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# *A Novel HASE Polymer For Challenged System In O/W Emulsion*

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## 1. Introduction

Simplified formulation emerges in response to sensitive skin and clean beauty demanding, in sensitive skin care products only indispensable ingredients are introduced to the system. However, it is challenging to formulate effective emulsions with a good balance between stability and sensory. On the other hand, to achieve good skin efficacy and sensory journey, some formulations are designed with complex systems, which bring a great challenge to emulsion robustness. A novel hydrophobically modified alkali-swellable emulsion (HASE) polymer, Acrylates/Steareth-20 Methacrylate Copolymer (ASMC), is designed for these extreme oil-in-water (O/W) emulsion systems. Applying this ASMC in formulation, robust stability and fresh sensory can be expected in high oil loading/emulsifier free/complex electrolyte contained O/W emulsion.

## 2. Materials and Methods

*Materials*

Polymer: Acrylates/Steareth-20 Methacrylate Copolymer (ASMC) was used as an aqueous solution with 30% active level, Sphingomonas Ferment Extract (DG) and Carbomer used as rheology modifier reference; Caprylic/Capric Triglyceride (and) Hydrogenated Poly(C6-20 Olefin) (and) HDI/Trimethylol Hexyllactone Crosspolymer (5SCC) was used as oil phase rheology modifier.

Emollient: Butyrospermum Parkii Butter (Shear butter), Dimethicone (5cSt), Diisopropyl Adipate (DIA), Diisopropyl Sebacate (DIS), Isopropyl Isostearate (318), Neopentyl Glycol Diethylhexanoate (NGDO), Pentaerythrityl Stearate/Caprate/Caprylate/Adipate(CATC CN), Polyglyceryl-3Laurate (TGL).

Others: Phenoxyethanol (and) Ethylhexyl Glycerin (PEHG), Dipotassium Glycyrrhizate, Sodium Chloride, Glycerin, Disodium EDTA, Sodium Hydroxide were used as supplied.

*Method*

Emulsion preparation: Mixing water phase A via over-head stirrer at 400 rpm under 50 ºC till fully homogenous. Neutralizer, phase B was added to phase A, pH adjusted to 6-6.5. Oil phase added to neutralized aqueous phase under stirring. The mixture (A+B+C) was subjected to homogenized at 3,000 rpm for 3 min. Cooling main vessel to 40 °C, then, phase D was introduced into mixture under stirring until fully homogenous **Table 1.** Formulation Table of ASMC simple emulsion with Emollients.

| Phase | Ingredient Name | Weight % |
|---|---|---|
| A | Deionized Water | To 100 |
| | Phenoxyethanol (and) Ethylhexyl Glycerin (PEHG) | 0.50 |
| | Glycerin | 5.00 |
| | Acrylates/Steareth-20 Methacrylate Copolymer (ASMC) | 1.50 |
| | Carbomer | 0/0.15 |
| | Sphingomonas Ferment Extract (DG) | 0/0.375 |
| B | Sodium Hydroxide | To pH 6-6.5 |
| C | Emollient | 5-30 |
| D | Disodium EDTA | 0.1 |

**Table 2.** Formulation Table of ASMC simple emulsion with Electrolytes.

| Phase | Ingredient Name | Weight % |
|---|---|---|
| A | Deionized Water | To 100 |
| | Phenoxyethanol (and) Ethylhexyl Glycerin (PEHG) | 0.50 |
| | Glycerin | 5.00 |
| | Acrylates/Steareth-20 Methacrylate Copolymer (ASMC) | 1.50 |
| B | Sodium Hydroxide | To pH 6-6.5 |
| C | Caprylic/Capric Triglyceride (CCT) | 20 |
| D | Disodium EDTA | 0.1 |
| | Electrolytes (Dipotassium Glycyrrhizate/Sodium Chloride) | 0-1% |

