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## ***Tailoring the Rheological Behavior of Oil-Based ZnO Dispersions via Multi-surfactant Approach***

**Nisa Ergin<sup>1,\*</sup>, M. Tumerkan Kesim<sup>2</sup>, Ender Suvacı<sup>1,2</sup>**

<sup>1</sup> Eskişehir Technical University, Materials Science and Engineering Dept., 2 Eylül Kampusu 26555, Eskişehir/Türkiye; <sup>2</sup> Entekno Industrial, Technological and Nano Materials Corp., Eskişehir Organized Industrial Zone 7. St. No.: 50 Odunpazarı, 26110, Eskişehir/ Türkiye

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### **1. Introduction**

The importance of effective sun care has become increasingly evident with the growing awareness of the harmful effects of ultraviolet (UV) radiation. Both UVA (320–400 nm) and UVB (290–320 nm) rays contribute to skin damage, with UVB being primarily responsible for sunburn and direct DNA damage, while UVA penetrates more deeply, accelerating skin aging and playing a significant role in the development of skin cancers. Broad-spectrum protection, therefore, is essential in preventing both acute and chronic effects of sun exposure [1,2]. Sunscreen filters, active agents in sun care formulations, are generally categorized into organic (chemical) and inorganic (physical) types. Inorganic UV filters, particularly titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO), have garnered increasing attention due to their favorable safety profiles. These particles function by reflecting, scattering and absorbing UV radiation. Unlike organic filters, which absorb UV radiation and undergo photochemical reactions, inorganic filters remain on the skin's surface and provide immediate, and long-lasting stable protection. Furthermore, inorganic filters are considered ideal alternatives for sensitive skin. Their minimal potential to cause irritation or allergic reactions has significantly contributed to their increased acceptance in dermatologically safe sunscreen formulations [3]. Among inorganic filters, ZnO is particularly preferred due to its ability to cover a broader spectrum of wavelength, offering superior UVA protection compared to TiO<sub>2</sub>, which is more efficient in the UVB range. This broader coverage makes ZnO a more versatile choice, especially in formulations specifically designed for comprehensive sun protection [4].

Inorganic powders such as TiO<sub>2</sub> and ZnO are routinely incorporated into a wide range of cosmetic formats [5] including but not limited to emulsions, sticks, gels, aerosol sprays and other anhydrous suspensions. However, formulating dry powder form can be challenging to formulators due to the aggregation propensity of high surface energy particles, which makes careful

control of particle distribution indispensable. Accordingly, achieving a truly homogeneous dispersion of  $\text{TiO}_2$  and  $\text{ZnO}$  is paramount for maximizing light-scattering efficiency and, in turn, for realizing their full contribution to Sun Protection Factor (SPF) performance.

Introducing these materials in pre-dispersed form circumvents the initial aggregation hurdle and provides uniform particle distribution within the matrix. Dispersions containing inorganic powders offer improved processability, whose formulation nevertheless necessitates rigorous optimisation to secure both functional performance and long-term stability. Although dispersions of inorganic powders are easier to process, their formulation still demands careful optimization to guarantee consistent performance and long-term stability. Parameters such as particle size, surface treatment, the dispersion medium, and the dispersant system all influence the final performance. Especially in the case of micron-sized particles, long-term stability becomes a critical concern. Simple wetting cannot maintain stability over time, as particles tend to sediment or re-agglomerate due to gravity and van der Waals interactions. The inclusion of appropriate surfactants, dispersing agents or rheology modifiers is essential to enhance steric or electrostatic stabilization, prevent sedimentation, and ensure that the active material remains evenly distributed in the formulation throughout the shelf life of products.

The aim of this study is to investigate and compare the effects of selecting appropriate surfactants/dispersing agents on the rheological properties of  $\text{ZnO}$  dispersions with micron-sized, platelet-shaped particles, focusing on how the structural characteristics of surfactants influence the homogeneous distribution of these particles in oil-based systems and providing insights into their potential for long-term stabilization.

