Understanding the Effects of Particle Size and Anisotropy on Microstructural and Rheological Properties of Suspoemulsions

Ergin, Nisa[1]; Sapan, Zuhal[2]; Kesim, M. Tumerkan[2*]; Suvaci, Ender[1,2]

[1]Materials Science and Engineering Dept., Eskisehir Technical University, 2 Eylul Kampusu, 26555, Eskisehir, Turkey

[2]Entekno Industrial, Technological and Nano Materials Corp., Eskisehir Organized Industrial Zone 7. St. No: 50, Odunpazari, 26110, Eskisehir, Turkey

*Corresponding Author: M. Tumerkan Kesim, tumerkan@enteknomaterials.com

Abstract

UV radiation can cause serious problems such as skin aging, cancer and suppresion of immune system. Traditionally used chemical/organic UV filters in sunscreens or cosmetics with UV protection raises health concerns due to potential allergic effects and risk of skin penetration. Mineral/physical metal oxide UV filters such as titanium dioxide and zinc oxide (ZnO) are safer alternatives to chemical filters. However, there can be difficulties in formulating emulsion systems with mineral filters because mineral filters are incorporated as an additional phase in the emulsion suspended in water and/or oil phases forming a suspoemulsion system. In this study, the changes in structural and physicochemical properties of O/W and W/O emulsions as a result of the interaction of emollients and emulsifiers with different mineral filters (size and morphology) were investigated. Anisotropic, micron-sized platelet-shaped particles in W/O emulsions exhibit higher zero shear viscosity compared to conventional spherical nano particles. Overall, the performance of inorganic filters in cosmetic formulations with UV protection depends on the complex interplay of formulation ingredients and processing conditions. UV protection performance is directly related to film forming ability of applied formulation and agglomeration state of inorganic filters which in turn determine the efficacy of the prepared emulsion. Chemically identical inorganic filters with different size and shape can exhibit vastly different properties in emulsion enabling the formulator to exploit morphological differences to design high performance and stable products with good sensory profile.

Keywords: inorganic UV filters; suspoemulsions; rheological properties; sunscreen

Introduction

UV radiation can cause mild to severe health problems including skin aging, cancer, suppresion of immune system, wrinkles and spots [1]. With the increase of such health concerns, consumers become more aware and demand safe cosmetic and personal care products to protect themselves from exposure to UV and even other types of radiation from sun (high energy visible light & infrared). As a result, not only the suncreen products contain actives that filter UV rays, but also daily and make up cosmetics commonly include UV filters. Conventionally used chemical/organic UV filters in sunscreens raises health concerns due to their potential of being allergenic, risk of skin penetration and to enter bloodstream [2, 3]. Mineral/inorganic UV filters such as titanium dioxide and zinc oxide are typically safer alternatives to chemical filters and offer high UV protection. Zinc Oxide (ZnO) is the only globally approved natural, mineral-based UV filter that provides broad spectrum protection against both UVA and UVB rays and it can offer great solutions as a cosmetic ingredient, whereas titanium dioxide (TiO_2) offers superior UVB protection and hence provides very high SPF per mass of powder used [4]. Compared to conventional organic filters, the inclusion of mineral filters in suncare products requires careful design of formulations to obtain stable and high performance products that are aesthetically pleasing and do not compromise the sensorial characteristics consumers demand.

Mostly used form of cosmetic and personal care products is emulsion systems. The ability to combine two (or more) liquid phases in a single product allows the manufacturer to further functionalize the product by using actives, deliverables, and their combinations that otherwise unavailable in a single-phase formulation. Additionally, the flexibility in designing of an emulsion system makes it possible to obtain formulations with wide range of physical (viscosity, skin feel, etc.) and chemical properties (composition, pH, etc.) suitable for all types of cosmetics and personal care products [5].

Suspoemulsions are specific type of emulsions that contain an additional solid phase suspended/dispersed in liquid phases of standard emulsions. They found use in industries such as paint, agriculture, cosmetics, and pharmaceuticals. Perhaps the ultimate challenge of formulating suspoemulsions is the stability and efficacy of the end product. Introduction of an additional solid phase in the emulsion, which is already thermodynamically unstable by its nature, adds even more complexicity by introducing new interfaces and surfaces. Particle agglomeration and particle-emulsifier interactions may lead to destabilization and/or diminished efficacy of the emulsion system [6]. On the other hand, there might be cases

where the inclusion of solid particles positively affect the overall stability. Pickering emulsions (or Pickering stabilization) are suspoemulsion systems where particles are decorated at the interphase interface and strenghten the continuous and dispersed liquid phase interface lowering the interfacial energy, similar to how emulsifiers function. With the use of inorganic particles such as silica, clay, chitosan, carbon black, etc., reduced use of surfactants or surfactant-free stable emulsions were reported [7]. There are various parameters affecting physical properties of Pickering emulsions such as concentration, hydrophilic/hydrophobic nature, size and shape anisotropy of particles. Nanowires, nanorods, flakes, cylinders, and other particles with various shapes and active surface areas were utilized to stabilize emulsions [7–10]. It was also reported that common organic emulsion components including rheology modifiers and waxes can also stabilize emulsions via Pickering effect [11, 12]. Crystallization of such components may lead to stabilization effect.

