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"The Future of Hair Care: detangling the knots of innovation"

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1. Introduction

The global personal care industry is undergoing a significant transformation, driven by increasing consumer awareness of environmental sustainability and health-related concerns (Pletnev, 2004). Shampoos, one of the most widely used personal care products, are under increasing scrutiny for their ecological footprint. Conventional formulations often contain petroleum-based and synthetic materials such as surfactants, thickeners, and silicones. While these components contribute to the product performance, their concerns related to biodegradability, aquatic toxicity, skin irritation and long-term environmental accumulation are rising. In response to these concerns, there is a growing interest in the development of shampoos formulated with naturally derived, environmentally friendly ingredients. However, achieving comparable performance using green alternatives remains a key challenge for formulators, particularly in maintaining viscosity, sensory appeal, heat protection, and frizz control.

Viscosity plays a critical role in the sensory experience and perceived quality of shampoo (Lisa Gandolfi, 2015). Consumers often associate a thicker consistency with higher efficacy, better cleansing performance, and a more luxurious or premium product. Moreover, viscosity impacts product stability, shelf life, and user control during application - factors that influence repeat purchase decisions. For formulators aiming to create biosurfactant-based shampoos, achieving the desired viscosity using thickeners poses a challenge, as these materials must deliver both functional performance and sensory appeal.

In addition to cleansing effectiveness, the trends of shampoos are increasingly expected to deliver other hair treatment benefits, particularly in areas such as heat protection and frizz control. Heat protection is one of key functions in hair care formulations which can cause keratin denaturation, cuticle degradation, and increased porosity (Y. Zhou, 2011). Heat protectants mitigate this damage by forming protective films that reduce water loss and limit thermal conductivity. Common agents include silicones, quaternized polymers, and hydrolyzed proteins, which enhance heat resistance while maintaining fiber integrity (da Gama, 2011). Similarly, frizz control remains a critical concern, particularly for consumers with curly, wavy, or chemically treated hair. Frizz is primarily caused by moisture imbalance and cuticle disruption, causing an irregular hair fiber alignment and surface roughness (Sang-Hun Song, 2024). Environmental factors such as humidity exacerbate this phenomenon by promoting water uptake

into the hair shaft, leading to fiber swelling and structural disarray. Conventional frizz-control strategies rely on silicones, conditioning agents, and film-forming polymers to smooth the hair surface and limit moisture permeability (S.M Badiul Alam Siddiqui, 2022). However, increasing regulatory has catalyzed the pursuit of biodegradable, bio-derived alternatives. Consequently, there is a growing drive to develop sustainable ingredients capable of delivering effective heat protection and frizz control.

Despite the existing limitations and challenges associated with biosurfactant-based hair care formulations, this study seeks to investigate novel strategies to enhance performance. Part 1 of this study focuses on evaluating the potential of a newly-developed associative thickener. Part 2 investigates green heat-protecting agents and green frizz-controlling compositions. Collectively, these investigations are intended to address critical formulation gaps while aligning with principles of green chemistry, thereby contributing to the advancement of sustainable, safe, and consumer-centric innovations in the personal care industry.

2. Materials and Methods

Part 1: The shampoo formulations in this study were developed using a combination of sophorolipid (60% active) as a biosurfactant, polysorbate 80 (100% active) and cocamidopropyl betaine (CAPB, 30% active). The newly developed associative thickener was used as the primary viscosity modifier. Its performance was compared with several conventional thickeners commonly used in personal care formulations as shown in Table 1. All percentages used in this work are by weight percentage (wt%).

Table 1 Physical properties of studied thickeners

Thickener	Melting point (°C)	Appearance	%Solid
New associative thickener	N/A	Paste	70-70
Xanthan gum	N/A	Powder	100
Acrylates/C10-30 alkyl acrylate cross polymer	N/A	Powder	100
PEG-150 distearate	52-57	Flake	100
PEG-135	60	Flake	100

Mixing: Shampoo formulations were mixed using an overhead mixer and left overnight to assure complete mixing before viscosity measurement.

Viscosity measurement: Shampoo formulation viscosity was measured using a Brookfield DV2 VT viscometer, spindle LV 3 at 20 rpm. The temperature was maintained constant at $22\pm0.2^\circ\text{C}$ through the study.