**Table 3.** Formulation Table of ASMC emulsion with co-stabilizer

| Phase | Ingredient Name | Weight % |
|---|---|---|
| A | Deionized Water | To 100 |
| | Phenoxyethanol (and) Ethylhexyl Glycerin (PEHG) | 0.50 |

| | | |
|---|---|---|
| | Glycerin | 5.00 |
| | Polyglyceryl-3 Laurate (TGL) | 0/0.5 |
| | Acrylates/Steareth-20 Methacrylate Copolymer (ASMC) | 1.50 |
| B | Sodium Hydroxide | To pH 6-6.5 |
| C | Emollient | 5-20 |
| | Caprylic/Capric Triglyceride (and) Hydrogenated Poly(C6-20 Olefin) (and) HDI/Trimethylol Hexyllactone Crosspolymer (5SCC) | 0/0.3 |
| D | Disodium EDTA | 0.1 |

*Equipment*

The formulations are prepared by overhead mixers T25 digital Ultra-Turrax® from IKA and homogenizer is subject as LBX TYPE R from Prmix.

*Stability measurement*

The stability of emulsion is evaluated under room temperature (RT), 50 °C for 1 month, and centrifugation test under 3,000 rpm for 30 min. pH is measured by pH meter at 24 h RT, 1 month 50 °C. Viscosity is measured by viscometer at 20 rpm at room temperature. The emulsion apparent stability is assessed by visual inspection.

*Microscope analysis*

Emulsion microstructure is observed by optical microscopy. Apply minute quantity of emulsion on microscope slide and cover a cover glass slip. Bright filed and polarized light at 200 times magnification are used for sample characterization.

## 3. Results

*ASMC simple emulsion with different emollients*

Simple emulsion without emulsifier is prepared as **Table 1.** The O/W simple emulsion is made by 20%(wt.) emollients with different polarity. The emollients vary from low polarity Dimethicone(5cst) and 318; medium polarity as NGDO and CATC CN; high polarity emollients as DIS and DIA. The permittivity is conventionally used for description emollients' polarity. Generally, Caprylic/Capric Triglyceride is recognized as medium polarity emollient, with permittivity 3.40. The permittivity of applied emollients is listed in **Table 4**.

The formulated simple emulsions are white thin textured emulsions, possess viscosity around 7,000 to 11,000 mPa·s. Microscope and full set stability test are employed to evaluate emulsion microstructure and stability. **Figure 1** shows that Dimethicone (5cSt) emulsion is not well emulsified, with more obvious oil droplets, and size of droplets varies with high polydispersity. 318, NGDO, CATC CN, DIS and DIA emulsions microstructure are homogeneous. In stability tracking, except Dimethicone (5cSt) one, all other emulsions passed full-stability test. Dimethicone (5cSt) sample failed in five freeze-thaw cycles and 50 °C incubation. The texture of stable samples was well maintained during all the tracking conditions.

**Table 4.** Emollient permittivity

| Polarity classification | Emollient | Permittivity |
|---|---|---|
| Low polarity (Permittivity: 2-3) | Dimethicone (5cSt) | 2.20 |
| | Isopropyl Isostearate (318) | 3.00 |
| Medium polarity (Permittivity: 3-4) | Neopentyl Glycol Diethylhexanoate (NGDO) | 3.30 |
| | Pentaerythrityl Stea-rate/Caprate/Capry-late/Adipate(CATC CN) | 3.46 |
| High polarity (Permittivity>4) | Diisopropyl Adipate (DIA) | 4.70 |
| | Diisopropyl Sebacate (DIS) | 4.20 |