Considering all the above-mentioned aspects of suspoemulsions, designing UV shielding cosmetic formulations with mineral filters requires; (i) detailed understanding of interactions between inorganic particles and formulation components, and (ii) the final properties as a result of such interactions. There are key requirements when using mineral filters in formulations with UV protection from a consumer perspective:

- The formulation should not leave a white-cast (non-whitening),
- Formulation should ideally offer broad spectrum protection,
- Skin feel and rheology should be optimized for easy and comfortable application during rub-in and rub-out,
- High UV protection efficacy (high protection per unit mass of active used),
- Safe and non-toxic mineral filter.

Some of the listed characteristics can be linked to one another. For instance, high efficacy formulations typically use less amount of mineral filters to achieve the desired SPF/UVAPF which can also improve the skin feel and transparency due to lower amount of inorganics in the formulation. The key to address these characteristics is through understanding the complex interactions in suspoemulsions. There are various analytical characterization tools available to a cosmetic scientist to understand the effect of formulation ingredients and

processing paramaters on microstructural, physicochemical and rheological properties of cosmetic and personal care emulsions. The distribution of particles and droplets can be observed with an optical microscope to provide information about the stability, film-forming effectiveness, droplet distrubiton and coalescence of the emulsion system. Tensiometers can be used to investigate interfacial tension of liquid-liquid and solid-liquid interfaces and gives crucial compementary information about the stability of the system [13]. On the other hand, rheological measurements offer a plethora of information. Observing viscosity changes under shear provide information about the flow behavior of the emulsion. Osicallation tests such as amplitude variation, frequency variation, time dependence and temperature dependence provide information about storage, thermal and transport stability, applicability, sensorial aspects, etc. [14–16]. Combined with spectroscopic techniques and typical measurements of emulsion properties (pH, conductivity, surface charge), it is possible to understand processing, structure and property relationship in cosmetic and personal care emulsions. Ultimately, the cosmetic scientist can use these information to maximize the performance of the product depending on the type of application.

The main objective of the current study is to understand how inclusion of different mineral filters with different size and particle morphology in suncare formulations affect the structural characteristics and UV protection performance. Micron-sized anisotropic ZnO platelets and nano-sized isotropic TiO_2 particles are utilized in different model emulsion systems (O/W and W/O). It was found that Pickering type stabilization can be observed when the external/continuous phase is water. Compared to emulsions without mineral filters, the droplet size in suspoemulsions were decreased and some of the particles were located at water-oil interface. On the other hand, ZnO particles dispersed homogeneously in the oil phase away from the oil-water interface in W/O emulsions. Results suggest that particle anisotropy and size are cruical parameters to affect suspoemulsion characteristics and detailed rheological analyses are needed to elucidate underlying interaction mechanisms.

Materials and Methods

Powder Characterization

ZnO and TiO_2 are the two types of UV filters used herein. ZnO particles employed are micron-sized anisotropic platelets (obtained from Entekno Materials). On the other hand, TiO_2 powders used in this study is obtained from a local manufacturer and mostly contains sub-micron to nano sphere-like isotropic particles. Structural analyses were carried out using a Bruker D2 Phaser X-ray diffractometer under 30 kV of operating voltage and 10 mA of current. Tests were performed in 2θ range of 10°-80° with a scanning rate of 10°/min using Cu $K\alpha_1$ radiation. Particle size of ZnO and TiO_2 powders were obtained using laser scattering and dynamic light scattering methods, respectively. Particle size of ZnO platelets were measured using a Horiba LA960 laser scattering system. Average of 5 measurements were obtained and equivalent spherical diameters and particle size distribution were reported. On the other hand, smaller TiO_2 particles were analysed using a Malvern Zeta Sizer Nano-ZS. Total of 6 runs were recorded and the results were plotted. Note that dynamic light scattering is much more suitable for size measurements of nano particles compared to light scattering, and it was the preferred technique for characterization of TiO_2 particles.

Formulation Preparation and Characterization

The physical, structural and UV filtering characteristics of formulations with mineral filters were tested in standard W/O and O/W emulsion systems. The formulation ingredients of both type of emulsions are indicated in **Table *1*** & **Table *2***. The O/W sunscreen formulation given in **Table *1*** includes 8 wt% mineral filter, whereas W/O formulation (**Table *2***) contains 20 wt% powder. The preparation procedures of O/W emulsions is as follows: Phase A is heated to 80°C. Meanwhile, xanthan gum is dissolved in glycerin and heated to 80°C by adding deionized water. Phase C is added to Phase A slowly and mixed for 3 minutes at 2000 rpm with a three-blade propeller stirrer. Then, Phase A+C is added slowly into Phase B and the product is homogenized at 3000 rpm for 30 min. Stirring was continued using an anchor-type propeller until the temperature of the cream reached 30°C before terminating the process.

For W/O emulsions, Phase A and B were heated in separate beakers to 80°C. Phase B then added to Phase A under stirring using a three-blade propeller for 10 minutes at 2000 rpm.

The mixtre was homogenized at 3000 rpm for 5 minutes. Phase C was slowly added into the A-B mixture and homogenized at 3000 rpm vigorously for 20 minutes. Stirring was continued using an anchored-type propeller until the temperature drops down to 40°C before adding Phase D which was also pre-heated to 40°C. The process was terminated when temperature reached to 30°C.

Table 1. Formulation ingredients and their respective phases for the O/W emulsion system.