## 2. Materials and Methods

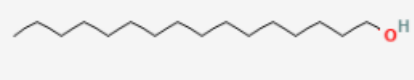
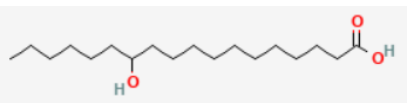
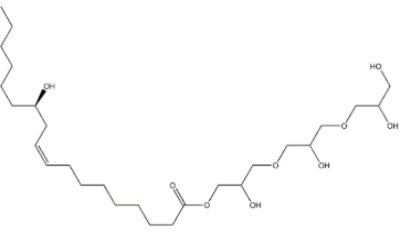
### *Selection of Ingredients*

In this study, Caprylic/Capric Triglyceride (CCT), a commonly used ingredient in commercial sunscreens, was selected as the primary base due to its compatibility with both natural formulations and certifications like COSMOS. Known for its emollient and solvent properties, CCT plays a critical role in stabilizing emulsions and enhancing the dispersion of active ingredients, such as micron-sized  $\text{ZnO}$ , in oil-based systems. Additionally, Polyhydroxystearic Acid (PHSA) was chosen as the key surfactant due to its ability to efficiently stabilize and disperse commercial inorganic UV filters. PHSA's structure, which includes both hydrophilic and lipophilic components, makes it particularly effective in maintaining the long-term stability of  $\text{ZnO}$  dispersions in the oily phase, ensuring the desired high performance of sunscreen formulations. Based on these factors, Cetyl Alcohol (CA), Hydroxy Stearic Acid (HAS), and Polyglyceryl-3 Polyricinoleate (PGPR) were selected as co-surfactants due to their differences in molecular structures and compatibility with PHSA in  $\text{ZnO}$ -containing systems, as shown in Table 1.

Cetyl alcohol (hexadecan-1-ol), a long-chain fatty alcohol with a molecular weight of approximately 247 g/mol, is widely used in cosmetic formulations as a thickening agent contributing to the viscosity and stability of emulsions. Hydroxystearic acid (12-hydroxyoctadecanoic acid), with a molecular weight of about 300 g/mol, serves as an emollient and thickener in cosmetic products, enhancing the texture and consistency of formulations. Polyglyceryl-3 Polyricinoleate (PGPR), an ester of polyglycerol and ricinoleic acid with a molecular weight of around 520.7 g/mol, functions as an emulsifier and viscosity controller in cosmetics, facilitating the formation

of stable emulsions. The structural complementarity and molecular weight compatibility of these co-surfactants with PHSA are considered as key factors in their cooperative behavior, improving the overall stabilization and homogeneity of the ZnO dispersion.

**Table 1.** Chemical properties and structures of selected secondary surfactants.

Surfactants selected as a second surfactant	Molecular Formula	Molecular Weight (g/mol)	Structure	References
Cetyl Alcohol (CA)	$C_{16}H_{34}O$	242.44		[6]
Hydroxystearic Acid (HAS)	$C_{18}H_{36}O_3$	300.5		[7]
Polyglyceryl 3 Polyricinoleate (PGPR)	$C_{27}H_{52}O_9$	520.7		[8]

### Preparation of Dispersions

During the dispersion preparation process, the secondary surfactants and PHSA were combined with Caprylic/Capric Triglyceride and maintained at 80 °C until the surfactants melted before the mixture was stirred. Following this, the ZnO powder was gradually added under mechanical mixing to ensure a uniform mixture, and the dispersion was then homogenized at 3000 rpm for one hour with Silverson LM5 without external heating. Finally, mixing was continued until the dispersion was cooled to the room temperature.

### Characterization of Dispersions

The viscosity and elastic (storage) modulus ( $G'$ ) values of the resulting dispersions were measured using a NETZSCH Kinexus Rheometer. The rheological properties, specifically the viscosity and the elastic modulus ( $G'$ ), were evaluated to understand the flow behavior and structural integrity of the dispersions, which are crucial for assessing the stability and performance of the formulation. In addition, the particle distribution was examined under an optical microscope (ZEISS Axioscope 5) to verify the uniformity of the ZnO dispersion within the oil phase. This step is essential and effective for ensuring that the ZnO particles are adequately dispersed

