require cationic functionality to enhance polymer properties. Commonly used cationic polymers in personal care products, such as cationic guar (catGuar) and cationic hydroxyethyl cellulose (catHEC), have limitations in biodegradation and aquatic toxicity.

Polyelectrolyte—surfactant complexes form various structures influenced by the properties of both components, including chain stiffness, charge density, and molecular weight [1-3]. While catGuar and catHEC complexes have been extensively studied, limited research exists on dual cationically modified dextran polymers (dual catDex) complexes.

The present research expands upon previous studies by investigating the morphology and deposition of dual cationically modified dextran polymers with surfactant mixtures used in industrial applications such as shampoos and detergents [4]. The study initially compares the performance in rinse off hair care applications of dual catDex complexes with surfactants and silicone oils to those formed between catGuar with shampoo formulations. The superior performance of dual catDex polymer-surfactant complexation is explained via high-throughput imaging to understand the phase behavior. Other than liquid-liquid phase separation (LLPS), the appearance of novel nanometric complexes of dual catDex-surfactants throughout a relevant dilution process is presented, along with insights into the size and morphology of dual catDex—surfactant complexes. The adsorption behaviors of the complexes onto silica-coated sensors are studied using quartz crystal microbalance with dissipation (QCM-D). The results demonstrate that dual catDex polymers can significantly increase the deposition of silicone from a model shampoo compared to catGuar technologies via two mechanisms, guiding the formulation of products that rely on polycation—surfactant complexes to benefit the skin and hair.

## 2. Materials and Methods

*Table 1. List of cationic polymers used in the study*

No.	Material	INCI
1.	dual catDex	Dextran Hydroxypropyltrimonium/ Laurdimonium Chloride
2.	catDex	Dextran Hydroxypropyltrimonium Chloride
3.	catGuar	Guar Hydroxypropyltrimonium chloride

### Model Shampoo Formulation:

Shampoos were prepared by first adding polymer to Max 60 Long FlackTek cups. Then, surfactant solutions and water were added. Finally, the shampoo was mixed for 2 minutes at 1950 rpm using a SpeedMixer (FlackTek, Inc., Landrum, South Carolina, USA), and placed on a hematology mixer (Medmark Technologies LLC , Pennsylvania, USA) to further mix overnight.

*Table 1. Model Shampoo Formulation Used in the Present Study.*

Name	Description	wt% active in Formula-tion
<b>Water</b>		balance
<b>Sodium Laureth Sulfate</b>	Primary Surfactant: Cleaning	9.00%
<b>Cationic Polymer</b>	Deposition Aid	0.30%
<b>Cocamidopropyl Beta-ine</b>	Co-Surfactant	2.00%
	Preservative	0.25%

### Model Commercial Shampoo formulation:

*Table 2 A sulfate shampoo example with Dual catDex*

Phase	INCI name	Wt. %
A	Water / aqua	q.s.
	Sodium Laureth Sulfate	30.00
	<b>Dextran Hydroxypropyltrimonium/ Laurdimonium Chloride</b>	<b>1.12</b>
	Tetrasodium EDTA	0.20
B	PEG-150 Pentaerythrityl Tetraesteate	0.8
	Cocamide MEA	1.00
C	Cocamidopropyl Betaine	6.30
D	<b>Amodimethicone (and) C11-15 Alketh-12 (and) C11-15 Alketh-7</b>	<b>2</b>
	Phenoxyethanol and Ethylhexylglycerin	0.50

### Process

1. Add phase A ingredients to water and start heating to 70 °C while stirring.
2. Add phase B ingredients in order listed. Mix for an additional 10 minutes and then start cooling down to room temperature.
3. While stirring, add phase C ingredient and mix for three minutes.
4. When temperature is below 40 °C, add phase D ingredients and adjust to pH 5.5. Mix for an additional 10 minutes.

