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Enhanced Natural Oil Deposition Using Acrylic Copolymers

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Synopsis

Natural oils have become increasingly prevalent in hair care products over the past decade and continue to gain traction in the market. While analytical methods exist in the field to understand the deposition and mechanism of action for silicone emulsions, which are chemically distinct from hair fibers, the visualization of natural oils on the hair surface has been an analytical challenge. In this work we showcase a new class of oil-soluble acrylic copolymers that structure coconut oil and enhance the deposition of the active onto the hair fibers. Additionally, we highlight the use of secondary ion mass spectrometry and depth profiling of the hair fibers to visualize the deposition of structure oils onto the hair surface. Lastly, we explore the utility of these structured oils in hair conditioning applications.

INTRODUCTION

In recent years, coconut oil has been a very popular ingredient in personal care formulations. This triglyceride oil is extracted from the coconut palm (*Cocos nucifera*) and is a source of long-chain saturated fatty acids (1). Over the past decade, the use of coconut oil in hair care products has grown in popularity across big and small labels all around the globe (2). Coconut oil has been shown to reduce hair damage when used as a prewash conditioner to improve the appearance of bleached, damaged hair (3). Data also show coconut oil outperformed sunflower oil and mineral oil, and coconut oil was the only oil that reduced protein loss due to excessive brushing and combing (4).

As this natural oil becomes increasingly popular in shampoos and rinse-off conditioners, the need to efficiently deposit this material on the hair fiber is important. While cationic deposition aid technologies can be used to increase the deposition efficiency of the emulsified oils (5), we hypothesized that structured oil would have greater persistence on the hair surface. To this end, oil-soluble acrylic copolymers that can swell in the presence of natural oils were developed to provide structuring and increased viscosity of the oil phase (Figure 1). These polymers contain a lightly cross-linked hydrophobic acrylic backbone that is compatible with triglyceride oils. Once dispersed in the oil, the polymer swells and provides viscosity through a space-filling mechanism. Excellent thickening efficiency and

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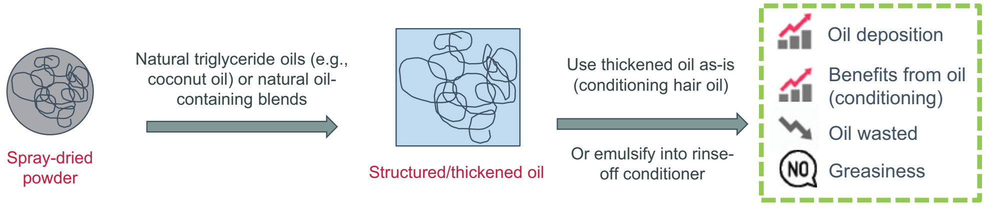

Figure 1. Mechanism for structuring natural oils with acrylic copolymers.

shear-thinning profiles along with high clarity in a range of different natural triglyceride oils and their blends with other ingredients have been observed (6).

The way oil deposits on the surface of hair can greatly impact the consumer perception in slipperiness, smoothness, and overall quality of the hair fibers (7). Quantification of natural oils is relatively straightforward using standard gas chromatography–mass spectrometry (GC–MS) techniques, but understanding the homogeneity of the oil deposition can be challenging to visualize, although it can have a profound impact on friction along the hair tress. In this study, we have demonstrated the utility of these acrylic cross-polymers and the improvements observed in coconut oil deposition, and we showcase visualization tools that further our understanding of the codeposition of acrylic copolymer with coconut oil.

METHODS

MATERIALS

Methacrylic acid (MAA) was supplied by Dow Chemical (Collegeville, Pennsylvania, USA). Isobutyl methacrylate (IBMA), 2-ethylhexyl methacrylate (EHMA), and trimethylolpropane diallyl ether (TMPDE) were supplied by Sigma Aldrich (St. Louis, Missouri, USA). Three gram tresses of European hair, 8 hour bleached, 1 inch wide, was purchased from International Hair Importers (Glendale, New York, USA). Refined coconut oil was purchased from Sigma Aldrich.

