NOVEL FORMULATION TECHNIQUE FOR BI-PHASE SYSTEMS FOR PRODUCT CUSTOMIZATION

Chen, Ye[1]; Yeung, Joey[1]; Yao, Ge[1]; Qu, Xianghua[2]; **Liu, Xin[2*]**

[1] Lubrizol Life Science, Lubrizol Southeast Asia (Pte) Ltd, Singapore.

[2] Lubrizol Life Science, Lubrizol Management (Shanghai) Co. Ltd, Shanghai, China.

* Liu, Xin, 6F, No.3. The New Bund World Trade Centre, Lane 227 Dong Yu Road, Pudong New Area, Shanghai, 200126, China. +86 21 3866 0504, xin.liu@lubrizol.com

Abstract

Background: Bi-phase products are one of the highly demanded product categories in skin care because of their unique and attractive appearances. They are an ideal product format for customization, engaging users and offering specific needs without conventional homogeneity requirements. A formulation technique that gives a special appearance of two different phases with a great variable tolerance, generates a universal interest among formulators.

Methods: Polyurethane-62 was tested as the stabilizer for such a bi-phase system. Formulation variables, including polymer concentration, emollient type and use level, and water phase properties, were investigated in terms of their influence on product appearance, separation profile, and storage stability. A simple formulation process was established to test the robustness and flexibility of the system.

Results: A three-step formulation process was set up and validated by different formulation variables and process parameters. The clarity of the lower water phase is mainly dependent on the use level of Polyurethane-62. A higher use level of the polymer displays a slower separation profile, and the stronger the electrolyte strength, the faster the separation. pH of the water phase did not show a significant impact on the phase separation profile.

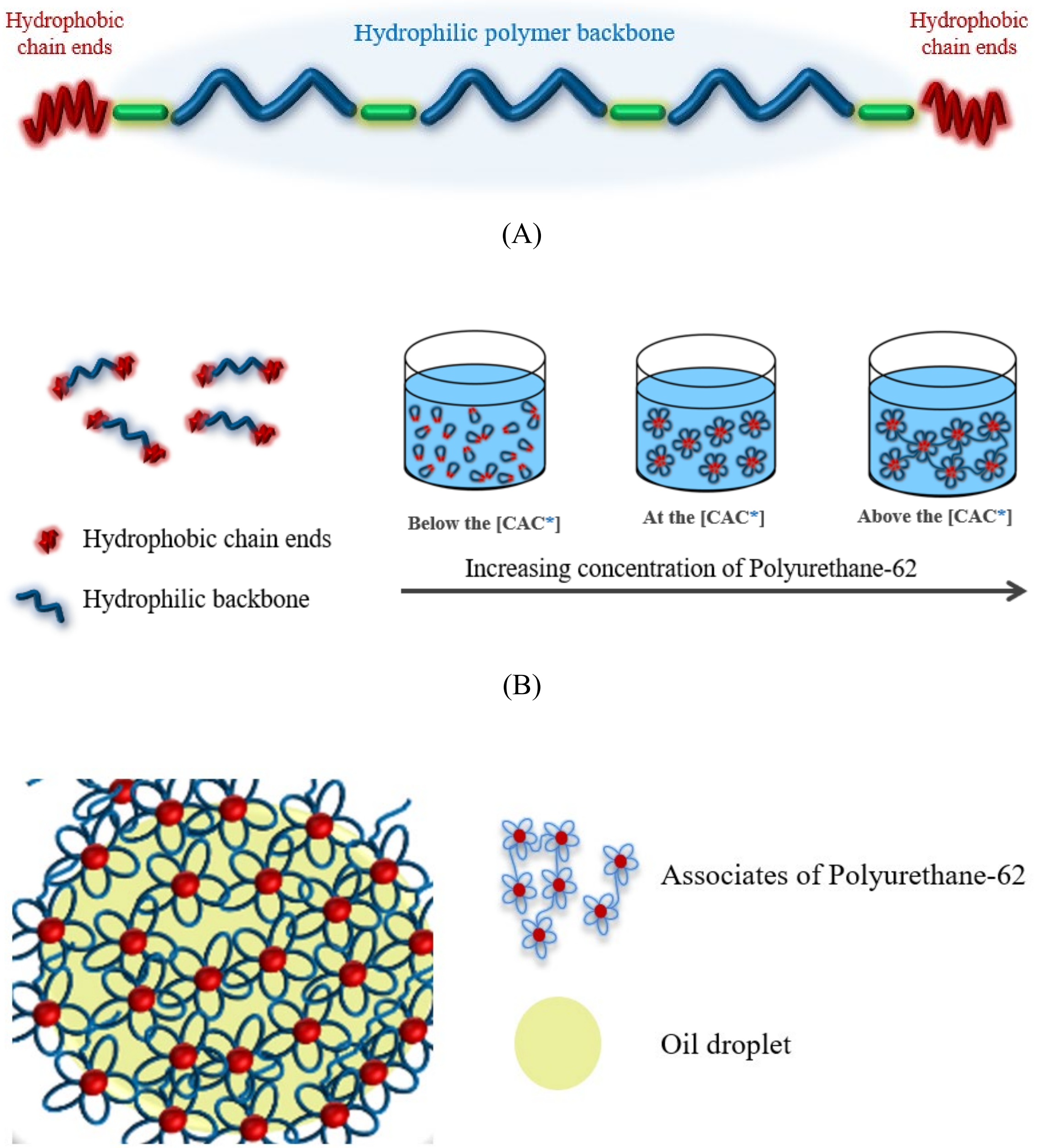
Conclusion: Polyurethane-62 provides an adequate emulsification capability and is applicable to a wide range of oil components. Such bi-phase products can be customized in terms of colour, contrast of appearance, and active components. Furthermore, Polyurethane-62 offers a soft and powdery sensory. Such a technique is simple and straightforward enough to empower product customization or even personalization by consumers themselves.