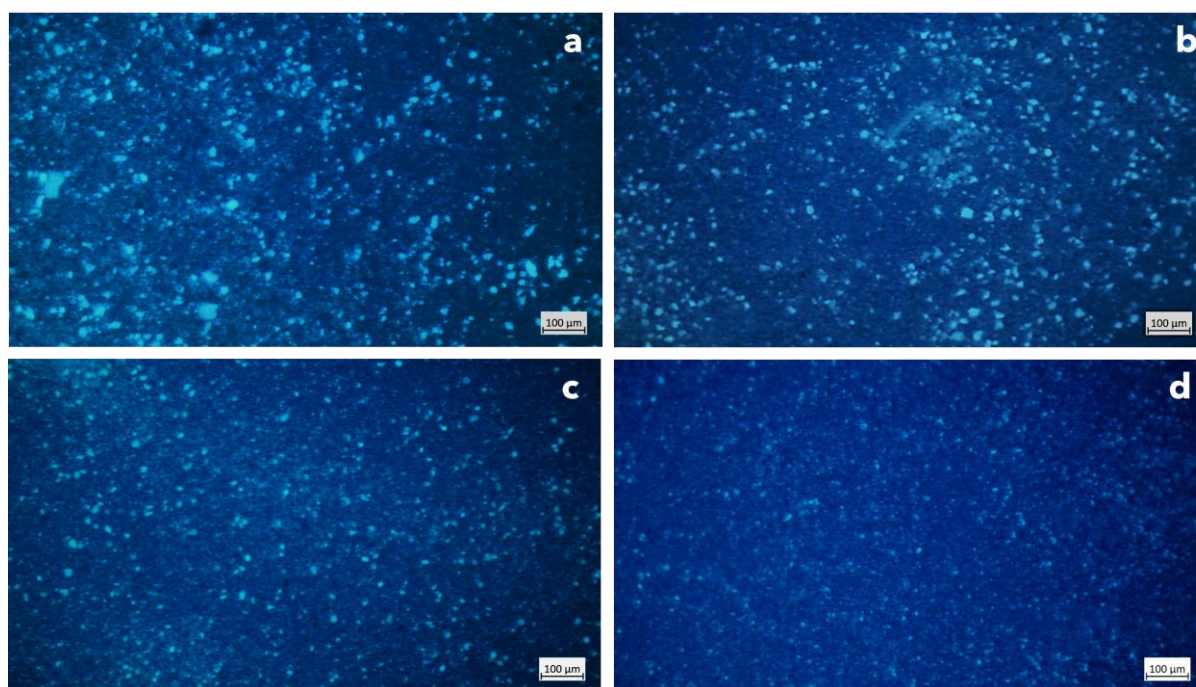
without aggregation, which could negatively impact both the effectiveness of the sunscreen and its aesthetic appeal.

### 3. Results

Dispersion samples were prepared to identify the optimum PHSA / secondary-surfactant ratio for improving particle distribution and stability in a carrier system composed of caprylic/capric triglyceride (CCT) and ZnO, with polyhydroxystearic acid (PHSA) serving as the primary dispersant. The PHSA-to-secondary-surfactant ratios investigated were 4.9, 3, 1, 0.3 and 0 (i.e., formulations containing only the secondary surfactant). While these ratios were varied, the total surfactant concentration (PHSA and secondary surfactant) was fixed at 3 wt% for all compositions for the addition of 65 wt% ZnO. Viscosity measurements and optical-microscopy images were used to determine the ratio that yielded the lowest viscosity and the most homogeneous particle dispersion. For the PHSA / polyglyceryl-3 polyricinoleate (PGPR) series, viscosity changed only slightly across the entire ratio range, and PGPR alone was able to disperse the particles satisfactorily; the minimum viscosity was observed at a PHSA / PGPR ratio of 3. In the PHSA / hydroxy-stearic-acid (HSA) series, the lowest viscosity was achieved at a ratio of 1. At a ratio of 0.3 and when HSA was used as the only surfactant in dispersion, viscosity rose sharply with preventing the incorporation of ZnO particles. For the PHSA / CA series, the minimum viscosity occurred at a ratio of 4.9. A pronounced viscosity increase was noted at a ratio of 0.3, and when CA was used alone, the viscosity became so high that ZnO particles could not be added to the system.