STRUCTURED OIL PREPARATION AND HAIR TRESS TREATMENT

The acrylic copolymer used in this study was prepared using the process detailed in patent WO2020092032A1 with a composition of 79.5 IBMA/19.5 EHMA/1 MAA/0.10 TMPDE by weight. Latex emulsion was spray-dried and used as prepared. Spray-dried copolymers powders and coconut oil were heated to 50°C and mixed with an overhead mixer at 500 rpm for 1 hour to prepare the structured coconut oil.

The prewashed 8 hour bleached hair tresses were treated with coconut oil (as supplied) or structured coconut oil (2% acrylic copolymers in coconut oil), left to dry overnight, and then washed with shampoo the next day. Coconut oil retained on the hair was quantified by GC–MS after extraction in hexanes, derivatization, and comparison to calibration standards. The extracted coconut oil was converted to the methyl esters (KOH/MeOH) and quantified by GC–MS using calibration standards prepared from coconut oil following the same derivatization protocol.

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Table I
Rinse-Off Conditioner Formulation Used for the Studies

	Control	Coconut oil only	6% acrylic copolymer in coconut oil gel
Ingredient (INCI name)	wt%	wt%	wt%
Water	95.8	93.8	93.8
Hydroxyethyl cellulose	1.5	1.5	1.5
Tetrasodium EDTA	0.2	0.2	0.2
Cetearyl alcohol	1.0	1.0	1.0
PEG-100 stearate and glyceryl stearate	1.0	1.0	1.0
Oil or oil gel	0.0	2.0	2.0
Phenoxyethanol and methylisothiazolinone	0.5	0.5	0.5

EDTA: ethylenediaminetetraacetic acid; INCI: International Nomenclature Cosmetic Ingredients.

RINSE-OFF CONDITIONER FORMULATION

The rinse-off conditioner formulation used for the studies is found in Table I.

Deionized water was added to the mixing vessel and heated to 70°C. With moderate agitation, the hydroxyethyl cellulose was dispersed until fully dissolved. The temperature was decreased to 60°C, and cetearyl alcohol and PEG-100 stearate, glyceryl stearate, and oil or oil gel were added. The conditioner was mixed for 3 min, and then tetrasodium EDTA was added and mixed for 3 min. When the temperature was below 40°C, the phenoxyethanol and methylisothiazolinone was added. Additional water was added, and the final pH of all conditioners was approximately 5.

SECONDARY ION MASS SPECTROMETRY IMAGING

Organic depth profiling of deposited layers can be accomplished using secondary ion mass spectrometry (SIMS). This method utilizes an Ar cluster ion beam (gas cluster ion beam) to gently etch the surface followed by analysis with a Bi_3^+ ion beam with sensitivity to the molecular and elemental composition of the top 2 nm. In this case delayed extraction was used to obtain high-resolution images during depth profiling.

Data were collected using an IONTOF V SIMS (IONTOF, Münster, Germany) instrument with a primary analysis beam operating at 30 kV using bunched Bi_3^+ ions in a 200 μm random raster with 256 × 256 pixels. Depth profiling was accomplished using a 2.5 kV Ar_{1000}^+ ion beam in noninterlaced mode with 1 scan/1 sputter cycle across 500 μm square raster areas. Data were analyzed using Surface Lab 7.2.125200 (IONTOF, Münster, Germany).

RESULTS

The main component of coconut oil is the ester of lauric acid, a saturated, linear dodecyl (C12) hydrophobe. To target the greatest compatibility with coconut oil, which contains mostly short-chain fatty esters, we selected a polymer composition with 80% IBMA and 20% EHMA, stabilized with a small level of MAA and lightly cross-linked for maximum viscosity enhancement. The compatibility of these acrylic copolymers is highlighted in