Keywords: Bi-phase; Polyurethane; Emulsion; Creaming; Customization; Skin care

Introduction.

With more and more intensified market competition and increased difficulty in technological differentiation, there has been a rising demand for customizable skin care products with innovative formats. Customization in skin care is an effective approach to offering skin care solutions designed for consumers to address various needs. Furthermore, greater diversity and inclusivity within skin care are gaining popularity, and customization can be a useful attempt to align the values of a product with that of an individual [1]. Bi-phase products are one of the most suitable types of products to do customization because of consumers' high tolerance towards their instability. A typical bi-phase skin care product consists of two immiscible phases–an oil phase and a water phase. Colour dyes can be added to either or both phases to make the whole pack more appealing. Such conventional biphasic products often appear as two transparent layers. It is difficult to get a relatively stable bi-phase product with one phase opaque (cream layer) and the other crystal clear due to the difficulty in controlling the emulsification and stabilizing floccules or creaming phase against a complete oil phase separation. It is of even greater interest if such a format is customizable.

A novel hydrophobically-modified ethylene-oxide urethane rheology modifier (HEUR), Polyurethane-62 (PU-62), has been developed to address such unmet needs (**Figure 1A**). Polyurethane-62 is amphiphilic, and it can form a floret network when above its critical aggregation concentration (CAC) (**Figure 1B**). When used below its CAC, hydrophobic chain ends associate and hydrophilic backbone forms loops in an aqueous phase. When in contact with oil droplets, the hydrophobic end groups of PU-62 polymer align on the oil droplet surface with the loop formed by hydrophilic backbone in the water phase. Such associates offer very limited yet sufficient "stabilization" power to hold oil droplets on top of a clear water phase. Moreover, the polyurethane, without compromising the clarity of the lower water phase, provides an adequate stabilization capability under various conditions, making such a system applicable to a customizable product.



(A)

(B)

(C)

Figure 1. (A) A schematic diagram of the polymer structure of Polyurethane-62. (B) Associative behaviour of Polyurethane-62 in an aqueous solution. (CAC*: Critical Aggregation Concentration) (C) A dynamic network formed by Polyurethane-62 associates on an oil droplet.

The mechanism of such emulsion/solution bi-phase preparation is very different from the conventional oil/water bi-phase formulation. The conventional oil/water bi-phase product is using the liquid-liquid immiscibility—the force of attraction within the substances is greater than the force of attraction between two substances. Phase separation behaviour of thermodynamically immiscible substances has been discussed in many literatures [2-4]. A "stable" emulsion/solution-based bi-phase system is new to the industry with limited understanding of such phase behaviour and relative stability. Although such creaming behaviour is not preferred in many cases, such long-term (month and years) stability of the cream layer (visual non-uniformity) offers a novel texture in skin care field, attractive to consumers. Researchers have concluded that creaming behaviour can be attributed to the spinodal decomposition of the system [5].

Although the creaming process has been intensively researched in the food industry, it is new to the personal care industry and there are still progresses to be made in understanding the influence of processing conditions to make it an attractive type of products.

In this study, a Polyurethane-62-based bi-phase platform was evaluated in depth to investigate its potential for customization to a wide extent. A simple formulation process was established to test the robustness and flexibility of the system. An example of ingredient level customization was illustrated with Polyurethan-62 as the stabilizer and oil components and actives tailored to a few different contexts reflecting consumer needs.

Materials and Methods.

Material

Polyurethane-62 was supplied as a combination (AF-6) of Polyurethane-62 and Trideth-6. Ingredients as Isopropyl Isostearate (318), Lauryl Lactate (LL), Triolein (Algapur), Cocoyl Adipic Acid/Trimethylolpropane Copolymer (CATC), Caprylic/Capric Triglyceride (CCT), Dimethicone, Glycerin, Methyl Gluceth-20 (E-20), Sodium Chloride, Disodium EDTA, Ethylhexyl Glycerin, and Phenoxyethanol were used as supply. Neutralizers, sodium hydroxide and citric acid, were used in dilutions.

Method

Preparation of emulsion samples

The water phase was first prepared by stirring at 400-500 rpm until homogenous and the oil phase was added into the water phase under stirring. The additive phase was added at last.

Table 1. Formulation tables for the evaluation of different formulation variables: concentration of PU-62 (A), concentration of oil phase (B), electrolyte strength (C), pH of the water phase (D), selection of oil components (E), customized bi-phase prototypes (F).