INCI Name	Amount (wt%)	Phase
Cetearyl Alcohol	6	A
Butyrospermum Parkii (Shea) Butter	2	
PEG-30 Dipolyhydroxystearate	2	
Glyceryl Stearate (and) Ceteareth-20 (and) Ceteareth-12 (and) Cetearyl Alcohol (and) Cetyl Palmitate	3	
C12-15 Alkyl Benzoate	10	
Zinc Oxide/Titanium dioxide	8	C
Xanthan Gum	0,2	B
Glycerin	5	
Deionized Water	63,8	

In-vitro UV protection performance and visible light transparency characteristics of emulsions were evaluated on polymethylmethacrylate plates (Helioscreen HD6) using a UV-VIS-NIR spectrophotometer (Shimadzu UV-3600 plus) with a double beam optical system following a procedure adapted from Colipa guidelines [17]. NPC-603A multi-purpose large sample compartment attachment with a built-in integrating sphere was used for in-vitro measurements. 1.3 mg/cm^2 cream was rubbed on the PMMA plate and 9 measurements from each plate were obtained between 260-750 nm wavelength. Total of 3 different plates were

used for analyses. SPF, coefficient of variation (CoV), UVAPF, UVA/UVB, and critical wavelength (CW) values were obtained from the measured transmittance curves using a manufacturer supplied built-in software (UVProbe 2.61). Optical images of formulations were obtained with a Zeiss-Primotech microscope. 0.01 gr sample were transferred in between double glass slides and a slight pressure is applied by hand to even out the sample. Images were taken with fluorescent and polarized light. Viscosity measurements were taken with an Anton Paar-MCR 102 Rheometer using a cone-plate geometry and a measuring distance of 0.5 mm.

Table 2. Formulation ingredients and their respective phases for the O/W emulsion system.

INCI Name	Amount (wt%)	Phase
Olea Europaea (Olive) Fruit Oil	15	A
Butyrospermum Parkii (Shea) Butter	5	
PEG-30 Dipolyhydroxystearate	3	
Cera Alba	1	
Cetearyl Alcohol	1	
Polyglyceryl-3 Diisostearate	4	
Polyhydroxystearic Acid	3	
Panthenol	2	D
Aloe barbadensis leaf juice	2	
Tocopheryl Acetate	2	
Zinc Oxide/Titanium Dioxide	20	C
Xanthan Gum	0,1	B
Glycerin	2	
Deionized Water	39,9	

Results

The XRD results and particle size data of ZnO and TiO_2 powders used in this study are presented in **Figure *1***. X-ray diffractograms revealed that zinc oxide and titanium dioxide powders exhibit phase pure hexagonal wurtzite structure and rutile phase, respectively. No other impurity phases and/or different structural symmetry were seen in neither of the results. The average platelet size of zinc oxide powders is 4.07 µm, whereas the average particle diameter of sub-micron TiO_2 powders is slightly above 200nm. The size distrubution of TiO_2 powders also showed that there were nano-sized particles (80 nm to 100nm) also present in the powder batch.

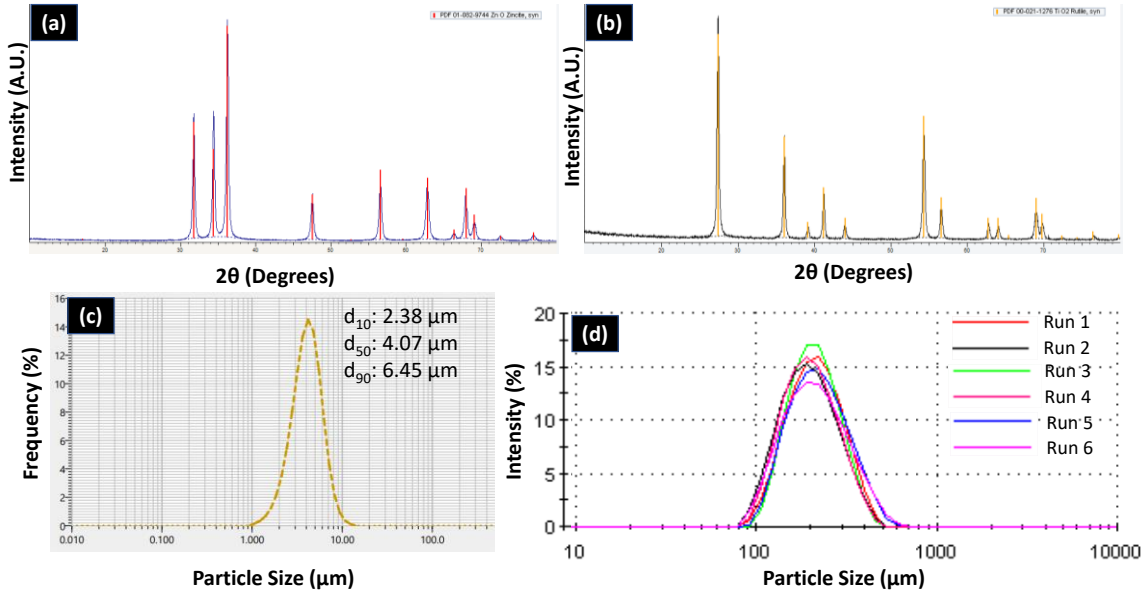

Figure 1. XRD results of (a) ZnO and (b) TiO_2 and particle size distribution data of (c) ZnO and (d) TiO_2 powders.

In-vitro UV protection performance and visible light transparency of emulsions are shown in **Table *3***. Formulations without mineral filters (base) were also included for comparison. It can be seen from **Table *3*** that inclusion of TiO_2 and ZnO to base formulations increases the SPF and UVAPF values as expected. The protection performance of O/W formulations were poorer compared to that of W/O formulations due to water being the external phase. The evaporation of water during application somewhat hinders the formation of a perfect film for UV protection and hence lowers the efficacy. Note that the SPF value of W/O emulsion with TiO_2 particles was not included for comparison in **Table *3*** due to unrealistically high

obtained values. The spectrum indeed showed that the absorbance reached spectrophotometer's maximum absorbance limit and hence not reliable.