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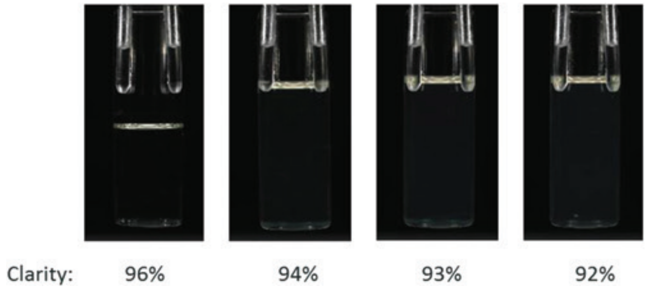

Figure 2. Images of refined coconut oil (first panel), 2% acrylic copolymer in coconut oil (second panel), 4% acrylic polymer in coconut oil (third panel), and 6% acrylic polymer in coconut oil (fourth panel).

Figure 2, and the rheological profile is presented in Figure 3. The clarity of the structured coconut oil is comparable to the native coconut oil, but the viscosity, particularly at low-shear rates, was increased by two to four orders of magnitude when 4% or 6% acrylic copolymer was used, respectively.

To demonstrate the effectiveness of structured coconut oil for improved deposition, we first compared an unstructured oil with a structured oil for deposition and retention on bleached hair tresses. Shown below in Figure 4, hair tresses were treated with coconut oil or structured coconut oil (containing 2% acrylic copolymer), left to dry overnight, and then washed with shampoo the following day. Six tresses were used for each condition, and the level of oil retained on the hair fibers was observed to be 2.5 times that of the unstructured coconut oil. Interestingly, despite slight changes in polymer composition, a similar 2 to 3 times increase was observed for all polymers in this class of oil structurants.

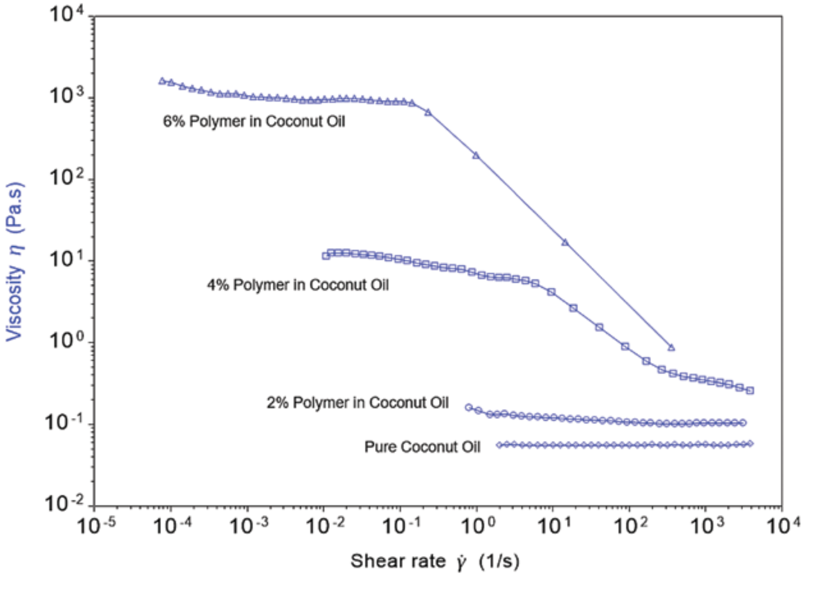

Figure 3. Overlay of flow curves of (refined) coconut oil containing acrylic copolymer samples at different concentrations.

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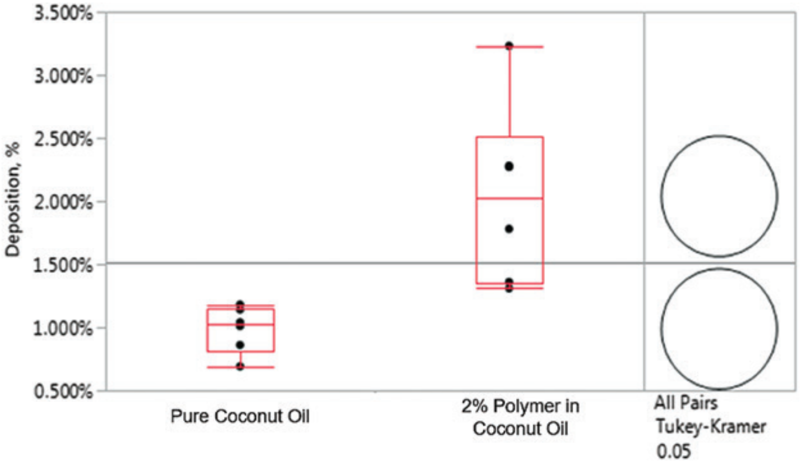