(A)	Ingredient	Weight %
Water phase	Deionized water	Q.S. to 100
	AF-6	0.20/0.30/0.50/0.80/1.00
	Glycerin	3.00
	E-20	2.00
	Disodium EDTA	0.05
	PEHG	0.60
Oil phase	318	20.00
Additive phase	Sodium Chloride	1.00

(B)	Ingredient	Weight %
Water phase	Deionized water	Q.S. to 100
	AF-6	0.20
	Glycerin	3.00
	E-20	2.00
	Disodium EDTA	0.05
	PEHG	0.60
Oil phase	318	5/10/20/30/40/50/60
Additive phase	Sodium Chloride	1.00

(C)	Ingredient	Weight %
Water phase	Deionized water	Q.S. to 100
	AF-6	0.20
	Glycerin	3.00
	E-20	2.00
	Disodium EDTA	0.05
	PEHG	0.60
Oil phase	318	20.00

Additive phase	Sodium Chloride	1/2/3/4/5

(D)	Ingredient	Weight %
Water phase	Deionized water	Q.S. to 100
	AF-6	0.20
	Glycerin	3.00
	E-20	2.00
	Disodium EDTA	0.05
	PEHG	0.60
Oil phase	318	20.00
Additive phase	Sodium Chloride	1.00
	Sodium Hydroxide	pH 6/6.5/7
	Citric Acid	pH 4/4.5/5

(E)	Ingredient	Weight %
Water phase	Deionized water	Q.S. to 100
	AF-6	0.20
	Glycerin	3.00
	E-20	2.00
	Disodium EDTA	0.05
	PEHG	0.60
Oil phase	Emollient*	20.00
Additive phase	Sodium Chloride	1.00

*Emollient: Isopropyl Isostearate (318), Lauryl Lactate (LL), Triolein (Algapur), Cocoyl Adipic Acid/Trimethylolpropane Copolymer (CATC), Caprylic/Capric Triglyceride (CCT), Dimethicone (DM).

(F)	Peach Macchiato	Cheering Beer	Crystal Grape Juice
Ingredient	wt%	wt%	wt%
DI water	70.69	65.79	71.69
Glycerin, Water (Aqua), Stevia Rebaudiana Leaf/Stem Extract	0.00	5.00	0.00
Glycerin, Water (Aqua), Crocus Sativus Flower Extract	2.00	0.00	2.00
Glycerin, Water (Aqua), Thymus Citriodorus Flower/Leaf Extract	0.00	2.00	0.00
AF-6	0.20	0.20	0.20

Glycerin	3.00	3.00	3.00
E-20	2.00	2.00	2.00
1,2-Hexanediol	0.50	0.50	0.50
Hydroxyacetophenone	0.50	0.50	0.50
318	20.00	20.00	0.00
Dimethicone	0.00	0.00	20.00
Sodium Chloride	1.00	1.00	0.00
Red (solution)	0.10	0.00	0.00
Violet dye (solution)	0.00	0.00	0.10
Fragrance	0.01	0.01	0.01

Characterisation of emulsion

pH of the samples was determined by a pH meter. The conductivity of the water phase alone (C) was measured by a conductivity meter at room temperature.

Characterisation of creaming

The boundary height of samples was measured by a vertical ruler at each time interval and used to define the endpoint of creaming: no further movement of the lower boundary and a clear lower continuous phase.

Microscope analysis

Optical microscopy was used to examine the packing of droplets in the emulsion samples. A small amount of emulsion sample on the very top layer (cream layer) was placed on a microscope slide without dilution and covered by a cover glass slip. The lower phase of 0.8% and 1.0% AF-6 samples was also subjected to microstructure analysis. Samples were observed under transmitted light at 500 times magnification.

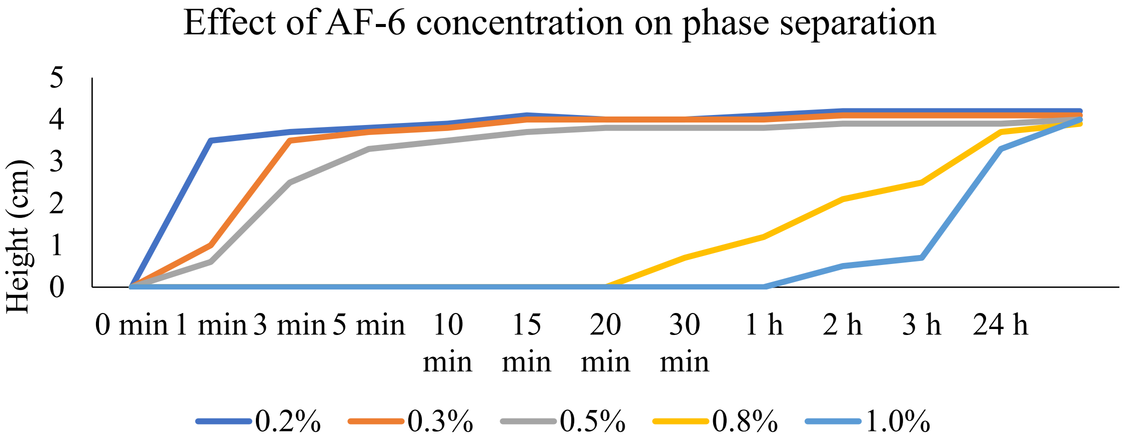
Results.

A three-step formulation process was set up and validated by different formulation variables and process parameters. Upon mixing or shaking, a milky lotion can be generated which separates after standing still.