Table 3. In-vitro UV protection characteristics and visible light transparency of O/W and W/O emulsions w/ and w/out mineral filters.

Sample	SPF	CoV (%)	UVAPF	UVA/UVB	Critical Wavelength (nm)	%T @440 nm	%T @550 nm
O/W Base	1,09	1,38	1,06	0,97	371	99,12	99,85
O/W TiO_2 (8wt%)	9,97	10,11	6,20	0,82	381	50,15	61,48
O/W ZnO (8wt%)	4,99	3,16	4,13	0,93	374	78,24	86,76
W/O Base	1,04	3,54	0,99	0,94	302	99,14	99,88
W/O ZnO (20wt%)	41,44	13,02	20,74	0,78	374	60,59	74,26

Figure *2* shows the zero-shear and sheared ($100s^{-1}$) viscosity of W/O and O/W emulsions with and without inclusion of ZnO and TiO_2. The zero-shear viscosity of O/W formulation with TiO_2 is almost three times larger than that of emulsion with ZnO. Under shear, the viscosity values of both emulsions were almost identical. On the other hand, the findings for W/O emulsions were quite interesting. The viscosity at rest for formulation with ZnO was almost an order of magnitude larger than that of formulation with TiO_2 (**Figure *2*c**). Both formulations exhibited viscosities larger than base formulations. In other words, the viscosity values increase with the addition of powders. The flow behavior significantly changes when samples are sheared (**Figure *2*d**). Viscosity of emulsion with TiO_2 particles drops to values close to 6000 mPa.s due to shear thinning. This value is almost twice as much as the viscosity of emulsion with ZnO which means that the shear thinning effect is much more pronounced for emulsion with ZnO due to the larger magnitude of change before and after shearing.

The representative optical microscope images of emulsions obtained under fluorescent light is shown in **Figure *3***. The oil and water droplets can be seen in all images. The regions with

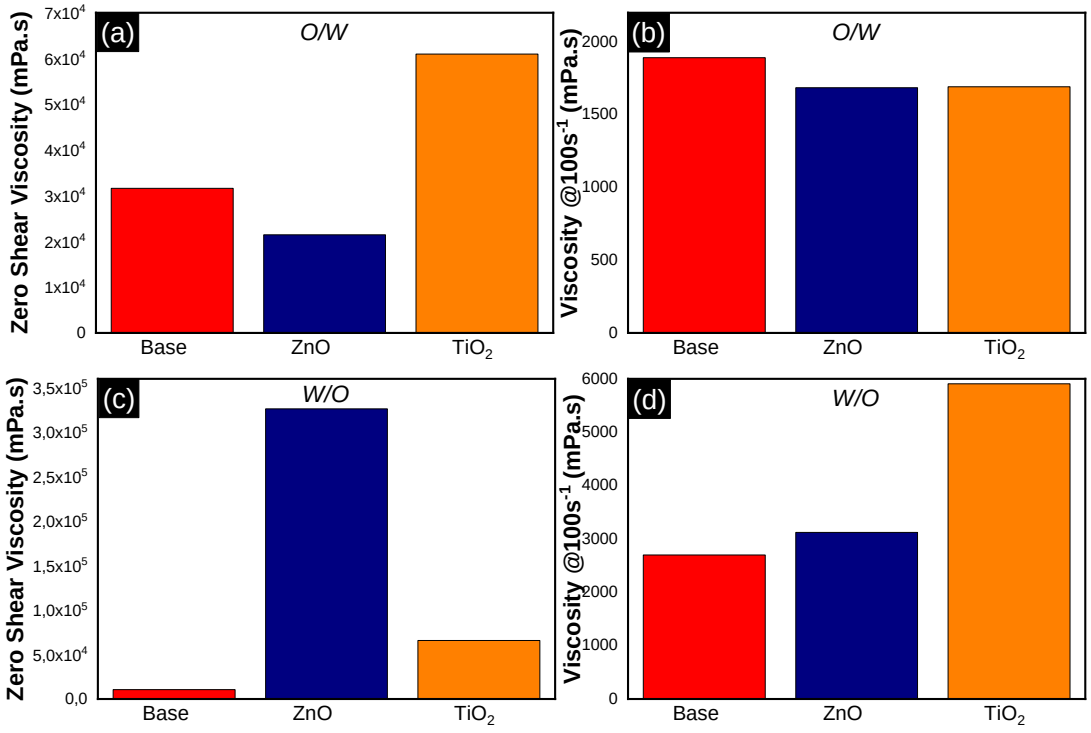

Figure 2. Viscosity of O/W formulations w/ and w/out mineral filters (a) at zero shear and (b) at $100s^{-1}$ shear. Viscosity of W/O formulations (c) at zero shear and (d) at $100s^{-1}$ shear.