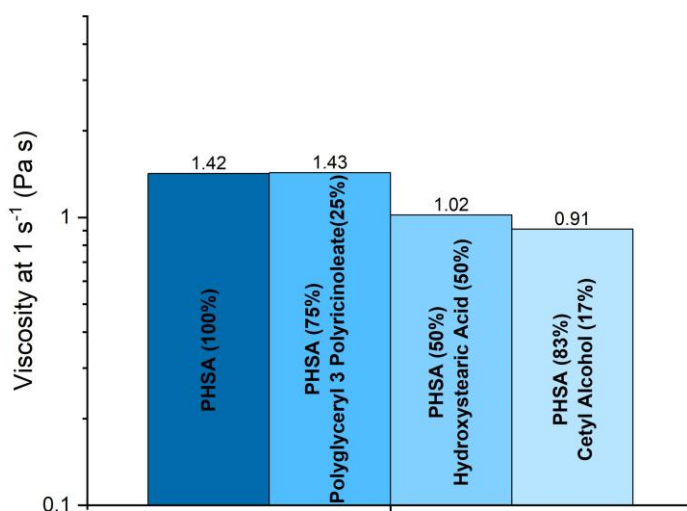
#### *Dispersibility of Particles*

Figure 1 compares particle distribution from the optical micrographs as a function of the surfactant ratios that exhibited the lowest viscosity and, for reference, at the same total surfactant level using PHSA alone (i.e., without any secondary surfactant). Notably, the addition of hydroxy-stearic acid (Figure 1-c) or cetyl alcohol (Figure 1-d) as secondary surfactants led to a visibly improved dispersion of ZnO particles relative to the PHSA-only system (Figure 1-a).



**Figure 1.** Optical micrographs of dispersion formulations with (a) 3% PHSA only and (b) polyglyceryl 3 polyricinoleate as a co-surfactant, (b) hydroxystearic acid as a co-surfactant, and (c) cetyl alcohol as a co-surfactant.

Figure 2 presents the viscosity at  $1 \text{ s}^{-1}$  for the formulations that exhibited the lowest overall viscosity in each surfactant series. The minimum value is observed in the system containing cetyl alcohol, whereas hydroxy-stearic-acid-containing dispersions also show lower viscosity than either the PGPR-containing sample or the PHSA-only control. The improved particle distribution shown in Figure 1 correlates directly with these reductions in viscosity.



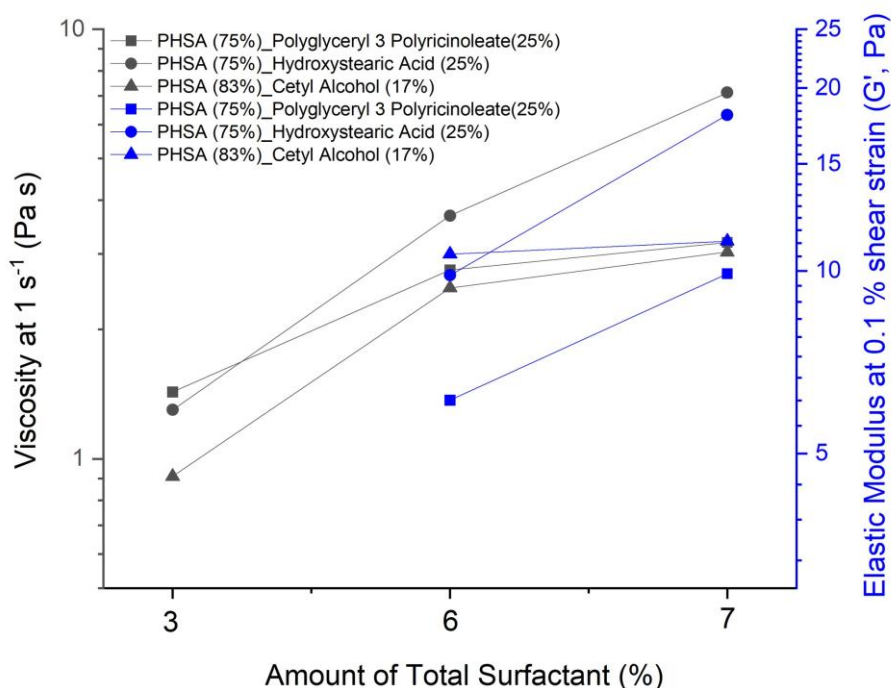
**Figure 2.** Viscosities at  $1 \text{ s}^{-1}$  for PHSA and for the PHSA / secondary-surfactant ratios that exhibited the lowest viscosities in each series.