Part 2: Isoamyl caprylate/caprate, isoamyl cocoate, and isoamyl palmitate/stearate were tested for heat protection and frizz control management. The isoamyl esters were compared to C13-15 alkane (known as hemisqualane) and bis-cetearyl amodimethicone as common thermal hair protectants.

Thermal protection analysis: differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and microscopy were used as analytical techniques. The DSC is a thermal analysis technique that measures the energy difference supplied to a substance and a thermally stable reference material as a function of temperature, while both are subjected to a controlled temperature program. The TGA provides information on mass changes as a function

of time and/or temperature under a specific atmosphere. The resulting curves offer insights into the composition and thermal stability of the sample, intermediate products, and the residue formed. A microscopy, on a micrometric scale, was applied to visualize the film formed on the hair fiber.

To determine if the film formation for thermal protection was effective, different heat protectant formulas were prepared as shown in Table 2, mixed until homogenous, applied to hair tresses and then analyzed by microscopy and DSC.

Table 2 Heat protectant shampoo formulations

Component	Range (%)
Cyclopentasiloxane	50-80
Dimethiconol	2.0-5.0
Ethylhexyl methoxycinnamate	2.0-5.0
Simmondsia chinensis seed oil	0.1-1.0
Thermal protection agent	1.0

Caucasian Type 2 virgin hair tresses were standardized by washing with a 20% sodium lauryl ether sulfate solution and then treated with the application of 0.4 grams of the heat protectant formulas. After drying ($25^{\circ}\text{C} \pm 2^{\circ}\text{C}$; $60\% \pm 5\%$ RH), a 250°C flat iron was applied to the entire strand for evaluation under optical microscopy, using an Olympus BX51 microscope at a scale of 20 micrometers.

The same hair strands were used for DSC analysis. The analysis was carried out in a DSC under a nitrogen gas atmosphere at a flow rate of 50 mL/min, with a heating rate of $10^{\circ}\text{C}/\text{min}$ and a temperature range of 25 to 400°C in a sealed aluminum crucible containing around 3.0 mg of sample. The data was evaluated in terms of the intensity of the signal emitted in ΔH and analyzed as follows: the first event is related to hydration degradation, which takes place around $40-185^{\circ}\text{C}$. The higher the signal, the greater the hydration protection attributed to the sample. The second and third events refer to α -keratin degradation, which takes place around $225-250^{\circ}\text{C}$. The higher the signal modulus, the greater the α -keratin protection attributed to the sample.

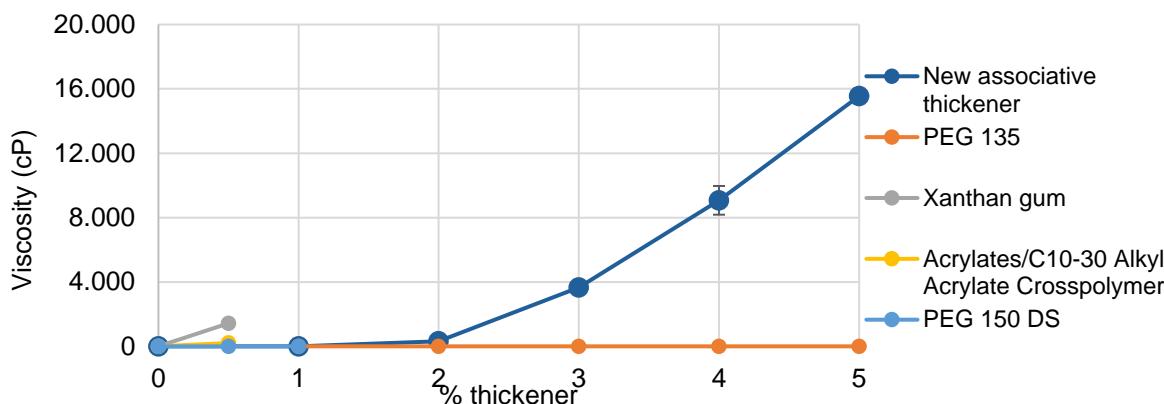
Frizz control was evaluated using Caucasian Type 2 virgin hair tresses, with five tresses per treatment. The heat protectant formulas were applied at a volume of 0.2g on damp tresses, which were then dried for 24 hours at $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $60\% \pm 5\%$ RH. Pictures of the tresses were taken using a digital camera. Image analysis was conducted using GIMP software, and frizz was quantified by applying a filter to identify the total area of the tresses and the frizz area in pixels. The pixel count was further analyzed through the image histogram to determine the extent of frizz.