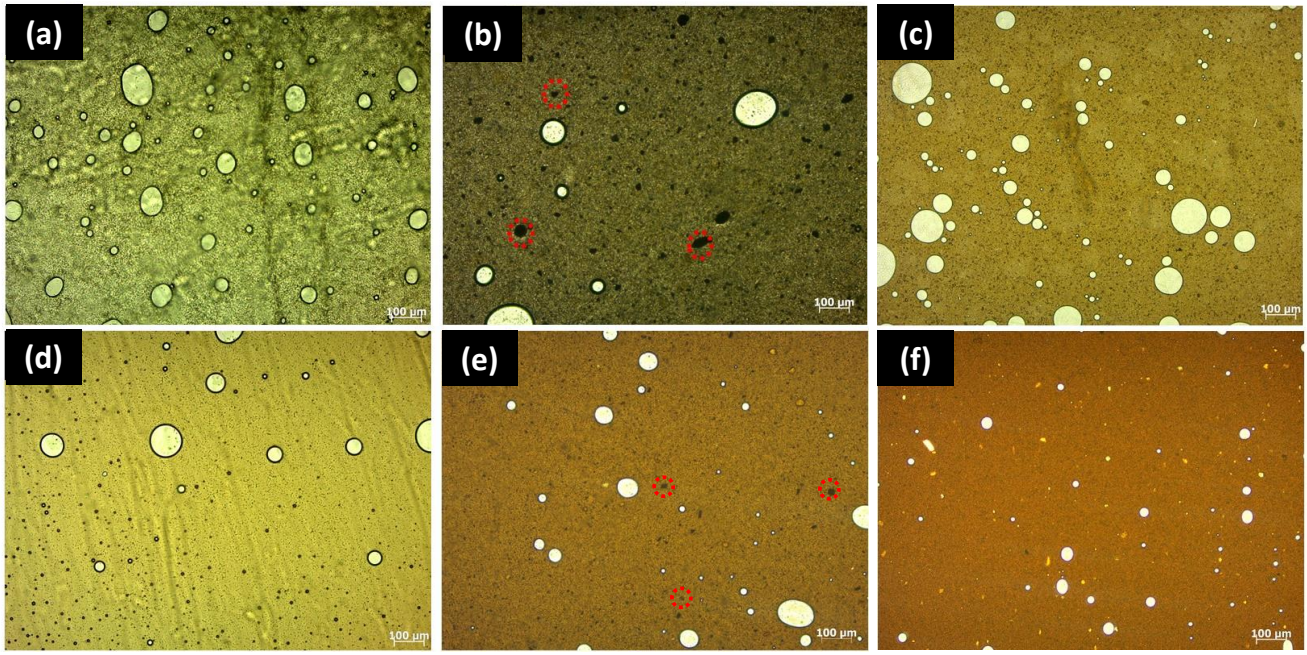

Figure 3. Representative optical images of O/W formulations (a) without powders, (b) with ZnO, and (c) with TiO_2. Representative optical images of W/O formulations (d) without powders, (e) with ZnO, and (f) with TiO_2.

dark contrast in formulations with ZnO represents ZnO particles. The reason such features are absent in images of emulsions with TiO_2 is that resolution of the optical microscope is not high enough to distinguish nano-sized features which is one of the main limitations of optical microscope imaging of suncare formulations with nano UV filters. Note that the micron sized ZnO platelets in O/W emulsions are located in the continuous water phase. The droplet diameters calculated from the optical microscope images of emulsions with and without mineral filters are plotted in **Figure *4***. The base O/W formulation exhibited the highest mean droplet size and standard deviation (75.28±40.72) among all samples. The incorporation of mineral filters in O/W emulsions decreases the mean droplet diameters and their standard deviation which is more pronounced in sample with TiO_2 (41.14±29.54). In contrast, base W/O formulation showed the lowest droplet diameter. Inclusion of powders increased the droplet diameter which is especially notable for emulsion with ZnO.

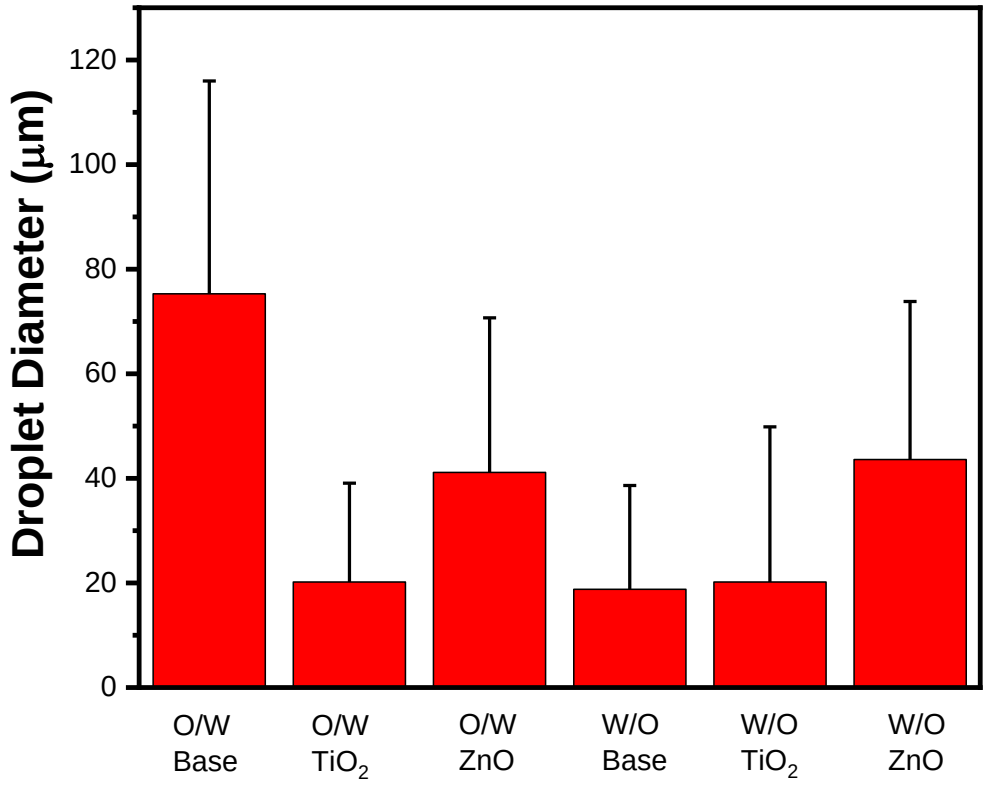

Figure 4. Droplet diameters of emulsions w/ and w/out mineral filters calculated from representative optical microscope images.