## Hair tresses and treatment

Hair tresses used in this study were virgin brown hair and Caucasian bleached hair provided by International Hair Importers & Products, USA. Tresses were 2.5 cm wide, 15 cm length and 2 grams each. Prior to applying the formulation, each tress was pre-washed under running tap water with a 9% Sodium Lauryl Sulfate (SLS) solution. The tresses were massaged gently with fingers for 30 seconds, then rinsed under running tap water for 1 minute to remove SLS. Excess water was removed by squeezing the tresses with two fingers. Test shampoos were applied at 0.4 grams of material per gram of hair. The tresses were massage for 1 minute and then rinsed for 30 seconds. The tresses were left to air dry overnight in a controlled room at 50% humidity.

## Tribology

A Diastron miniature tensile tester model MTT175 was used to measure Coefficient of Friction (COF) on the hair tress. COF correlates with perceived smoothness and conditioning as a result of silicone and oil deposition on hair. Results with dual catDex were compared to formulations without a deposition aid and with catGuar. An Instron model 3342 measured Average Combing Load (ACL) to evaluate the reduction in wet/dry combing load. The same tresses from the friction test were used for this measurement.

## X-ray Photoelectron Spectroscopy (XPS):

Samples were analyzed as received by taping sections of hair tresses to double-sided tape. Data were taken from regions where no underlying tape was optically visible. X-ray photoelectron spectroscopy (XPS) gives quantitative elemental and chemical state information from the top 10 nm. XPS data were acquired from four areas across 1 cm × 3 mm from the center of the tress. Instrument parameters can be found below.

## Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D):

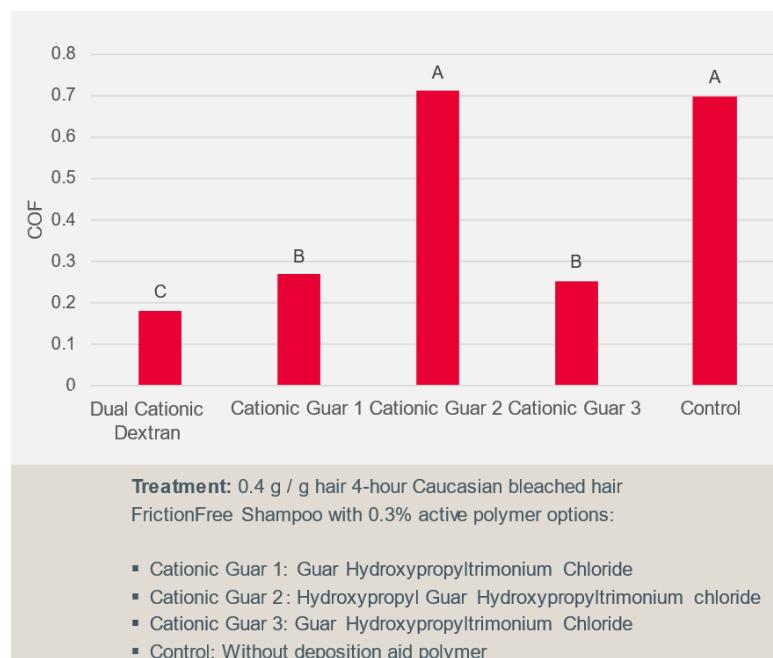
QCM-D measurements were performed with QSense Analyzer (Biolin Scientific) using SiO<sub>2</sub> coated sensors purchased from Biolin Scientific Instruments (QSensors QSX 303). The sensors were cleaned using the recommended manufacturers' sensor cleaning protocol to obtain stable and reproducible baselines. Initial baseline conditions were set with ultrapure water flow for 30 minutes. For experiments where shampoo was introduced, frequency data was collected continuously, and the pump flow paused briefly to exchange feed solutions from an ultrapure water flow.