Figure 4. Comparison of coconut oil quantification on bleached hair with and without acrylic copolymer.

With evidence that the acrylic copolymers aid in the deposition and retention of the coconut oil on the bleached hair fibers, we next sought to understand the localization of each component on the hair fiber. SIMS is a powerful analytical tool that is capable of chemical imaging of surfaces. SIMS images are shown in Figure 5. The total ion image is influenced by the topography (left panel), which is why the cuticles are easily seen, as well as changes in chemistry. In this case the chemistry has negligible effect. Polymer signal from the methacrylate monomers ($C_4H_5O_2$, middle panel) is detected on all regions of the hair, but seems to be concentrated in some smaller regions, in particular on the top hair. Coconut oil ($C_{12}H_{23}O_2$, right panel) appears to have a uniform distribution; this image is affected by the topography of the hair.

Using two ion beams, where one beam is used for analysis and the second is used for etching, a depth profile can be constructed to characterize any layering in the deposited layer on hair. For this treatment, a depth profile, as shown in Figure 6, shows lauryl sulfate

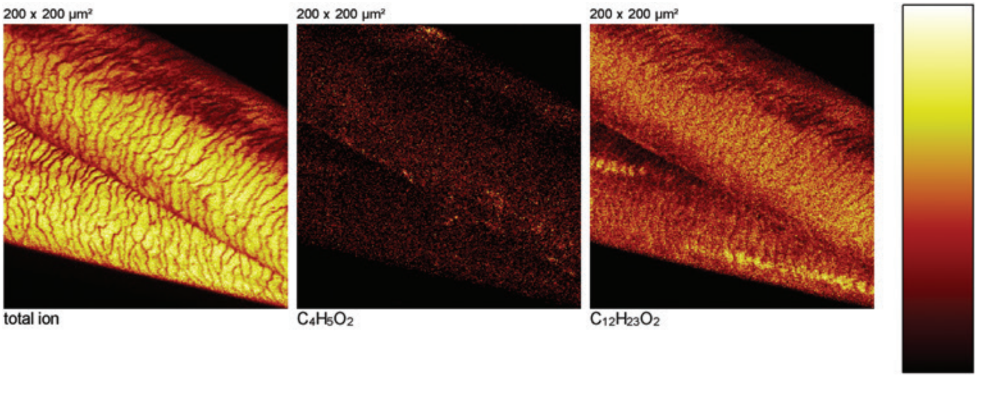

Figure 5. Negative ion SIMS images from structured coconut oil treated hair. $C_4H_5O_2$ is from methacrylates, and $C_{12}H_{23}O_2$ is from coconut oil. The field of view is 200 × 200 µm. The intensity scale for the images is shown to the right where black is no signal and white is the maximum signal.