Optical images of O/W and W/O suspoemulsions under polarized light are shown in ***Figure 5***. Black contrast regions are dispersed phase droplets, whereas the regions with white contrast are ZnO particles. Compared to optical micrographs in **Figure *3*b&e**, polarized light

imaging enables one to distinguish between particles and droplets much more clearly with better contrast on the same image. From ***Figure 5***, ZnO platelets in O/W suspoemulsions were slightly agglomerated and located in the continuous water phase and at the water-oil interface. On the contrary, particles are dispersed homogeneously in the external oil phase in W/O suspoemulsions. Also note that there were almost no particles present at the water-oil interface. **Figure *6*** shows the mean size of ZnO particles in O/W and W/O suspoemulsions obtained from optical microscope images. The particle size of ZnO in O/W and W/O emulsions are 26.34±13.02 and 15±10.90, respectively.

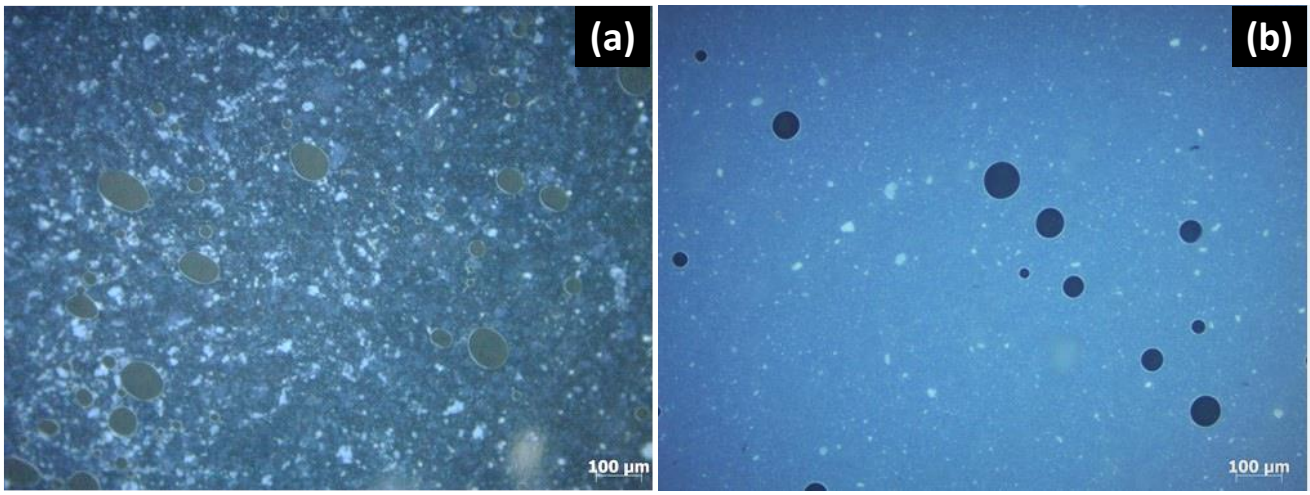

Figure 5. Optical images of (a) O/W and (b) W/O suspoemulsions with ZnO obtained under polarized light. Black contrast regions are dispersed phase droplets, whereas white contrast regions are ZnO particles.

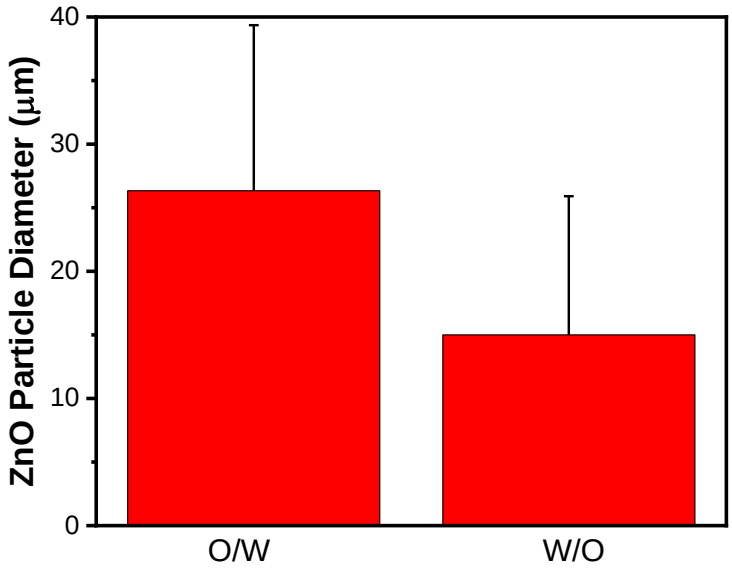

Figure 6. ZnO particle size in O/W and W/O suspoemulsions obtained from optical microscope images.