3. Results

3.1.1 Viscosity Performance Comparison

Biosurfactant-based shampoo consists of 6.03%wt sophorolipid, 3.75%wt polysorbate 80 and 3.75%wt CAPB with the %wt total surfactant of 13.53 which is about the average total surfactant concentration found in shampoos. The viscosity performance of various thickening agents from Table 1 was evaluated as a function of concentration as shown in Figure 1. The new

associative thickener exhibited a significant increase in viscosity with increasing dosage used, achieving over 16,000 cP at 5%, far surpassing all other tested thickeners. The commonly used thickener xanthan gum produced slight viscosity (about 1400 cP) at 0.5%. However, the formulation was slimy, which could associate with poor quality to consumers. Acrylates/C10-30 alkyl acrylate crosspolymer, which is another widely used thickener in personal care products, showed a gradual rise (200 cP) at 0.5%; however, the formulation was hazy, which is unpleasant for consumers. In contrast, PEG-150 DS and PEG 135 produced negligible viscosity increases across the entire concentration range.



1Figure 1 Viscosity enhancement comparison between new associative thickener vs. other conventional thickeners for biosurfactant-based shampoo formulations

3.1.2 Effect of Salt on Viscosity of Biosurfactant-Based Formulation

This work further explored the effect of adding sodium chloride (NaCl) on the viscosity enhancement of the biosurfactant-based shampoo formulations with PEG-150 DS and PEG-135 as illustrated in Figure 2. The results show that adding salt does not increase the viscosity of the formulations even up to 5%.

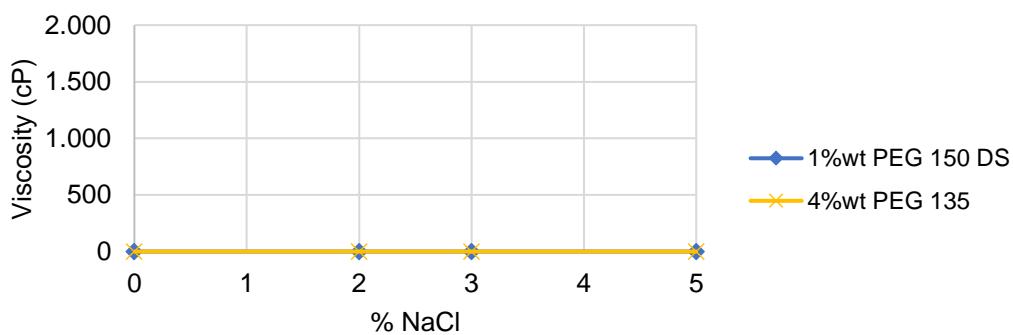


Figure 2 Effect of additional salt on viscosity of biosurfactant-based shampoo formulations with 1% PEG 150 DS and 4% PEG 135

3.1.3 Effect of pH on Viscosity of Biosurfactant-Based Shampoo Formulations

Figure 3 shows the effect of pH on the formulation viscosity. The formulations containing 3% and 4% associative thickener were selected for the evaluation due to their moderate and high viscosities. For both thickener concentrations, maximum viscosities were observed at approximately pH 6, reaching around 4,000 cP for the 3% formulation and approximately 9,000 cP for

the 4% formulation. Beyond this pH, viscosity decreased sharply, with values dropping below 1,000 cP at pH 10.