## 3. Results

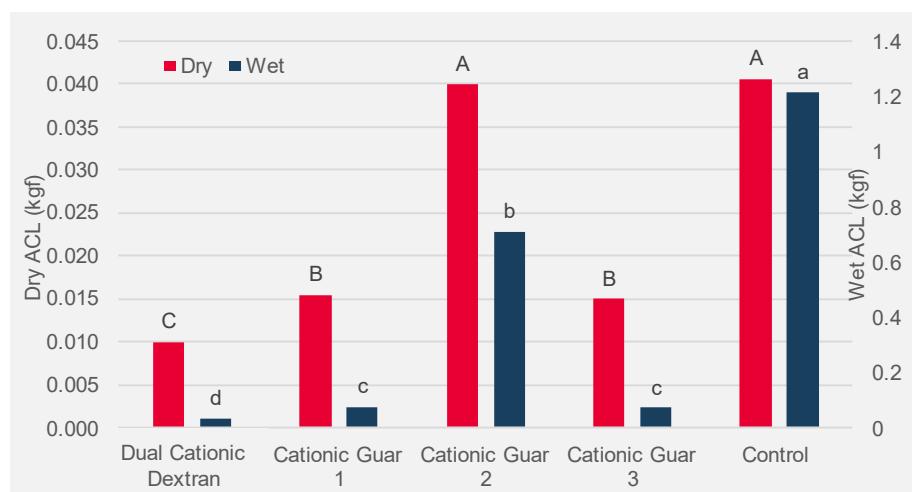
- Deposition aid polymer in sulfate shampoos

### Reduced coefficient of friction and dry/wet combing forces

Figure 1 demonstrates that dual catDex provides significant tribological benefits in terms of COF values at the same polymer use level with a value of  $0.18 \pm 0.01$  compared to Cationic guars with values of  $0.27 \pm 0.01$ ,  $0.25 \pm 0.02$  and  $0.70 \pm 0.02$  indicating a smoother, and lubricated feel of the hair. Similarly, Figure 2 shows significant lower dry and wet combing load measured on damaged hair with dual catDex polymer compared to other cationic polymers.



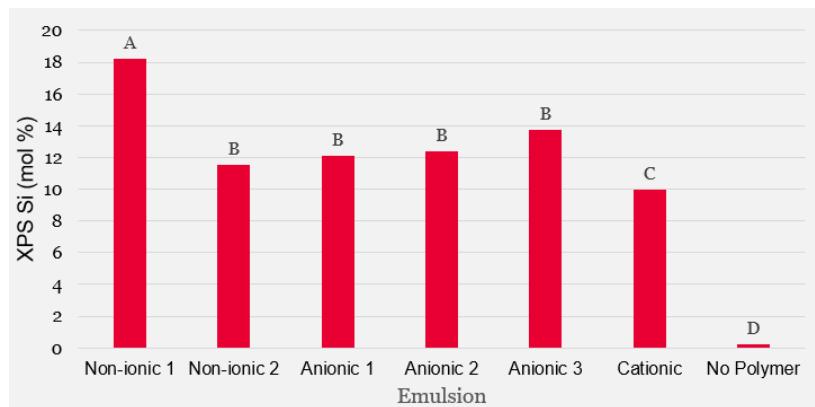
*Figure 1 Dual catDex significantly reduces friction compared to various cationic guars. Different letters show a statistical difference at 95% confidence*



*Figure 2 Dual catDex significantly reduces wet and dry combing load compared to various cationic guars. Different letters show a statistical difference at 95% confidence.*

#### Versatility with different silicone emulsions

We also found high deposition of silicone on 4 hr bleached hair regardless of silicone or surfactant charge type, as shown in Figure 3. The formulations were prepared with shampoo, as tabulated in Table 2 and Table 3, using different silicones.



*Figure 3 Deposition versatility with different silicone emulsion. Different letters show a statistical difference at 95% confidence.*