Discussion

There is a very significant difference between the rheological profiles of different mineral filters when used in the same formulation. Although the UV filters investigated here are chemically different, the most notable difference affecting rheology seem to be their particle morphology. The most striking difference in viscosity values and degree of shear thinning were observed in W/O formulations with ZnO and TiO_2 (**Figure *2*c&d**). The platelet shaped micron sized ZnO exhibited a higher resistance to flow at rest, whereas under $100s^{-1}$ shear, it flows even more easier than emulsion with TiO_2. It is known that anisotropic particles exhibit high zero-shear viscosity compared to isotropic, sphere-like particles. When both are deformed under shear, the viscosity of elongated particles would be lower than isotropic particles [18]. At rest, elongated ZnO platelets were randomly oriented in the emulsion system probably forming a dense network around the liquid phases. Considering that ZnO platelets' mean equivalent spherical diameter was 4.07 μm from laser scattering (**Figure *1*c**), and mean platelet size obtained in emulsions from optical micrographs was 15 μm, their network forming/interlocking effect is expected to be much greater compared to a nano sized spherical particle. Under shear, the platelets align themselves towards the flow direction and provide more efficient packing and easier flow compared to spherical particles, and hence provides a larger extent of shear thinning. This observation can also be critical when anisotropic particles are employed as UV filters in suncare formulations. High efficicent and easy packing under shear implies that film formation during rub-in is easier and should give a good skin feel. In addition, since the packing is efficient, the amount of UV filters required per unit mass is expected to be lower.

There is a different trend in the viscosity profiles of O/W formulations (**Figure *2*a&b**) prepared using the same filters. The viscosity of TiO_2 suspoemulsions at rest was three times greater than that of ZnO suspoemulsions. When both emulsions were sheared, their viscosity values became almost identical. As mentioned before, there seemed to be a slight agglomeration of ZnO in O/W emulsions and the mean particle diameter was 26.34±13.02 μm, from **Figure *6***. Note that the oil droplet size of the same emulsion was found to be ≈40 μm (**Figure *4***). Although ZnO platelets were dispersed in the oil phase during processing, they were located either in the continuous water phase or at the oil-water interface (**Figure**

5a). It is known that ZnO is hydrophilic and tends to migrate towards the water phase over time [19]. Moreover, since the platelet size was somewhat close to the droplet diameter, there is more driving force for platelets to migrate to water phase in the emulsion during processing. On the other hand, it was not possible to observe TiO_2 particles with an optical microscope. They were also added into the oil phase during emulsification. Considering that their mean size is around 200 nm, one would expect the internal oil phase to accommodate TiO_2 particles. One of the reasons why the viscosity at rest of TiO_2 suspoemulsions was high can be due to increased density of oil droplets compared to ZnO suspoemulsions in which internal oil phase was free of ZnO particles. Moreover, from **Figure *4***, mean droplet size of TiO_2 suspoemulsion was ≈20μm and smallest among the measured values. The decrease in droplet diameter is associated with an increase in the viscosity of the emulsions [20]. This can also be the other reason of high zero-shear viscosity found in this study.

Pickering type stabilization can be observed from the optical images given in **Figure 5** and from the calculated droplet diameters in **Figure *4*** for O/W suspoemulsions. The rather large mean dropet diameter and standard deviation for the base emulsions without particles decreased with inclusion of mineral filters for suspoemulsions. Systematic decrease in droplet size of O/W emulsions upon introduction of increasing amount of nanoparticles were reported previously [21]. ZnO particles at the oil-water interface seemed to help stabilize the suspensions and shrank the droplet diameters probably making them more resistant to coalescense. Although TiO_2 particles cannot be observed with the microscope in the current study, droplet diameters of TiO_2-O/W suspoemulsions got even smaller compared to that of ZnO suspoemulsions suggesting that Pickering stabilization can even be more pronounced in this case. Pickering-type stabilization using colloidal TiO_2 particles were also reported previously [22]. Compared to micron sized platelets, small spherical particles can be more effectively decorated on the droplet surface providing a better stabilization. The effective contact area of such particles is expected to be larger. Another interesting outcome of the results of suspoemulsions with ZnO platelets is that the formulation shown in **Table *1*** is stable over 2 years at room temperature. Initially, one might suspect that since ZnO is in the water phase and there was slight agglomeration, the stability of the formulation can be at risk. We believe that there is an interplay between Pickering stabilization in favor of stability and

ZnO-water interaction which is detrimental for stability due to potential solubility of ZnO in water and agglomeration. More detailed analyses are required to elucidate stabilization mechanisms and long-term stability of different O/W suspoemulsions with ZnO particles.

On the other hand, no findings suggesting Pickering type stabilization were observed in W/O suspoemulsions. There is a very small increase in mean droplet size of TiO_2 suspoemulsions compared to base formulations, whereas inclusion of ZnO in suspoemulsions increases the mean droplet diameters. The optical images of ZnO suspoemulsions clearly show that ZnO platelets are homogeneously dispersed in the external oil phase and no particles were found at the water-oil interface. It is believed that TiO_2 particles were also homogeneously dispersed in the oil phase as well. Note that the W/O formulation (**Table *2***) includes a specific dispersant (polyhydroxystearic acid; PHSA) in the oil phase that is quite effective in dispersing ZnO and TiO_2. PHSA might have helped preventing metal oxide surfaces to interact with emulsifiers at the water-oil interface and forced the particles to stay in the oil phase. We believe that this can be an important factor to achieve high efficacy and UV protection in W/O formulations. As mentioned before, film forming ability is expected to be better when the external phase is oil (which can also be seen from the UV protection performance shown in **Table *3***). A good agglomerate-free particle dispersion in the external oil phase implies good coverage upon cream application on skin and consequently high UV protection performance.