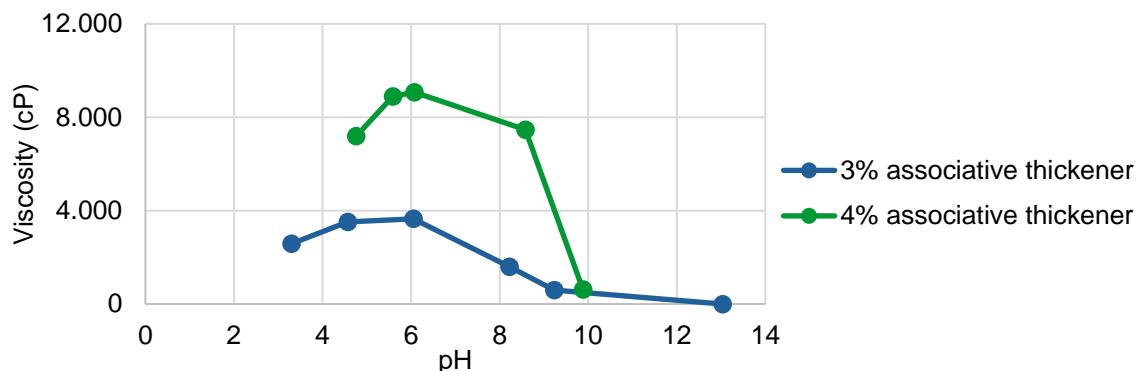


Figure 3 Impact of pH on the viscosity of biosurfactant-based shampoo formulations

3.1.4 Effect of Preservative on Viscosity of Biosurfactant-Based Shampoo Formulations

In personal care products, preservatives are always used to prevent microbial growth during shelf-life period. This work investigated the effect of two common cosmetic preservatives (0.5% sodium benzoate and 0.5% phenoxyethanol) on the viscosity of formulations containing 3% and 4% associative thickener (Figure 4). All samples were adjusted pH to 4.5 and 6.0 within the common pH range for personal care products. In the presence of sodium benzoate, a minimal decrease in viscosity both associative thickener concentrations was observed. However, adding phenoxyethanol resulted in a more pronounced reduction in viscosity than those of sodium benzoate.

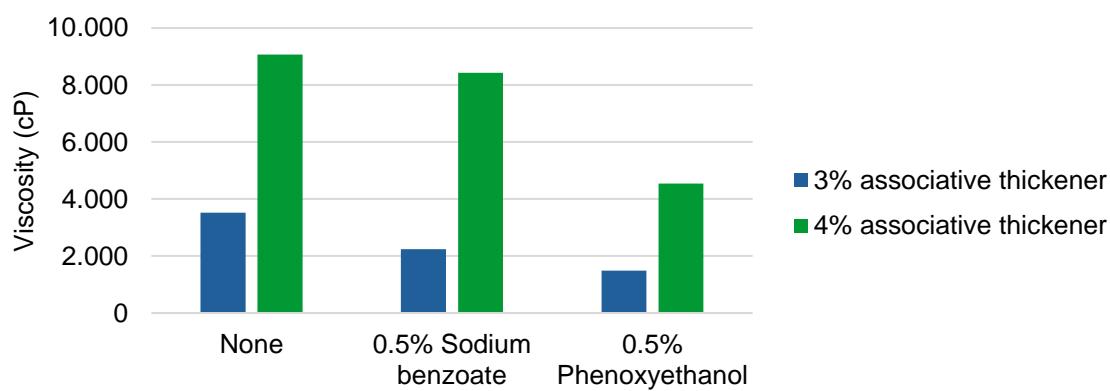


Figure 4 Effect of preservatives on the viscosity of biosurfactant-based shampoo formulation

3.2.1 Thermogravimetric Analysis (TGA)

TGA results (Table 4) show that bis-cetearyl amodimethicone exhibited thermal stability up to approximately 337°C with decomposition occurring over a broad temperature range up to about 634°C. C13-15 alkane (hemisqualane) began to decompose at a lower temperature with the onset of mass loss occurring around 26°C and continuing up to about 186°C. Isoamyl caprylate/caprate showed thermal stability up to about 26°C with decomposition occurring between 26°C and 206°C. Isoamyl cocoate demonstrated thermal stability up to approximately 25°C with decomposition taking place between 25°C and 280°C and isoamyl

palmitate/stearate exhibited thermal stability up to about 26°C with decomposition occurring between 26°C and 352°C.