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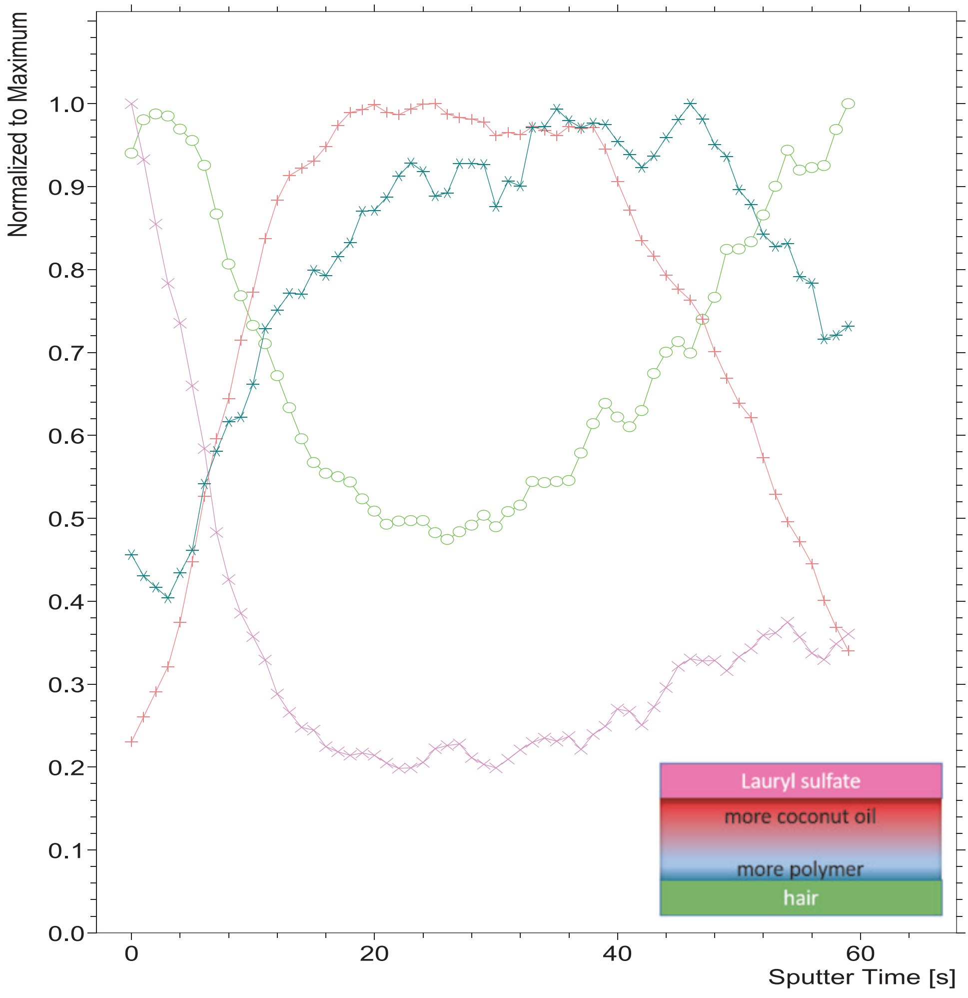

Figure 6. Negative ion depth profile from the top hair from Figure 5. Green circles are CN, red plus signs are coconut oil, pink x's are lauryl sulfate, and blue asterisks are methacrylic ions. Data are normalized to the maximum signal for each ion.

on the surface of the hair, presumably from the shampoo washing after the oil treatment. Under this layer there is a mixed layer that starts out richer in coconut oil and decreases toward the hair surface, where the concentration of methacrylate copolymer increases. This may describe a deposition mechanism where the copolymer acts somewhat as a primer, and this helps the coconut oil adhere to the hair, much like a primer helps paint stick to wood. As the copolymer is uniformly dispersed within the coconut oil, it is also possible that the smaller, more mobile coconut oil migrates toward the air interface and the copolymer stays localized closer to the hair fiber. CN is likely from proteins in hair or other organic nitrogen compounds, not necessarily from cyanide. At the deepest part of the profile toward the right, CN has a high concentration as the hair is etched. At the air interface, it is also richer, although the compounds that cause this enhancement are unclear.

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DISCUSSION

Through this work we have demonstrated that acrylic copolymer structured coconut oil is retained on the hair surface after washing at a higher level. Additionally, through SIMS we have shown that the structured oil is uniformly distributed over the hair fiber, providing a nice even coating. We next sought to understand the impact of this oil deposition on consumer perceivable benefits like combing, reduced friction, and improved feel of the hair. In this section we will describe two pieces of work: first, coconut oil leave-in treatments that are then washed with shampoo to reduce the greasy haptics; and second, the incorporation of these structured coconut oils in standard rinse-off conditioner applications.