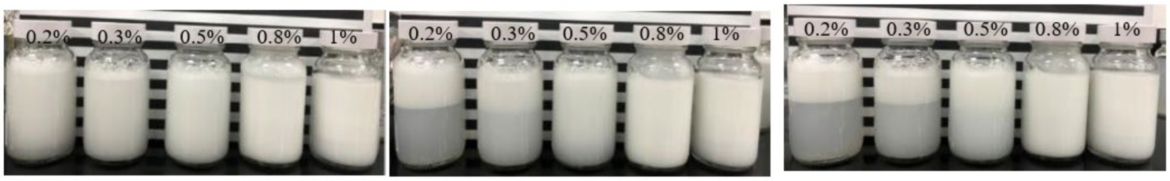
Effect of polymer concentration

Figure 2A showed the height of the lower boundary phase during the creaming of PU-62 stabilized Isopropyl Isostearate-in-water system. The creaming started immediately after shaking, droplets have moved up the container and some droplets have reached the cream layer, which created a sharp visible interface between them. The droplets are polydisperse in size (**Figure 2C**), and there is a diffuse boundary separating the emulsion phase from the serum layer. Although within the serum layer, the droplets are still moving at constant speed, the boundary line of the cream layer can be clearly observed (**Figure 2B**).

0.2% AF-6 showed the fastest creaming rate and transparent lower phase after 24 h, while 0.8% and 1% AF-6-based emulsions displayed a significant delay period, followed by a slow rearrangement and compaction in the cream layer. In this system, PU-62 dominates the interaction between droplets by adsorbing to the droplet surface and causing bridging flocculation and depletion (**Figure 2B**-(A), (B), (C)). The droplets formed aggregates creamed slowly. With a stronger depleting interaction (higher use levels of PU-62), the emulsion can form a single network structure. The cream layer underwent further compaction with time, and it finally became a uniform layer. In the microscopic analysis, the systems with 0.8% and 1% AF-6 exhibited a colloid-rich phase (**Figure 2C**-D1 and E1) and colloid-poor phases (**Figure 2C**-D2 and E2).



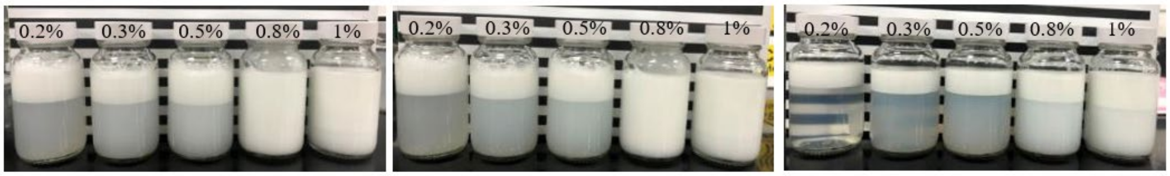
(A)



Shaked 10 times

After 3 min

After 5 min

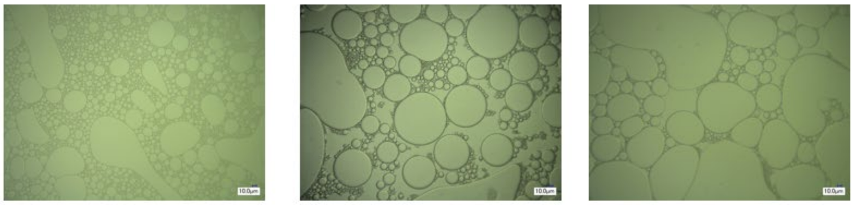


After 10 min

After 30 min

After 24 h

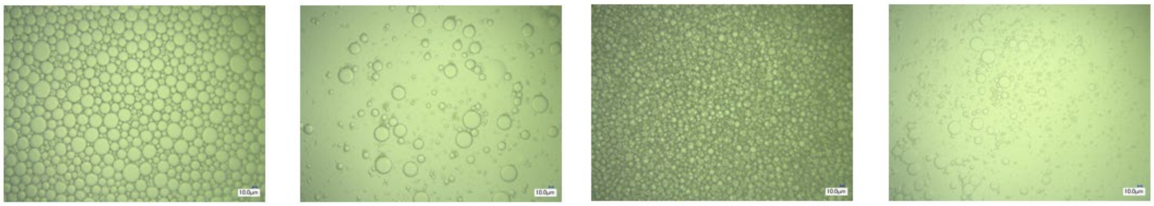
(B)



(A) 0.20% AF-6

(B) 0.30% AF-6

(C) 0.50% AF-6



(D1) 0.80% AF-6
(Cream layer)

(D2) 0.80% AF-6
(Lower layer)

(E1) 1.00% AF-6
(Cream layer)

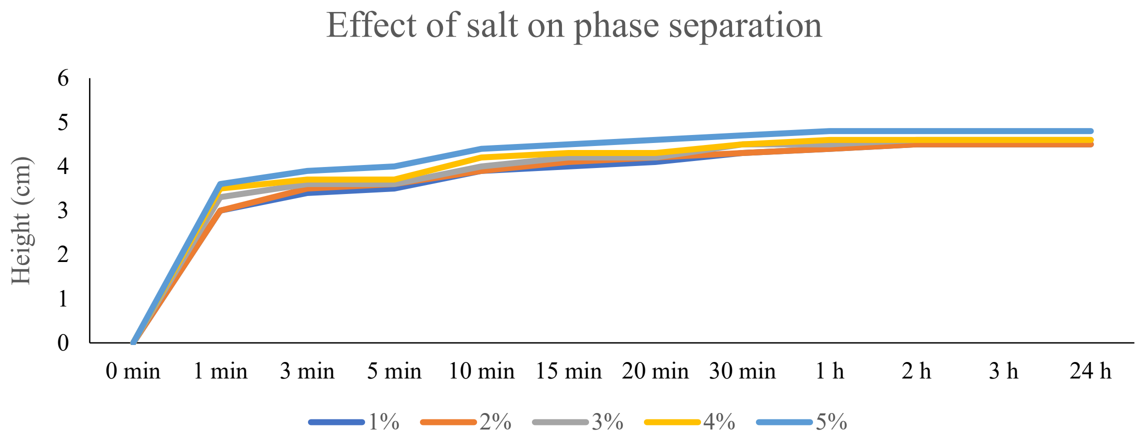
(E2) 1.00% AF-6
(Lower layer)