Table 4 TGA results of the film-forming ingredients tested

Film-forming ingredients	Event start temperature (°C)	Event end temperature (°C)
Bis-cetearyl amodimethicone	337.34	634.2
C13-15 alkane	25.84	185.78
Isoamyl caprylate/caprate	26.26	205.88
Isoamyl cocoate	25.42	280.4
Isoamyl palmitate/stearate	26.26	351.58

3.2.2 Optical Microscopy

Optical microscopy images (Figure 5) showed that the strands treated with isoamyl esters appeared natural and healthy. The strand treated with hemisqualane, however, showed signs of cuticle damage. Bis-cetearyl amodimethicone formed a characteristic silicone film on the hair fiber contributing to build-up. The strand treated with the base formulation which lacked of a film-forming agent and also exhibited cuticle damage.

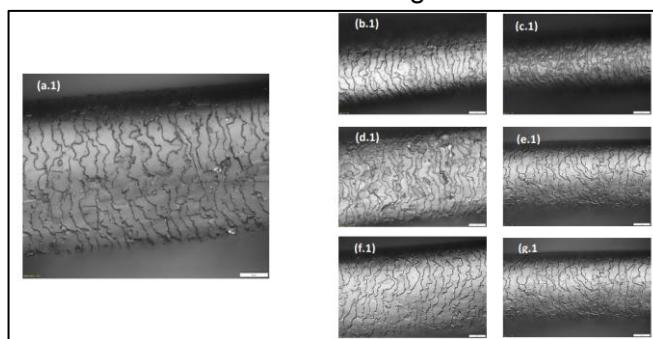


Figure 5 Optical Microscopy of hair strands after flat ironing: (a.1) Untreated hair strand; (b.1) Hair strand treated with a base formulation, without film-forming agent; (c.1) Hair strand treated with a base formulation with bis-cetearyl amodimethicone; (d.1) Hair strand treated with a base formulation with C13-15 alkane (hemisqualane); (e.1) Hair strand treated with a base formulation with isoamyl caprylate/caprate; (f.1) Hair strand treated with a base formulation with isoamyl cocoate; (g.1) Hair strand treated with a base formulation with isoamyl palmitate/stearate.

3.2.3 Differential Scanning Calorimetry (DSC)

Table 2 presents the results for moisturizing and α -keratin protection. The negative ΔH (J/g) value indicates the energy expended to degrade the material. Regarding hydration protection, isoamyl cocoate and isoamyl palmitate/stearate showed superior results, as the energy required to break down the water was higher. Isoamyl caprylate/caprate exhibited results very similar to bis-cetearyl amodimethicone. Conversely, C13-15 alkane (hemisqualane) demonstrated lower results than the blank formulation (without the film-forming agent) indicating that this material offers minimal hydration protection. In terms of α -keratin protection, isoamyl palmitate/stearate and bis-cetearyl amodimethicone achieved comparable results, while isoamyl cocoate performed even better. On the other hand, isoamyl caprylate/caprate and C13-15

alkane yielded inferior results, closely resembling the blank formulation without a film-forming agent, suggesting they provide low α -keratin protection.

Table 4 DSC Results

Samples	Event 1 - hydration		Event 2 - breakdown of α -keratin		Event 3 - breakdown of α -keratin		Events 2 and 3	
	ΔT	ΔH (J/g)	ΔT	ΔH (J/g)	ΔT	ΔH (J/g)	ΔT	ΔH (J/g)
Untreated hair	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Blank	51.6	-170.1	12.4	-6.6	13.3	-6.47	25.7	-13.07
Bis-cetearyl amodimethicone	96.1	-188.5	10.4	-7.5	14.9	-7.9	25.3	-15.4
C13-15 alkane	73.0	-139.2	10.8	-6.7	10.7	-5.0	21.5	-11.7
Isoamyl caprylate/caprate	76.8	-188.1	11.0	-6.5	13.4	-5.9	24.4	-12.4
Isoamyl cocoate	149.9	-258.9	11.4	-6.7	20.9	-10.0	32.3	-16.7
Isoamyl palmitate/stearate	116.5	-239.6	11.3	-7.3	18.6	-8.1	29.9	-15.4