Conclusion

It was shown that the rheology, structural characteristics, and final UV protection performance are highly dependent on the type and morphology of UV filters, as well as the type of emulsion system in the final product. Highly anisotropic micron sized platelets in W/O formulations exhibited higher viscosities at rest compared to that of emulsions with nano to sub-micron sized particles. Upon shearing, anisotropic particles align towards the flow direction resulting in reduction of high shear viscosity and became even lower than the viscosity of emulsions with isotropic particles. The larger extent of shear thinning of platelets can be exploited to obtain better skin feel, transparency, high coverage, and UV protection.

On the other hand, Pickering-type stabilization was evident for O/W suspoemulsions probably increasing long-term stability.

Acknowledgments

The authors would like to thank the Scientific and Technological Research Council of Turkey (TUBITAK) for supporting this work under the grant number of 119C163. In addition, they would like to thank Entekno Materials Corp. for supplying platelet shaped ZnO powders. They also thank Eskisehir Technical University Scientific Projects Commission for supporting this work under the grant number of 22ADP057.

Conflict of Interest Statement: None

References.

1. Wang SQ, Balagula Y, Osterwalder U (2010) Photoprotection: a Review of the Current and Future Technologies. Dermatol Ther 23:31–47.
2. Morabito K, Shapley NC, Steeley KG, Tripathi A (2011) Review of sunscreen and the emergence of non-conventional absorbers and their applications in ultraviolet protection. Int J Cosmet Sci 33:385–390.
3. Giokas DL, Salvador A, Chisvert A (2007) UV filters: From sunscreens to human body and the environment. TrAC - Trends Anal Chem 26:360–374.
4. Osmond MJ, Mccall MJ (2010) Zinc oxide nanoparticles in modern sunscreens: An analysis of potential exposure and hazard. Nanotoxicology 4:15–41.
5. Lodén M (2005) The clinical benefit of moisturizers. J Eur Acad Dermatology Venereol 19:672–688.
6. Hewitt J (2013) Formulating with Nanotechnology in Skin Care Opportunities and Challenges. In: Nasir A, Friedman A, Wang S (eds) Nanotechnology in Dermatology. Springer New York, New York, NY, pp 1–8
7. Yang Y, Fang Z, Chen X, et al (2017) An Overview of Pickering Emulsions: Solid-Particle Materials, Classification, Morphology, and Applications. Front Pharmacol 8:287.
8. He J, Zhang Q, Gupta S, et al (2007) Drying droplets: A window into the behavior of nanorods at interfaces. Small 3:1214–1217. https://doi.org/10.1002/smll.200700055

9. Yan H, Zhao B, Long Y, et al (2015) New pickering emulsions stabilized by silica nanowires. Colloids Surfaces A Physicochem Eng Asp 482:639–646.
10. Venkataramani D, Tsulaia A, Amin S (2020) Fundamentals and applications of particle stabilized emulsions in cosmetic formulations. Adv Colloid Interface Sci 283:102234.
11. Haj-shafiei S, Ghosh S, Rousseau D (2013) Kinetic stability and rheology of wax-stabilized water-in-oil emulsions at different water cuts. J Colloid Interface Sci 410:11–20.
12. Patel AR, Babaahmadi M, Lesaffer A, Dewettinck K (2015) Rheological Profiling of Organogels Prepared at Critical Gelling Concentrations of Natural Waxes in a Triacylglycerol Solvent. J Agric Food Chem 63:4862–4869.
13. Sharma T, Kumar GS, Chon BH, Sangwai JS (2015) Thermal stability of oil-in-water Pickering emulsion in the presence of nanoparticle, surfactant, and polymer. J Ind Eng Chem 22:324–334.
14. Wza X R.Brummer_Rheology Essentials of cosmetics and food emulsions
15. Yao ML, Patel JC (2001) Rheological characterization of body lotions. Appl Rheol 11:83–88.
16. Kwak M, Ahn H, Song K (2015) Rheological investigation of body cream and body lotion in actual application conditions. 27:241–251. https://doi.org/10.1007/s13367-015-0024-x
17. Moyal D, Alard V, Bertin C, et al (2013) The revised COLIPA in vitro UVA method. Int J Cosmet Sci 35:35–40. https://doi.org/10.1111/j.1468-2494.2012.00748.x
18. Hill A, Carrington S (2010) Understanding the Links Between Rheology and Particle Parameters. Surf Coatings Int 93:1–4
19. Anderson MW, Hewitt JP, Spruce SR (1997) Broad-Spectrum Physical Sunscreens: TItanium Dioxide and Zinc Oxide. In: Lowe NJ, Shaath NA, Pathak MA (eds) Sunscreens: Development, Evaluation and Regulatory Aspects, Second Ed. Marcel Dekker Inc., New York
20. Pal R (1996) Effect of Droplet Size on the Rheology of Emulsions. AIChE J 42:3181–3190

21. Zeng M, Li X, Zhang Y, et al (2020) Tailoring the droplet size of Pickering emulsions by PISA synthesized polymeric nanoparticles. Polymer (Guildf) 206:122853.
22. Wang J, Yu M, Yang C (2019) Colloidal TiO2 nanoparticles with near-neutral wettability: An efficient Pickering emulsifier. Colloids Surfaces A 570:224–232.