(C)

Figure 2. The effect of polymer concentration on the creaming behaviour. (A) The position of the lower boundary with time showing different creaming behaviour. (B) The appearance of samples at different time points after shaking 10 times. (C) The microscopic images of the upper cream layer (A, B, C, D1, E1) and the lower layer (D2 and E2) of the samples (×500 magnification).

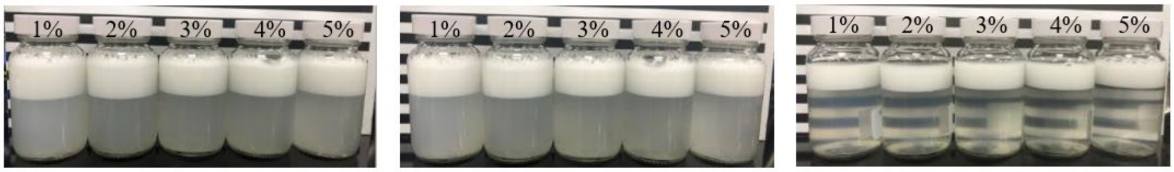
Effect of salt

Introducing salt into an emulsion system may lead to instability of emulsions, especially at high concentration. The addition of salt (sodium chloride in this study) increased the ionic strength of the aqueous system from 18.51 mS/cm (1% NaCl) to 76.2 mS/cm (5% NaCl) (tested without oil components) as well as the surface tension of the droplets. Moreover, the density of the aqueous phase can be raised by adding salt, which promotes the phase separation with a higher density difference. It can be seen that the separation rate, with the emulsion containing 5% NaCl as the fastest, decreases with the concentration gradient (**Figure 3A and 3B**). The phase separation profile can be manifested by controlling the amount of salt in the system.



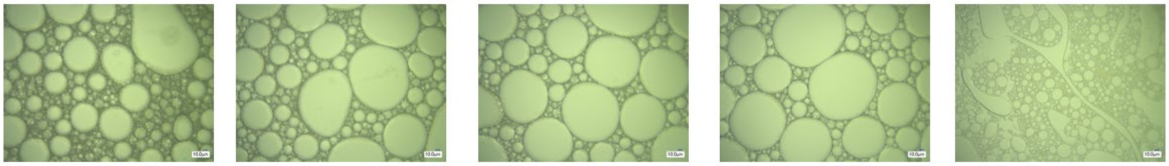
(A)

Shaked 10 times After 3 min After 5 min



After 10 min After 30 min After 24 h

(B)



1% NaCl 2% NaCl 3% NaCl 4% NaCl 5% NaCl

(C)

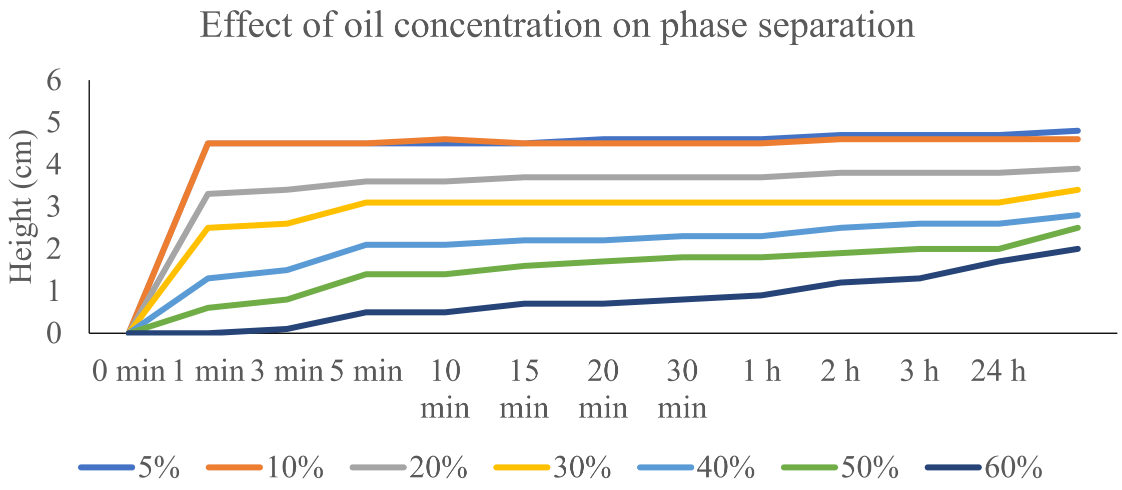
Figure 3. The effect of electrolyte strength on the creaming behaviour. (A) The position of the lower boundary with time showing different creaming rates. (B) The appearance of samples at different time points after shaking 10 times. (C) The microscopic images of the upper cream layer of the samples (×500 magnification).