3.2.3 Frizz Control

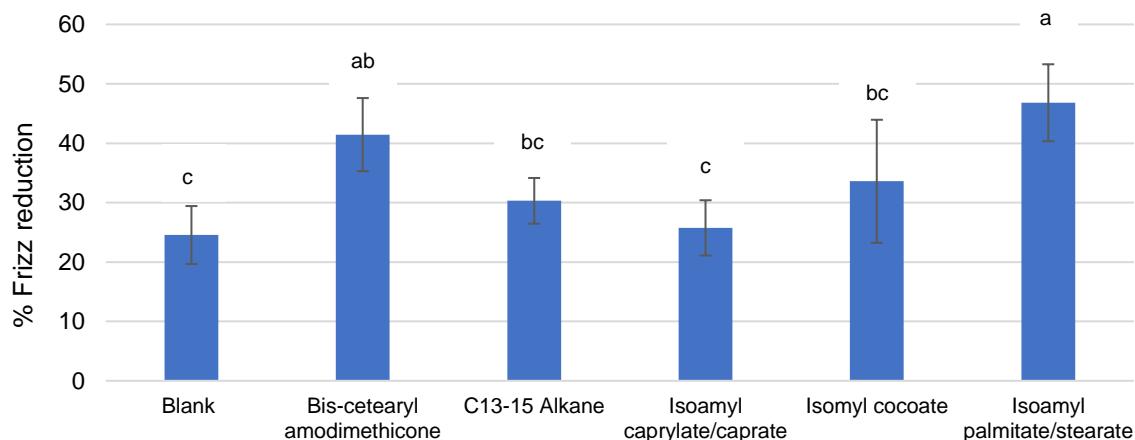


Figure 6 Percentage of frizz reduction for different heat protection agents

Figure 6 shows the percentage reduction in frizz for each different heat protection formulation: blank (without film forming agent), bis-cetearyl amodimethicone, isoamyl caprylate/caprate, isoamyl cocoate, and isoamyl palmitate/stearate. Statistical analysis was performed using one-way ANOVA followed by a multiple comparison test, with different letters above the bars indicating statistically distinct groups ($p<0.05$). The results reveal significant differences among the tested ingredients regarding their ability to reduce hair frizz. Isoamyl palmitate/stearate showed the highest frizz reduction (~47%), forming a group statistically different from all others (letter "a"). Bis-cetearyl amodimethicone also demonstrated high performance (~42%) and belonged to group "ab" indicating that this ingredient is not significantly different from either

isoamyl palmitate/stearate or C13-15 alkane. C13-15 alkane and isoamyl cocoate (group "bc") presented intermediate levels of frizz reduction (~30-35%) with no statistical difference between them or from bis-cetearyl amodimethicone. Isoamyl caprylate/caprate and the blank control (both in group "c") showed the lowest efficacy with frizz reduction (~25%) which is statistically lower than isoamyl palmitate/stearate and bis-cetearyl amodimethicone.

4. Discussion

The superior performance of the new associative thickener is evident across the entire concentration range tested in the biosurfactant-based shampoo formulaiton. Associative thickeners are known to self-assemble and interact with the hydrophobic portion of surfactants in complex formulations forming entangled or networked structures (Courtney J. Thompson, 2023) that contribute to strong thickening effects even at low concentrations. In contrast, xanthan gum, acrylates/C10-30 alkyl acrylate crosspolymer, PEG 135 and PEG 150 DS showed minimal contribution to viscosity possibly due to their lack of interpolymer or micellar association.

In traditional surfactant-based shampoo systems (e.g., those using sodium lauryl sulfate or sodium laureth sulfate combined with CAPB), salt addition is a well-established method for enhancing viscosity through micelle transformation (Xiao Xiao, 2022). However, in biosurfactant-based systems, this mechanism appears ineffective. The observed lack of salt response may be attributed to the nonionic or weakly anionic nature of biosurfactants which differ significantly from conventional anionic surfactants in terms of micellar behavior and sensitivity to ionic strength, thus diminishing the impact of salt on micelle packing and viscosity.

The associative thickener maintains excellent viscosity performance in the mildly acidic to neutral pH range (pH 4.5-7.5) which is a skin friendly pH range for all ages (Sarah G. Brooks, 2025) helping to preserve the stratum corneum, prevent irritation, and support the skin's microbiome. The viscosity relatively remained stable pHs between 4.5 and 7.5 suggesting robust thickening behavior where hydrophobic associations between the thickener and surfactant micelles remain intact due to minimal electrostatic disruption. The sharp decline in viscosity at alkaline pH values (above pH 8) limits the applicability of the thickener in high-pH systems such as some industrial cleaners, but underscores its suitability for personal care formulations where pH control is important.