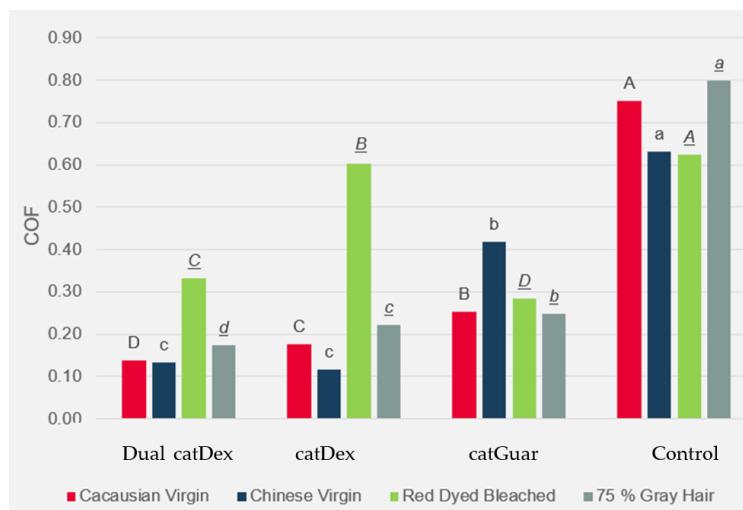
*Table 3 Silicone Type and charge for different products*

Emulsion Charge	Type of Silicone
Non-ionic 1	Amino functional silicone polymer
Non-ionic 2	High molecular weight divinyldimethicone/dimethicone copolymer
Anionic 1	High molecular weight polydimethylsiloxane
Anionic 2	High molecular weight polydimethylsiloxane
Anionic 3	High molecular weight polydimethylsiloxane
Cationic	Blend of Amodimethicone, Cetrimonium Chloride, and Trideceth-6

#### Performance on different hair types

To illustrate the polymer's versatility on different hair substrate, four distinct hair types were evaluated: Caucasian Virgin Hair, Chinese Virgin Hair, Red Dyed Hair, and 75% Gray Hair. Figure 4 demonstrates the performance data for a shampoo comparing the 4 different polymers. COF is lowest for dual catDex across all hair types and is comparable to catGuar on red dyed bleached hair (0.32 vs. 0.28), with similar trends observed in combing forces. The results

underscore the efficacy of dual catDex in enhancing hair manageability and appearance across diverse hair types.

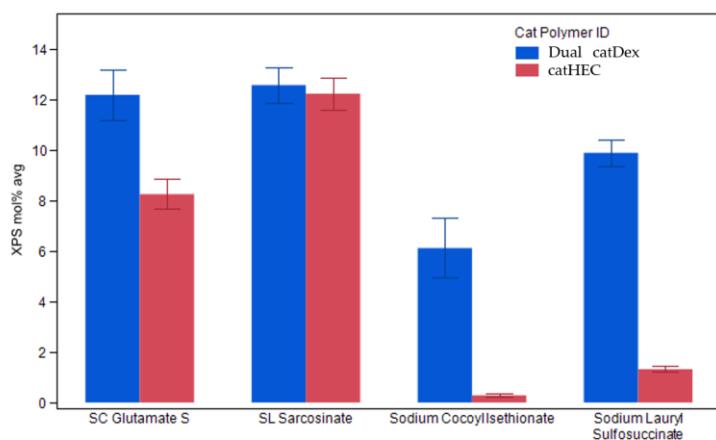


*Figure 4 Tribological performance measured on different hair types with shampoos made from Table 2. Different letters show a statistical difference at 95% confidence.*

b) Deposition aid polymer in sulfate-free shampoos

#### Efficient Silicone Deposition

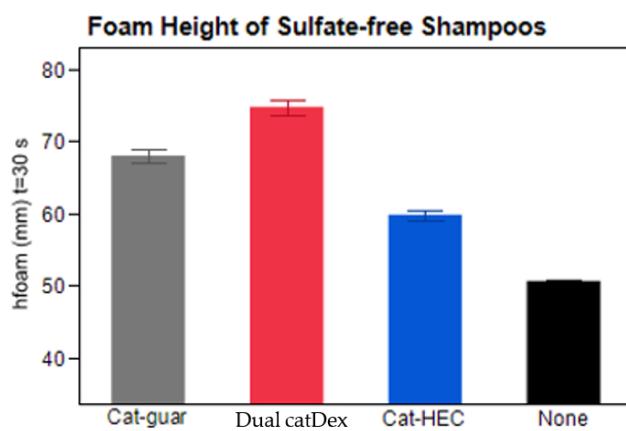
With shampoos containing various Anionic:Amphoteric surfactants in ratio (3:1) with 0.3 wt% dual CatDex, we confirmed the efficient deposition of silicone using X-Ray photoelectron spectroscopy (XPS). Figure 5 demonstrates a high deposition of silicone based on dual CatDex in comparison to catHEC.