Effect of oil concentration

When the oil volume was low, the position of the lower boundary was visible from the very beginning and rose fast (**Figure 4B**). By contrast, in the case that the oil volume was high, the position of the lower boundary was not visible at the beginning, suggesting a delay period followed by a slow rearrangement and compaction in the cream layer (**Figure 4A and 4B**).

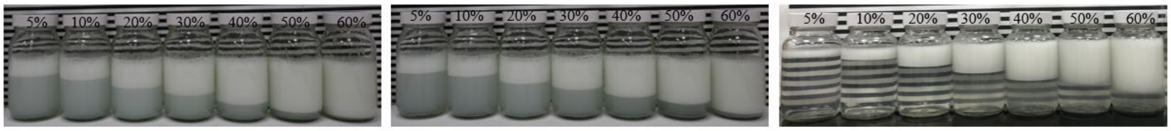
When the oil volume gets higher, the samples exhibited a delay phase, where no visible movement can be seen in the first few minutes, and then the network moved up steadily until the cream layer is reached (**Figure 4A and 4B**). The explanation is that the initial droplet network is stress-bearing and the volume fraction in the cream layer is lower than the close-packed one [5]. The oil droplets undergo further compaction with time until a uniform layer is formed at the end [5].

The position of the lower boundary with time, showing different creaming rates and suggesting a rearrangement in the cream layer depending on the level of oil volume in the system (**Figure 4A**).



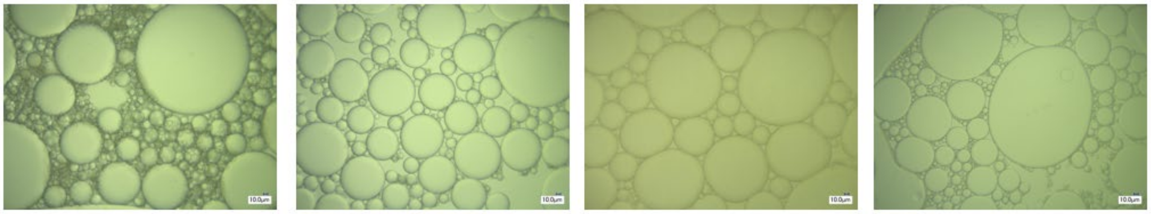
(A)

Shaked 10 times After 3 min After 5 min

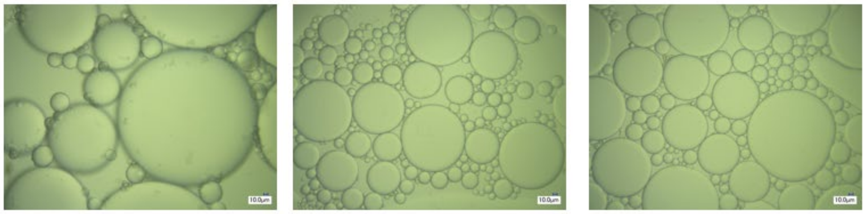


After 10 min After 30 min After 24 h

(B)



(A) 5% 318 (B) 10% 318 (C) 20% 318 (D) 30% 318



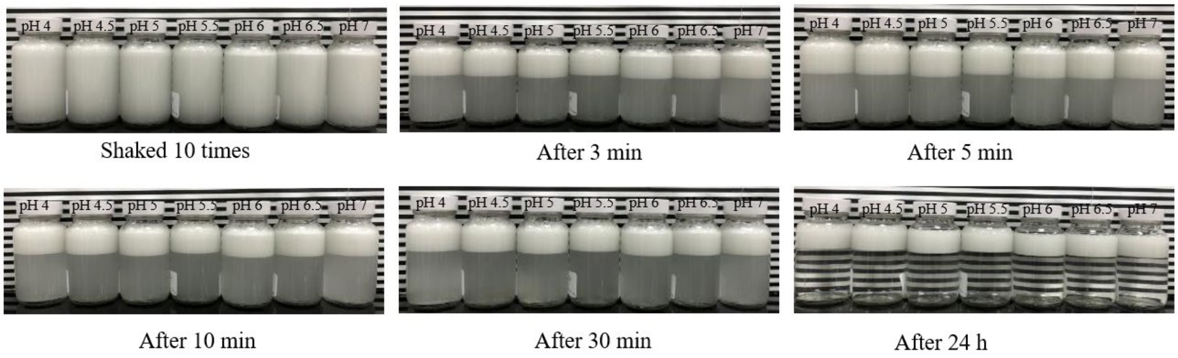
(E) 40% 318 (F) 50% 318 (G) 60% 318

(C)

Figure 4. The effect of oil concentration on the creaming behaviour. (A) The position of the lower boundary with time showing different creaming rates and behaviour. (B) The appearance of samples at different time points after shaking 10 times. (C) The microscopic images of the upper cream layer of the samples (×500 magnification).

Effect of pH

Polyurethane-62 is a non-ionic polymer, insensitive to pH environment. In 318-based emulsion systems, pH did not affect the performance and separation profile of PU-62 significantly.