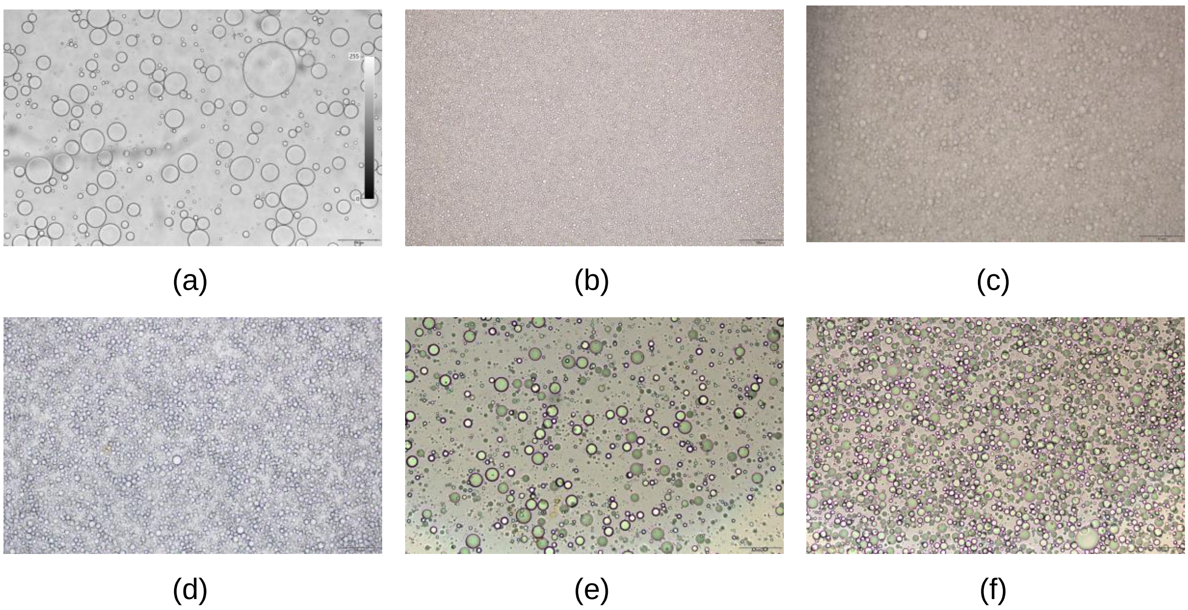


**Figure 1.** Microscope picture of ASMC simple emulsion with different emollients (magnification 200x): (a) Dimethicone (5cSt) simple emulsion; (b) 318 simple emulsion; (c) NGDO simple emulsion; (d) CATC CN simple emulsion; (e) DIA simple emulsion; (f) DIS simple emulsion.

*ASMC simple emulsion with variety emollient dosage*

The loading oil dosage leaves impact on emulsion texture and viscosity [1]. 5%,10%, 20% and 30% (wt.) emollient have been formulated as in **Table 1**. The 318, NGDO and DIS are picked out to represent low, medium and high polarity emollient. Texture evolution and viscosity behavior are illustrated in **Figure 2**.

As illustrated in **Figure 2**, all samples' viscosity increases aligned with emollient dosage, and texture get thickening as oil dosage increases. Sample varies from thin lotion to fine emulsion, then to soft cream, at 30% it reaches structured cream. According to stability tracking, NGDO and DIS all samples passed the stability test, but 318 samples with 5% and 10% dosage failed in five freeze-thaw cycles and 50 °C incubation. ACMS as an emulsion stabilizer, it shows excellent compatibility with medium to high polarity oil, ACMS stabilize low polarity oil when oil dosages above 10%. To ensure emulsion stability with limited amount of low polarity oil, the use of co-stabilizer is required to strengthen the system.

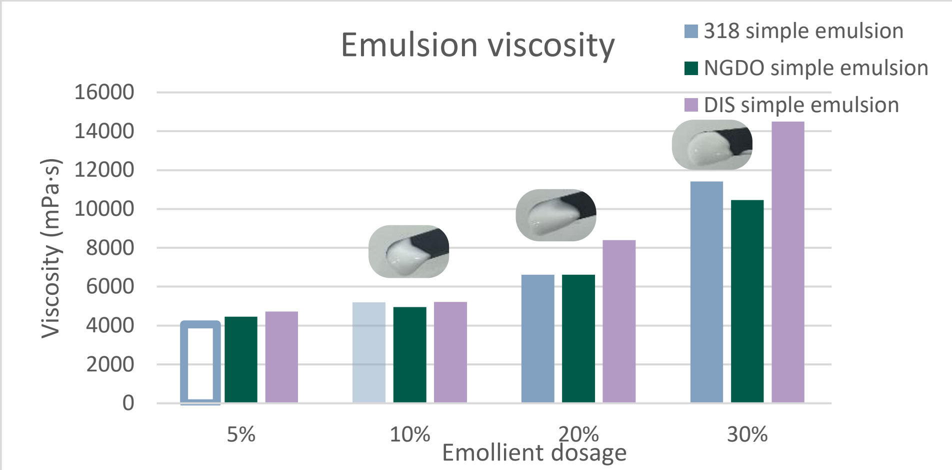


***Figure 2.*** *Emulsion texture and viscosity behavior with emollient dosage: (a) 318 simple emulsion; (b) DIS simple emulsion; (c) NGDO simple emulsion.*