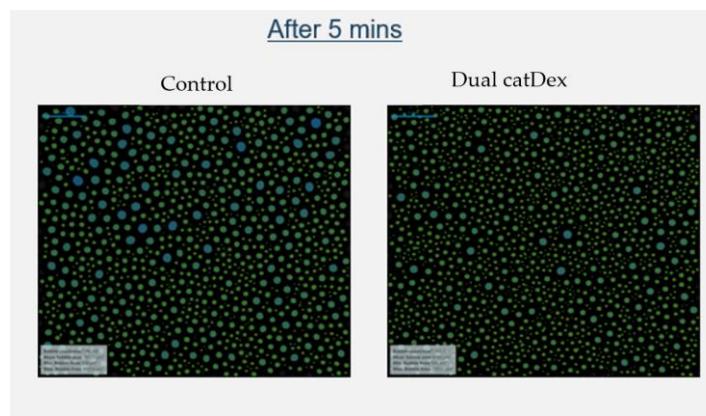
*Figure 5 Dual CatDex deposits more silicone on damaged hair than catHEC with 0.3% active polymer with 1% active silicone in different sulfate free surfactants shampoos. Measured via X-Ray photoelectron spectroscopy (XPS).*

#### Synergistic increase in foam height and quality

To reduce the impact on skin health caused by traditional sulfate-based surfactants, a common approach is to use a combination of milder biobased or biosurfactants consisting amino acid, sugar-based surfactants, sulfonates, and betaines. These alternatives also have lower environmental impact and improved sustainability. However, these formulations typically result in shampoos with lower foaming properties, such as foam height and stability, compared to SLS and SLES based shampoos. We found that several systems of sulfate free surfactants combined with dual catDex lead to a 30-50% increase in foam boosting in several sulfate-free surfactant chassis, as shown in Figure 6 upper and lower panels. Additionally, there was a 65% increase in bubble count per area with dual catDex, indicating a higher quality foam with more air trapped within a given space, as shown in Figure 7.



*Figure 6 Upper panel: synergistic increase in foam containing dual catDex and sulfate free surfactants in comparison to other cationic polymers for surfactant combination SL Sarcosinate: CB (3:1) 15 wt%. This was measured at 5 min mark with DFA Kruss Foam Analyzer.*

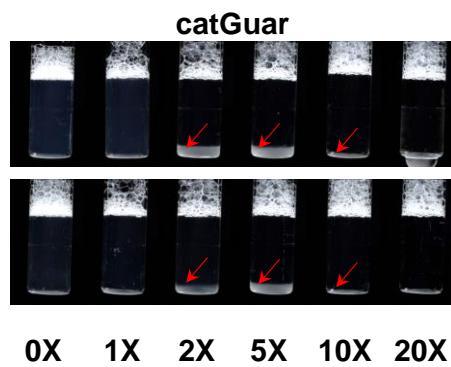


*Figure 7 Foam quality measured by probing the size of the bubble overtime for surfactant combination SL Sarcosinate: CB (3:1) 15 wt%. This was measured at 5 min mark with DFA Kruss Foam Analyzer.*

#### 4. Discussion

In shampoos that contain an excess of anionic surfactants compared to cationic polymer, less biodegradable polymers like cationic Guar or HEC systems showed a propensity for solid—