Shaked 10 times

After 3 min

After 5 min

After 10 min

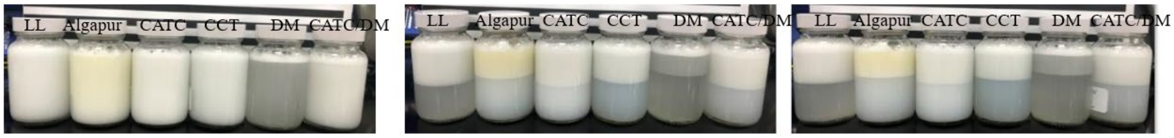
After 30 min

After 24 h

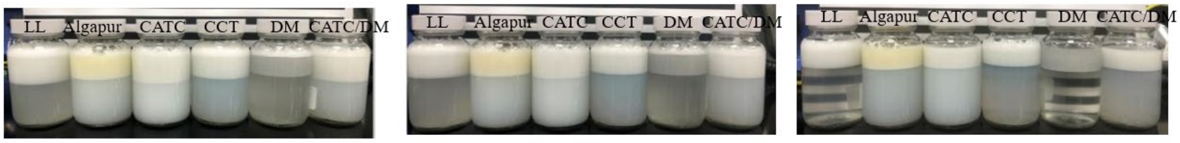
Figure 5. The effect of pH environment on the creaming behaviour. The appearance of samples at different time points after shaking 10 times.

Effect of oil type

Several oil emollients of different polarity and interfacial tensions were tested to monitor the creaming behaviour and all of them displayed creaming at rest after shaking. The difference lies in the appearance of the aqueous phase. CATC showed the opaquest lower layer and the cream layer of Dimethicone most translucent because of its unique refractive index, close to the refractive index of water. Therefore, different oil components can be selected to formulate a bi-phase product based on the requirement of the appearance.



Shaked 10 times After 3 min After 5 min

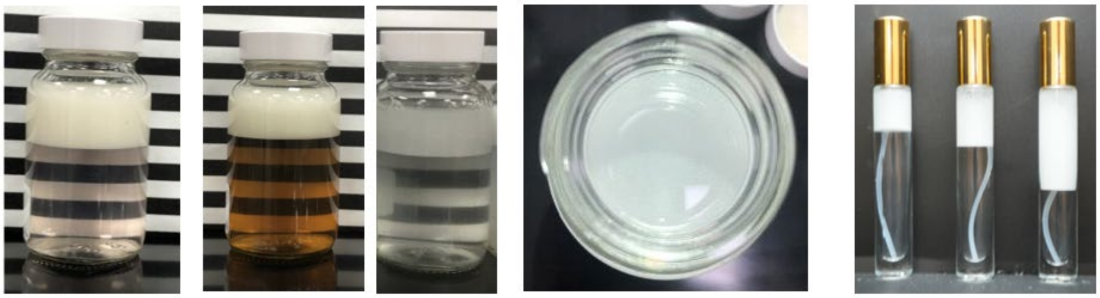


After 10 min After 30 min After 24 h

Figure 6. The effect of oil type on the creaming behaviour. The appearances of samples at different time points after shaking 10 times.

Customized prototypes

Based on the investigation results of formulation variables, the PU-62-based bi-phase products can be easily customized into different colours, different appearances (Dimethicone showed a natural glittering look without any additive), and different ratios between layers (**Figure 7**). With their high tolerance to pH and salt, many different kinds of actives can be added to either oil phase or water phase depending on the nature of the actives. Furthermore, the phase separation (creaming) rate can be well controlled, ensuring consistent product performance.



Peach Macchiato Cheering Bear Crystal Grape Juice (side/top view) Bi-phase at different ratio

Figure 7. Photos of customized PU-62-based bi-phase prototypes.

Discussion.

Based on the Stokes' law, the creaming rate is affected by the viscosity. PU-62 stabilizes emulsions via steric stabilization. As the concentration of PU-62 (0.2%) was below its CMC, there was no significant viscosity increase to slow down the Stokes' creaming rate. When the concentration of PU-62 was above its CMC, the network built and corresponding interactions between the polymer and the droplets resulted in a stable O/W emulsion without showing any creaming behaviour in a short period of time. Moreover, such a delay period can last for months or years with an optimized use level of PU-62.

The simple measurement of the boundary height gives information of creaming behaviour of different systems, and the diffusion profile of the boundary can be customized based on the product design. The clarity of the lower water phase depends on the use level of Polyurethane-62 and the selection of oil components. Higher use levels of the polymer and/or oil volumes display slower separation profiles. In addition, results show that the selection of oils can differentiate the product appearances.

On the other hand, a faster separation is observed with formulations of a stronger electrolyte strength. pH of the water phase does not show a significant impact on the phase separation profile. Based on the tests on these two most important water properties, it is conclusive that PU-62-based platform exhibits great feasibility with different pH environments and a complete “tolerance” to salt as salt only promotes the creaming process, which is preferable for such a product format.