LEAVE-IN COCONUT OIL TREATMENTS

In these experiments, coconut oil or structured coconut oil are used as leave-in conditioner treatments that are then washed off with shampoo. This is a common practice in India and the Middle East where coconut oil would be massaged into the hair before bed and washed the following morning. In Figure 7, the results show that coconut oil structured with acrylic copolymers provided an improvement in the reduction in dry combing force compared to the control formulation (coconut oil only) without such polymers. This impact was observed at copolymer use levels as low as 0.5% in the formulation despite having no impact on the viscosity at this use level. It was noted that when the acrylic copolymer was used at 6% in the structured oil gels that the retention on the surface was significant and negatively impacted the haptics of the hair tress. Given this behavior and the data in Figure 7, we hypothesize that there is optimal performance when the oil is slightly structured but not overly gelled in these leave-in treatments.

RINSE-OFF CONDITIONER TREATMENTS

After having demonstrated the utility of these structured oils, we explored if these benefits could be observed from rinse-off conditioners that contained coconut oil. While direct

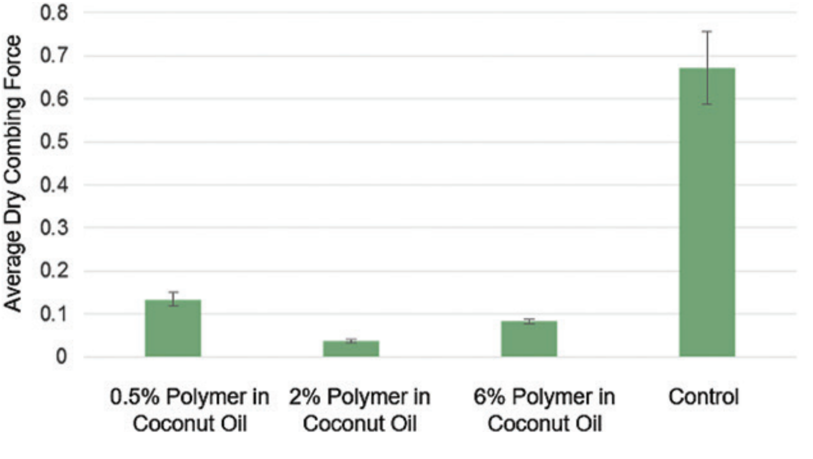

Figure 7. Average dry combing force on 8 hr bleached hair tresses after treatment with structured or unstructured coconut oil followed by shampooing. The control is coconut oil only.

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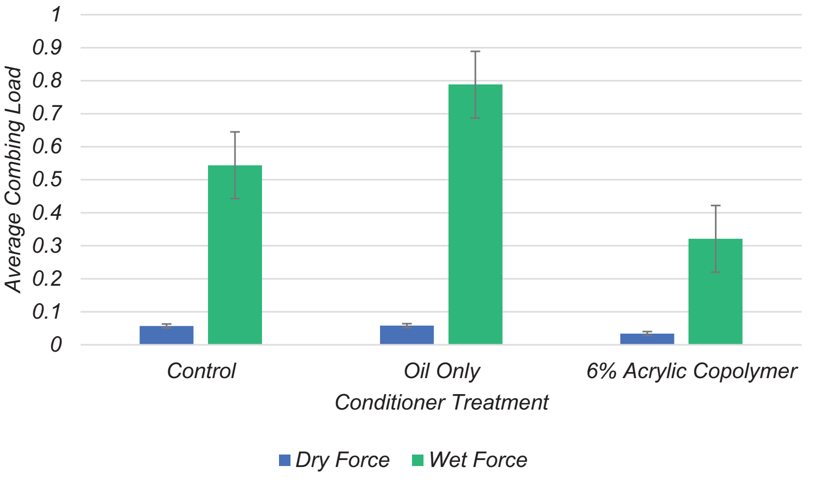

Figure 8. Average wet (green) and dry (blue) combing force on 8 hour bleached hair tresses after treatment with rinse-off conditioners containing structured or unstructured coconut oil.

leave-in treatment is common in a subset of the world, the inclusion of coconut oil in standard shampoos and conditioners is growing rapidly as consumers desire more natural benefit agents. In this section we explored a standard rinse-off conditioner that contained either 2% coconut oil or 2% coconut oil structured with 6% of acrylic copolymer. It is important to highlight that the polymer use level in these conditioners is a fraction of a percent, more specifically 0.12% by weight, of the finished formulation.