### Viscosity and Elastic Modulus of Dispersions

When the overall surfactant content was held at 3 wt% and the PHSA / secondary-surfactant ratios that gave satisfactory particle distribution were selected, all samples stored for one week at  $45^\circ\text{C}$  exhibited physical sedimentation. As illustrated in Figures 1-c and 1-d, even though the particles could initially be well dispersed, they agglomerated rapidly and settled. In other words, a total surfactant level of 3 wt% was insufficient to provide durable steric stabilization. New dispersions were prepared at the previously optimised ratios but with higher overall surfactant levels to improve steric hindrance and long-term stability. In the dispersion system with a PHSA / HSA ratio of 1, where the particles were well dispersed, increasing the total surfactant concentration to 6% or 7% caused the viscosity to increase so sharply that ZnO could not be incorporated/wetted. Consequently, the study was continued with the ratio of 3, which had shown (i) a particle distribution comparable to that of Figure 1-c and (ii) a viscosity of  $1.3 \text{ Pa s}$ , which is close to the value given for a ratio of 1 in Figure 2.



Figure 3 summarises how viscosity and storage modulus ( $G'$ ) changed when the total surfactant concentration was increased from 3 to 6 and 7 wt% at the ratios that previously afforded the best particle distribution. In all systems, viscosity increases with high surfactant amounts. In the PGPR and HAS containing dispersions,  $G'$  also increased with a higher amount of total surfactant, indicating a stronger elastic network, whereas the cetyl alcohol containing dispersion showed little change in elastic modulus.



**Figure 3.** Viscosity and elastic modulus values of PHSA (75%) - polyglyceryl 3 polyricinoleate (25%), PHSA (75%) - hydroxy stearic acid (25%), and PHSA (83%) - cetyl alcohol (17%) with total surfactant amounts of 3, 6 and 7.

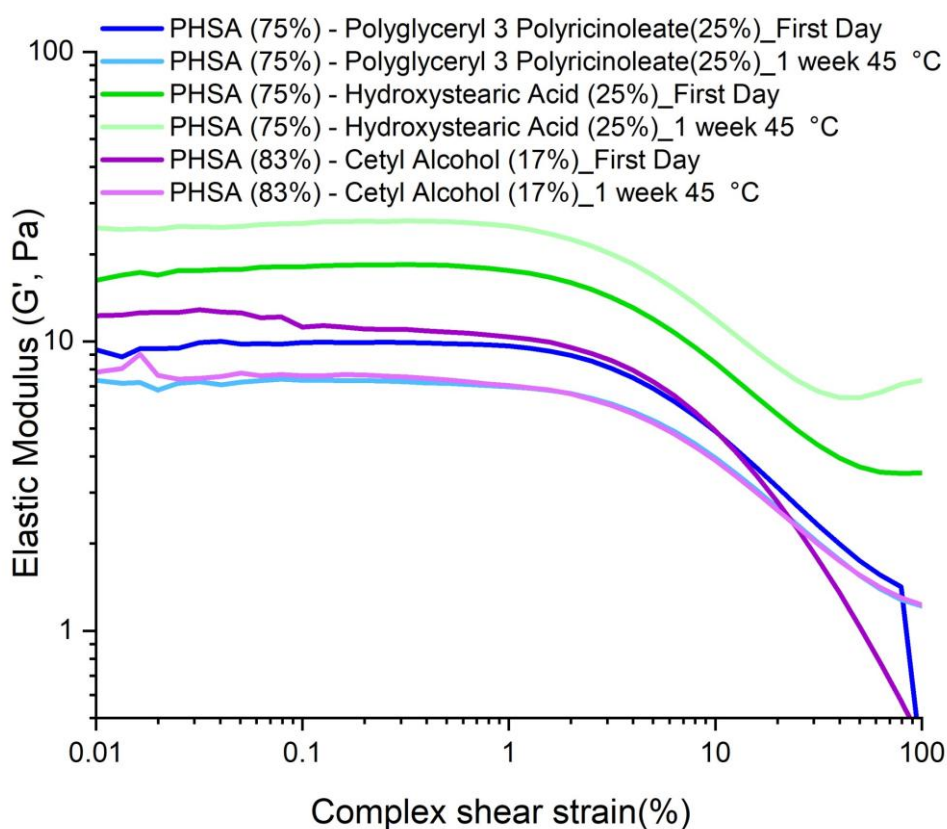
In dispersions formulated with a total surfactant content of 3 wt%, the sedimentation observed after one week at 45 °C persisted in the cetyl-alcohol system even after the overall surfactant level was increased. By contrast, in dispersions containing HSA or PGPR, sedimentation was observed after one month at 25°C and one month at 45°C. To translate the macroscopic observations into quantitative terms, the linear viscoelastic region (LVER) was determined and compared for all systems to comment stability of dispersion systems [9].