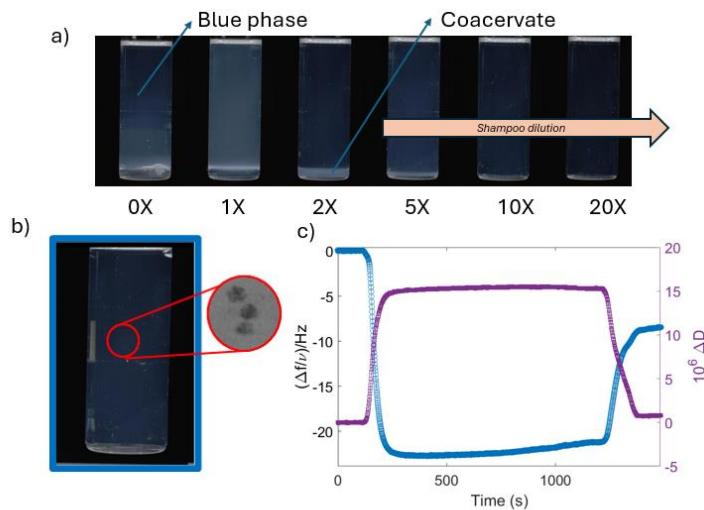
liquid or liquid-liquid phase separation at concentrations relevant to formulation of rinse-off personal care products. Classically, in the initial stage, the deposition polymer electrostatically interacts with surfactant micelles in the undiluted bulk formulation, forming a "string of pearls" complex. This complex is stabilized by the excess anionic surfactant. Upon dilution, the complex breaks down, leading to surfactant dissociation and the formation of a charge-balanced complex. This new complex precipitates out of solution, becoming hydrophobic due to the surfactant tail groups, which favorably interact with the hair's surface. In the third stage, further dilution during rinsing reduces the surfactant concentration below the critical micelle concentration (CMC), causing additional dissociation. The polymer then forms electrostatic interactions with the anionic hair strands, depositing onto the hair. Additionally, the cationic polymer aids in the deposition of other beneficial agents, such as silicone, by coating them and forming coacervate complexes. These complexes, once precipitated, allow both the polymer and silicone particles or droplets to be deposited onto the hair. This is shown as example through Figure 8 that shows dilution of catGuar with sodium laureth ether sulfate (SLES) surfactants shampoo (Model formulation based on Table 1). During a dilution of 2X-5X, which mimics rinse off dilutions, the phase separated medium is deposited at the bottom of the vial as shown by the arrows. These precipitates or coacervates are responsible for entraining silicone oils that are deposited on hair.



*Figure 8* Photographs of model shampoos throughout dilution with deionized water. The undiluted shampoos (marked as 0x) contained 9 wt% SLES 1EO (upper panel/ SLES 3EO (lower panel)) and 2 wt% CapB, and 0.3 wt% cationic guar. The dilution factor is given below each image on a volume basis. The red arrow points to solid precipitate observed at the bottom samples containing catGuar.

By contrast, dual datDex led to formation of blue turbid solutions as well as complex coacervates, a unique discovery made with dual cationic dextran polymers, indicating two channels of deposition of silicones. This is demonstrated in Figure 9a as the shampoo is diluted. For the undiluted shampoo that contained the blue phase, previously by dynamic light scattering (DLS), we measured an intensity average diameter of the particles that ranged between 100 and 200 nm at total surfactant concentrations between 60 and 150 mM [4]. We confirmed the size in this study by liquid phase transmission electron microscopy (LP TEM) in Figure 9b. The surface activity of nanometric complexes was confirmed by Quartz-Crystal Microbalance with Dissipation (QCM-D) on silica substrate. Silica mimics the zetapotential (-30 mV) and hydrophilicity of the hair fibers. As shown in Figure 9c, an increase in the resonance frequency