As shown in Figure 8, improvements in both dry combing and wet combing were observed when the coconut oil in the rinse-off conditioner formulation was structured with acrylic copolymer. The control is hair without any rinse-off conditioner treatment, "oil only" is the rinse-off conditioner with unstructured coconut oil, and the "6% acrylic copolymer" sample is the rinse-off conditioner with structured coconut oil. The results show that the polyacrylate-containing oil gels formulated in the rinse-off conditioners provided an improvement in the reduction in wet combing force compared to the control conditioner without such polymers. The conditioners containing the polyacrylate-containing oil gels are therefore capable of significantly improving the wet conditioning properties of hair. Additionally, statistically significant benefits were observed in dry combing, which can lead to easier brushing and overall reduced damage.

Lastly, the impact of the structured-oil rinse-off conditioner treatments were explored using a coefficient of friction study on dry hair. Conditioners containing the structured coconut oil containing 6% copolymer provided an improvement for reduced friction compared to the control conditioner with unstructured coconut oil (Figure 9). No benefit was observed for rinse-off conditioners containing structured coconut oil with only 2% copolymer (data not shown).

In summary, the impact of acrylic copolymers on the deposition and retention of coconut oil on hair fibers has been studied. We have shown that structuring coconut oil can increase the overall viscosity of the oil and increase the amount of oil that is retained on the hair after leave-in treatment followed by shampooing. GC–MS was used to quantify the amount retained on hair upon washing, and it was found to be roughly 2% of the amount

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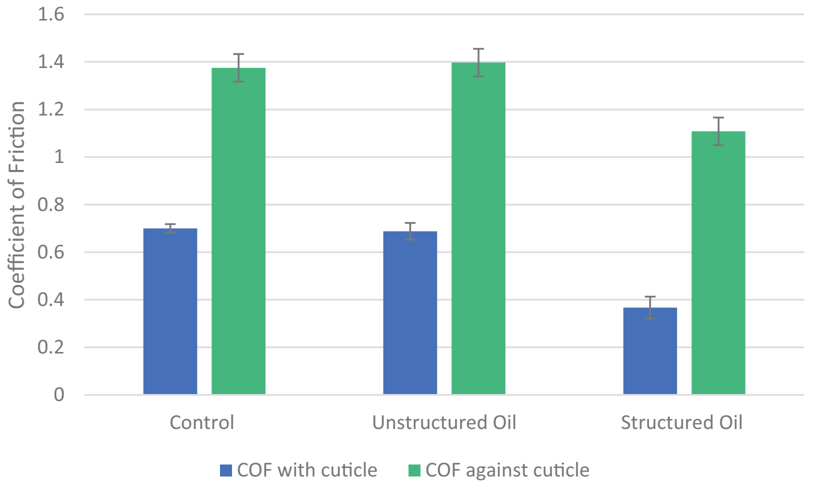

Figure 9. Coefficient of friction (COF) study on 8 hour bleached hair after rinse-off conditioner treatment.

applied, doubling the amount retained from the neat coconut oil treatment. Using SIMS, we have shown the colocalization of the acrylic copolymer and coconut oil, and through depth profiling, we have shown that the small, more migratory coconut oil is present in greater quantities at the air interface. We have explored the utility of those structured oil gels as neat leave-in treatments as well as the key benefit agent in rinse-off conditioners. In the leave-in treatments, we have shown significantly reduced dry combing force relative to unstructured coconut oil. For the rinse-off conditioners, benefits were observed for dry and wet combing, and reduced friction was measured with 0.12% acrylic copolymer in the formulation.

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