### **Stability of Dispersions included a higher amount of surfactant**

Figure 4 compares the linear viscoelastic regions (LVERs) of the dispersions containing 7 wt% total surfactant, recorded on the first day and after one week of storage at 45 °C. In the CA system, the initial strain sweep already exhibits a drop in  $G'$  at 0.1 % shear strain, showing poor long-term stability. After a one-week, 45°C stability test, the same sample shows a distinct

spike and collapse profile at  $G'$ , and these results are consistent with the apparent sedimentation observed on visual inspection. This behaviour is consistent with the relatively low viscosity of the CA-containing dispersion at 7 wt% surfactant (Figure 3).

In interpreting the LVER plots (Figure 4), not only the breadth of the linear region is critical for dispersion stability but also the absolute magnitude of  $G'$  must be considered. When the PGPR- and HSA-containing dispersions (both at 7 wt% % surfactant) are compared, the HSA system demonstrates superior stability, which correlates with its higher viscosity (Figure 3). After one week at 45 °C, the PGPR- and CA-containing samples both display reduced  $G'$  values. Because the post-storage rheology was measured on the undisturbed supernatant, the decrease in  $G'$  is attributable to diminished particle content in the probed region, consistent with partial sedimentation.



**Figure 4.** Linear viscoelastic regions of dispersion systems with a total surfactant content of 7 wt% on the first day and after 1 week of stability at 45 °C.

#### 4. Discussion

The present work systematically investigates how the molecular architecture and molecular weight of three secondary surfactants PGPR, HSA and CA modulate the dispersion and long-term stability of ZnO particles in CCT when PHSA ( $MW \approx 750\text{--}1200 \text{ g mol}^{-1}$ ) is employed as the primary dispersant. Holding the total surfactant concentration at 3 wt% while varying the

PHSA / secondary-surfactant ratio revealed that the optimum viscosity–dispersion balance depends strongly on both surfactant size and conformational flexibility. PGPR, whose branched polyricinoleate backbone and multi-hydroxylated polyglycerol segments closely resemble PHSA in molecular weight and functional group density, was able to wet and distribute ZnO effectively even in the absence of PHSA; viscosity remained low across all ratios and reached a minimum at PHSA / PGPR = 3. In contrast, smaller, less branched HSA and CA molecules with only a single hydroxyl polar head required the presence of PHSA to achieve acceptable dispersion. For HSA, the lowest viscosity occurred at PHSA / HSA = 1; at lower PHSA content (ratio 0.3) or with HSA alone, rapid viscosity increase prevented powder incorporation. The minimum viscosity was observed at PHSA / CA = 4.9 for cetyl alcohol.

Optical microscopy confirmed that these viscosity minima coincided with the most homogeneous particle distributions (Figure 1). Nonetheless, all dispersions formulated with 3 wt% total surfactant sedimented within one week at 45 °C, demonstrating that a critical surface coverage is required for durable steric hindrance and to achieve adequate viscosity to keep particles suspended. Increasing the overall surfactant level to 6–7 wt% enhanced stability but affected each system differently. In PGPR and HAS containing samples, the higher surfactant amount produced concurrent increases in viscosity and storage modulus ( $G'$ ), signalling the development of a more elastic interparticle network. However, the system included CA showed only a modest rise in  $G'$  despite viscosity growth, indicating that its linear chains thicken the continuous oil phase without forming an extensive elastic scaffold.