Preservatives can significantly influence the viscosity performance of thickeners (Rezarta Shkreli, 2022). In particular, phenoxyethanol had a more disruptive effect compared to sodium benzoate because phenoxyethanol is an alcohol acting as a solvent which can interfere with micelle formation and self-entangle network. Such interactions disrupt the balance between hydrophilic and hydrophobic interactions necessary for the formation of a stable thickening network. In contrast, sodium benzoate, a more polar and ionic preservative, appeared to have a less detrimental effect, possibly due to reduced interaction with the hydrophobic moieties of the thickener.

Regarding heat protection, among the film-forming agents evaluated, C13-15 alkane (hemisqualane) had the poorest results in all aspects. These findings show that isoamyl caprylate/caprate and bis-cetearyl amodimethicone exhibited very similar results in terms of hydration protection, while isoamyl palmitate/stearate and isoamyl cocoate demonstrated superior performance. Bis-cetearyl amodimethicone, isoamyl palmitate/stearate, and isoamyl cocoate also showed better results in protecting α -keratin. Considering that bis-cetearyl

amodimethicone is considered as a benchmark for thermal protection. This study reveals that isoamyl caprylate/caprate provided effective thermal protection against hair dehydration, while isoamyl cocoate and isoamyl palmitate/stearate offered effective thermal protection against dehydration and α -keratin degradation of the hair which is consistent with previous work (Lima, 2016; Pinheiro et al, 2007; Wrześniewska-Tosik et al., 2019). These results indicate that isoamyl esters can provide benefits in protecting hair hydration and α -keratin compared to other film-forming agents. TGA analysis indicates that the thermal stability of the isoamyl esters may be related to their molecular weight and chain length. Compounds with longer carbon chains, such as isoamyl palmitate/stearate, exhibit higher decomposition end temperatures compared to those with shorter chains(isoamyl caprylate/caprate). Bis-cetearyl amodimethicone showed a different behavior in comparison to the others, with different events that suggest a mixture of components.

In addition to providing heat protection, isoamyl esters, especially isoamyl palmitate/stearate showed the ability to reduce frizz similarly to bis-cetearyl amodimethicone. This is possibly due to their capacity to restore the hydrophobic external layer of the hair strand, forming a protective barrier that seals the cuticles. This prevents moisture absorption and protects the hair against frizz which is a responsible mechanism for maintaining the integrity of the cuticle and cortex layers under thermal stress (Lima, 2016).

5. Conclusion

Biosurfactant based shampoo was found to effectively thicken with the new associative thickener comparing to other typical thickeners. The new associative thickener showed to be robusted with the skin-friendly pH range between 4.5 and 7.5. Adding phenoxyethanol presented more negative impact on viscosity reduction than sodium benzoate. This finding proves that the efficiency and potential of the new associative thickener as a greener next-generation alternative, capable of delivering desirable thickener at lower usage levels for the biosurfactant-based shampoo formulation.

Among the different film-forming agents evaluated, C13-15 alkane (hemisqualane) demonstrated the poorest performance across all aspects. Conversely, isoamyl caprylate/caprate and bis-cetearyl amodimethicone exhibited similar results in terms of hydration protection, while isoamyl palmitate/stearate and isoamyl cocoate showed superior performance. Notably, bis-cetearyl amodimethicone, isoamyl palmitate/stearate, and isoamyl cocoate were more effective in protecting α -keratin. Furthermore, isoamyl esters, particularly isoamyl palmitate/stearate have demonstrated the ability to reduce frizz similarly to bis-cetearyl amodimethicone. Overall, the results indicate that isoamyl esters are promising agents for enhancing hair protection and maintaining hair health under thermal stress.

In summary, this work provides a significant step forward in the development of biosurfactant-based shampoo formulations , successfully achieving targeted viscosity, frizz control, and thermal protection to meet the performance demands of the hair care market.

6. References

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