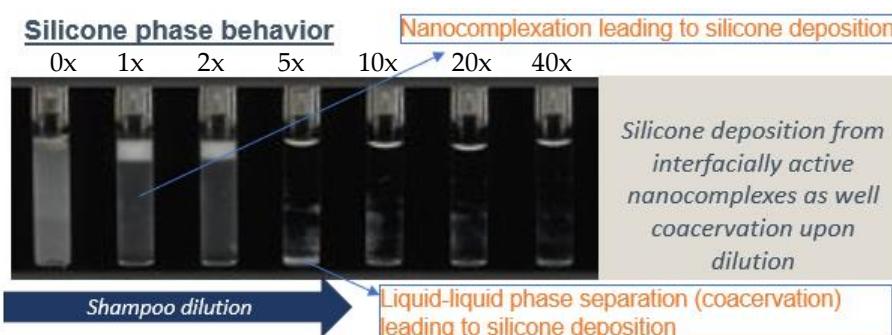
indicates mass deposition with undiluted shampoo. With this new nanostructure, the results indicated concentration-dependent deposition even in an undiluted shampoo (0X Dilution). As shown in Figure 9a, in the mid-range dilutions (2X-5X), we found the emergence of phase separation by coacervation as well. This behavior contrasts the deposition behavior observed previously for model shampoos formulated with other polysaccharides like catHEC or catGuar where the bulk of deposition takes place in a phase separated regime during dilution only through complex precipitation. We hypothesized that for dual catDex, both the surface-active polymer-surfactant complex as well charge-balanced complex would be responsible for deposition of benefiting agents like silicone.



*Unique surface-active microstructure identified on nm length scale*

*Figure 9 a) Photographs of model shampoos throughout dilution with deionized water. b) Undiluted shampoo imaged with liquid phase TEM to show the 200 nm nanocomplex morphology. c) Surface activity of nanocomplexes established by Quartz-Crystal Microbalance with Dissipation (QCM-D)*

The hypothesis was tested by adding a benefit agent like silicone oil to the model formulation as shown in Table 1. The shampoo dilutions confirmed the deposition of silicone oil through polymer-surfactant nanocomplex at undiluted stage. This is shown by the aggregation of silicone on the glass vial between 0-40x dilution. Deposition through coacervation also emerged in mid-range dilutions as shown in Figure 10.



*Figure 10 Photographs of model shampoos throughout dilution with deionized water. The undiluted shampoos (marked as 0x) contained 9 wt% SLES 1EO, 2 wt% CapB, 1 wt% silicone and 0.3 wt% dual catDex. The dilution is factor is given below each image on a volume basis.*

We ended this study by formulating shampoos with the two cationic deposition aid polymers (i.e., dual catDex, catGuar) according to the recipe outlined in *Table 2* simulating commercial shampoos, and characterizing the deposition of the silicone from the shampoos onto hair during washing. After washing, X-ray photoelectron spectroscopy (XPS) was used to quantify silicone deposition onto the tresses. The shampoos formulated with catGuar led to  $7.8 \pm 0.2$  for Si deposition for those containing SLES 1EO. Consistent with our hypothesis, shampoos formulated with dual catDex polymer deposited significantly more silicone onto the surface of hair than catGuar. The levels of deposition were  $18.2 \pm 0.7$  from SLES 1EO/ CapB shampoo. This data directly supports that cationic dextran polymers like dual catDex are a promising technology for replacement of less environmentally friendly cationic guar and cationic hydroxyethyl cellulose polymers.

## 5. Conclusion

The present research expands upon previous studies by investigating the morphology and deposition of dual cationically modified dextran polymers with surfactant mixtures used in industrial applications such as shampoos and detergents. The study initially compares the performance of dual catDex complexes with surfactants and silicone oils in rinse-off hair care applications to those formed between catGuar and shampoo formulations.. Superior performance of dual catDex polymer-surfactant complexation is explained via high throughput imaging. In addition to liquid-liquid phase separation (LLPS), the appearance of novel nanometric complexes of dual catDex-surfactants throughout a relevant dilution process is presented, along with insights into the size and morphology of dual catDex—surfactant complexes. The adsorption behaviors of the complexes onto silica-coated sensors are studied using quartz crystal microbalance with dissipation (QCM-D). The results demonstrate that dual catDex polymers can significantly increase the deposition of silicone from a model shampoo compared to catGuar technologies via two mechanisms, guiding the formulation of products that rely on polycation—surfactant complexes to benefit the skin and hair. Overall, the fundamentals described here can be extended to design products beyond personal care, such as electronic materials, pharmaceuticals, biotechnology, and food and nutrition.

## 6. References

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