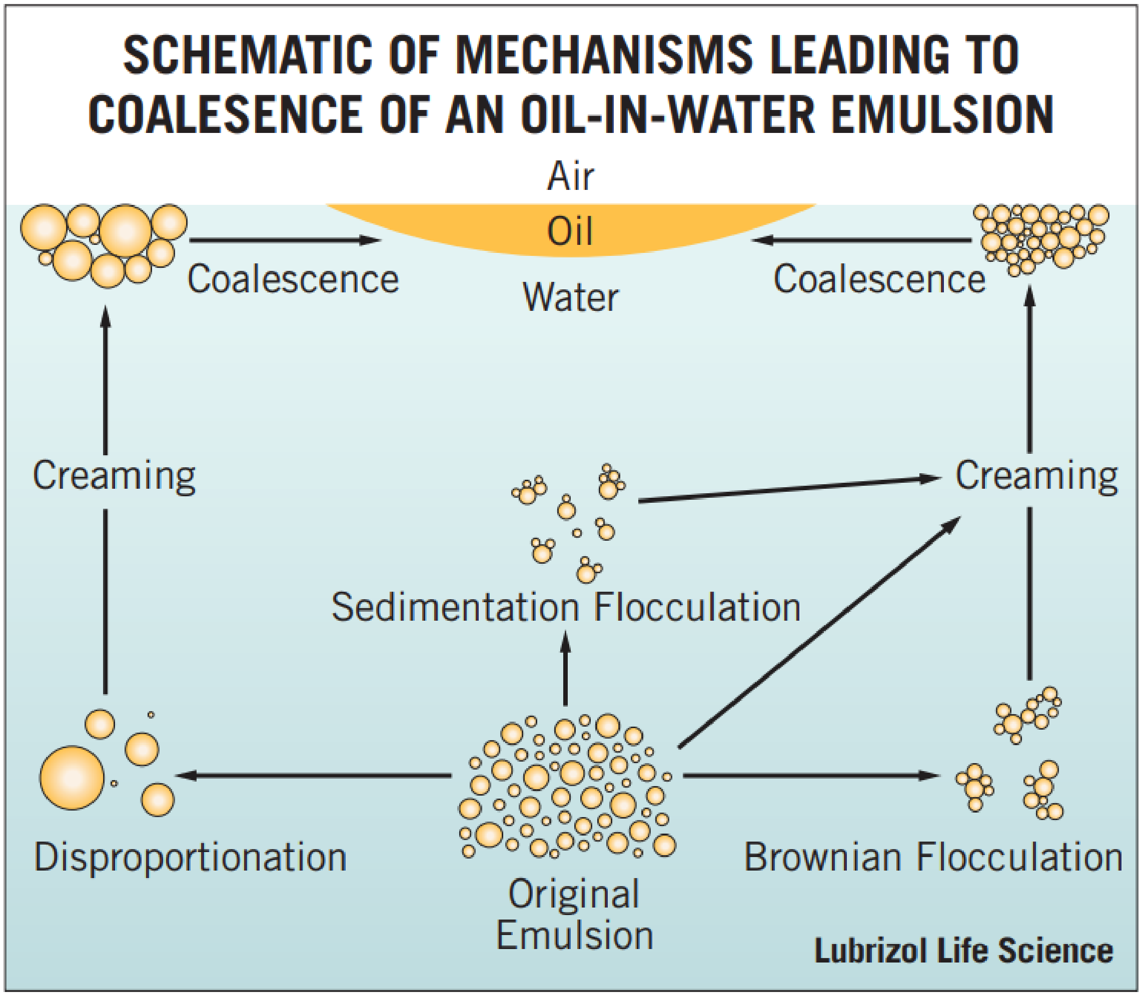


Figure 8. Schematic of mechanisms leading to coalescence of an oil-in-water emulsion. [6]

The creaming behaviour of PU-62-stabilized emulsions exhibit different forms, depending on the use level of PU-62, oil, and salt. Concentration effects cause hindrance, and creaming velocities are dependent on the polydispersity and inter-particle interaction [5].

Although coalescence may happen over time and eventually an oil separation may take place in the system (**Figure 8**), such a bi-phase product is supposed to be used frequently, and when used by consumers, the mechanical force applied can help restart the creaming process and prevent complete phase separation.

Conclusion.

Formulation technology using Polyurethane-62 is proposed with a comprehensive study of the impact of formulation variables. This study provides references that can be useful for developing appealing bi-phase products for skin care product customization and personalization.

The present study provides a good understanding of the factors that determine the product characteristics (creaming behaviour) of the Polyurethane-62 polymer-based bi-phase formulations and offers a novel formulation strategy to differentiate products effectively and incorporate various preferences or needs of consumers. Such a simple and flexible manufacturing process enables mass customization. Consumers can be integrated into the "production" of products during formulation tuning, product specification and co-design. Such consumer integration may increase the loyalty of consumers to brands.

Acknowledgments.

This work was supported by Lubrizol Advanced Materials. The authors gratefully acknowledge the assistance of Megan Lim and Michelle Lua on the experimental work.

Conflict of Interest Statement.

NONE.

References.

1. Dow A, Murphy M. Hispanic/Latinos and Skin care: Disparities in Product Development, Marketing, and Toxicity. J Drugs Dermatol 2020;19(12):1258-1260.
2. Chen, P. C., Gao, M., Yu, S., Jin, J., Song, C., Salmeron, M., ... & Yang, P. (2021). Revealing the phase separation behavior of thermodynamically immiscible elements in a nanoparticle. Nano letters, 21(15): 6684-6689.
3. Paige, M. F., & Ala'a, F. E. (2017). Phase-separated surfactant monolayers: Exploiting immiscibility of fluorocarbons and hydrocarbons to pattern interfaces. Advances in Colloid and Interface Science, 248: 129-146.
4. Thompson, A. B., Aerts, M., & Hack, A. C. (2007). Liquid immiscibility in silicate

melts and related systems. Reviews in Mineralogy and Geochemistry, 65(1): 99-127.

5. Robins, M. M. (2000). Emulsions—creaming phenomena. Current opinion in colloid & interface science, 5(5-6): 265-272.
6. HEALTH_RX_TB21_EMULSIONSTABILITY (2019) Lubrizol Life Science.