Linear-viscoelastic-region (LVER) measurements at 7 wt% total surfactant further discriminated among the systems. The CA formulation exhibited an early departure from linearity (strain  $\approx 0.1\%$ ) on the first day and, after one week at 45 °C, with a pronounced spike and collapse  $G'$  profile accompanied by visible sedimentation, which shows that the CA-induced viscosity increase is predominantly viscous rather than elastic and cannot prevent particle sedimentation. After one week at 45 °C, the  $G'$  values of the PGPR and CA dispersions decreased, whereas the HSA dispersion showed an increase. Because the rheological samples were taken from the undisturbed supernatant, the drop in  $G'$  for the PGPR and CA systems indicates that a portion of the ZnO had settled, leaving a particle content-reduced layer with lower elasticity. In contrast, the HSA formulation, whose smaller, more polar molecules raise the continuous phase viscosity and promote hydrogen bonding interactions with PHSA, retained more particles in suspension without sedimentation. Consequently, the resulting higher viscosity is related to an elevated  $G'$  after 1 week at 45 °C. Since sedimentation was observed in the CA system, long-term stability tests were not continued. Even though there was a decrease in the  $G'$  value in the PGPR system, the linear viscoelastic region appeared to be good in terms of stability. In the literature, the absence of change in the  $G'$  value has been associated with high stability [10]. Therefore, as a result of the 1-month 25 °C and 1-month 45 °C stability tests continued for PGPR and HA, sedimentation increased in PGPR and viscosity decreased compared to the viscosity of the first day. In the HA system, the viscosity measured at the end of 1 week at 45 °C increased approximately 3-fold compared to the first day viscosity, causing the system to become solid, i.e., its fluidity to deteriorate. Although reaching high viscosity is successful in preventing sedimentation, it is not a desired form since the dispersion is in solid form and it is difficult to include it in the systems where it will be used. Therefore, the 3-month stability tests were not continued.

These trends can be rationalised by considering interfacial assembly. PHSA and PGPR, owing to their comparable molecular weights, high branching and multiple hydroxyl functionalities,



co-adsorb onto ZnO surfaces and interpenetrate to create a thick, compliant, steric barrier that maintains low viscosity at high powder loadings and can provide an elastic network at higher concentrations. HSA, although much smaller, bears a hydroxyl group, which promotes hydrogen bonding with PHSA and ZnO. Although it can disperse particles even without PHSA due to its high molecular weight, a high amount of surfactant is needed to prevent sedimentation, but in this case, it causes a rapid increase in viscosity with time, especially as a result of 45 °C stabilization, causing loss of fluidity. CA lacks sufficient polar functionality and branching to adsorb strongly; instead, its linear C<sub>16</sub> chains self-assemble within CCT, raising the continuous-phase viscosity without furnishing an adsorbed elastic layer, so sedimentation persists despite higher surfactant amounts.

In summary, optimal dispersion and stability arise from a synergy between molecular weight, branching, and functional-group density. When PGPR is used in a system without PHSA, it shows a similar behavior to PHSA and allows the inclusion of high volumes of ZnO particles into the system, but despite the increased surfactant ratio, it does not create a strong steric effect around the particles and does not prevent sedimentation in the long term. Although the use of a small amount of CA in the system with PHSA improves the distribution of particles, it cannot provide the necessary steric effect to ensure long-term stabilization. The total amount of surfactant HSA effectively allows the viscosity increase and prevents the sedimentation of particles, but since it showed an excessive viscosity increase as a result of the 45 °C one-month stability and caused an undesirable solid form, i.e., deterioration of fluidity, it was not suitable for use with PHSA and CCT in high-rate ZnO loadings.

## 5. Conclusions

This study demonstrates that achieving long-term stability in dispersions containing high amounts of micron-sized ZnO depends not only on achieving a sufficiently high viscosity but also on providing sufficient steric stabilization through an elastic interface layer. Secondary surfactants whose molecular weight, branching, and functional-group density complement those of PHSA ( e.g., PGPR) can maintain low processing viscosity while promoting effective particle wetting. Smaller, less branched molecules such as HSA and CA require higher overall surfactant loadings; even then, CA affords only limited stability. These findings highlight the importance of the compatibility of carrier oil and surfactant pairs used for long-term stabilization in a nonaqueous dispersion system containing high levels of ZnO with homogeneous particle distribution, and the optimization of the total concentrations of the surfactants used and among themselves in the system.

For practical applications, a barrier must be created that provides a steric effect to prevent particles from settling and to maintain fluidity. Future work should combine rheology, interfacial spectroscopy, and long-term stability tests to elucidate how surfactant structure governs the formation, resiliency, and rearrangement of the adsorbed layers under shear, thermal stress and time. Such insights will be essential for designing dispersant systems long-term stability in high-solids content micron-sized ZnO formulations.

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