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*ASMC simple emulsion with variety electrolyte dosage*

0.1%, 0.2%, 0.3%, 0.5% and 1% NaCl have been added into ASMC simple emulsion, emulsifying 20% CCT emollient. Dipotassium Glycyrrhizate has also been introduced to simple emulsion. As shown in **Figure 3**, the simple emulsion viscosity increases with low amount of Dipotassium Glycyrrhizate, then decreasing aligned with potassium concentration. Emulsion texture varies from textured cream (up to 0.2% wt.) to yogurt texture (up to 0.5% wt.), then turn to fluid emulsion at high $K^+$ concentration (0.8% wt.). In $Na^+$ system, emulsion viscosity decreases at low amount of $Na^+$. When $Na^+$ reaches 0.2% wt. the emulsion viscosity drops, and texture vary from textured to fluid emulsion. According to **Figure 3,** ASMC simple emulsion shows better texture stability in $K^+$ system, emulsion texture and viscosity are well maintained at low to medium concentration.

ASMC simple emulsions with electrolytes have been analyzed via microscope and stability tracking. Microscope pictures illustrate in **Figure 4** that ASMC simple emulsion without electrolytes exhibits homogeneous and stable oil droplets. When 0.2% (wt.) $Na^+$ is introduced in the system, oil droplets become non-homogeneous with 50% viscosity drop, texture transfers to fluid lotion. With 0.5% $Na^+$ in the ASMC emulsion. The emulsion network is destabilizing, leading to coalescence of oil droplets and an increase in droplet size, emulsion texture turns into fluid lotion. In $Na^+$ contained system, emulsion stability is maintained within 0.3% NaCl; when $Na^+$ dosage is higher than 0.3% (wt.), emulsion instability signs have been observed under 50 °C and freeze-thaw test. In Dipotassium Glycyrrhizate contained simple emulsion, microstructure is maintained homogeneous up to 0.5% $K^+$ (wt), the oil droplets begin deforming and non-homogeneous up to 1%(wt.). The emulsion instability sign is noticed when $K^+$ reaches 1%, the oil coalescence is observed at 50 °C tracking.

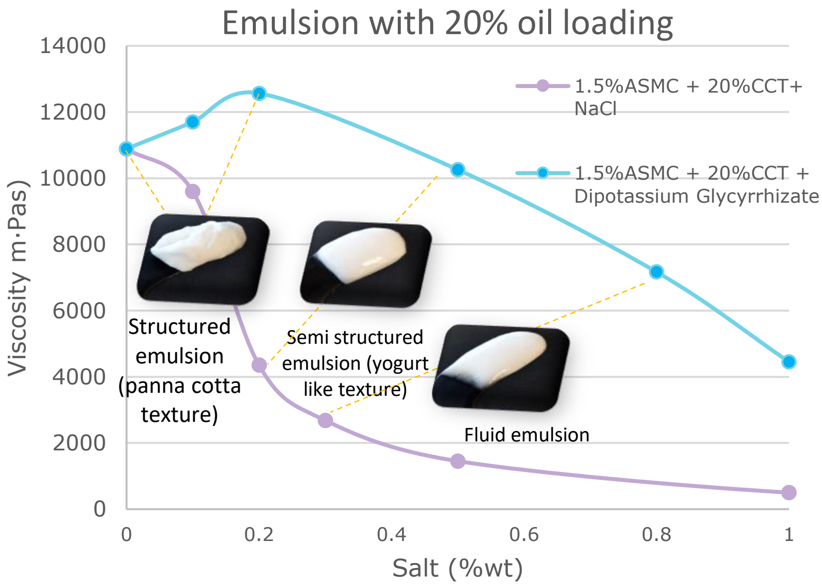



**Figure 3.** ASMC simple emulsion texture and viscosity behavior with electrolytes dosage

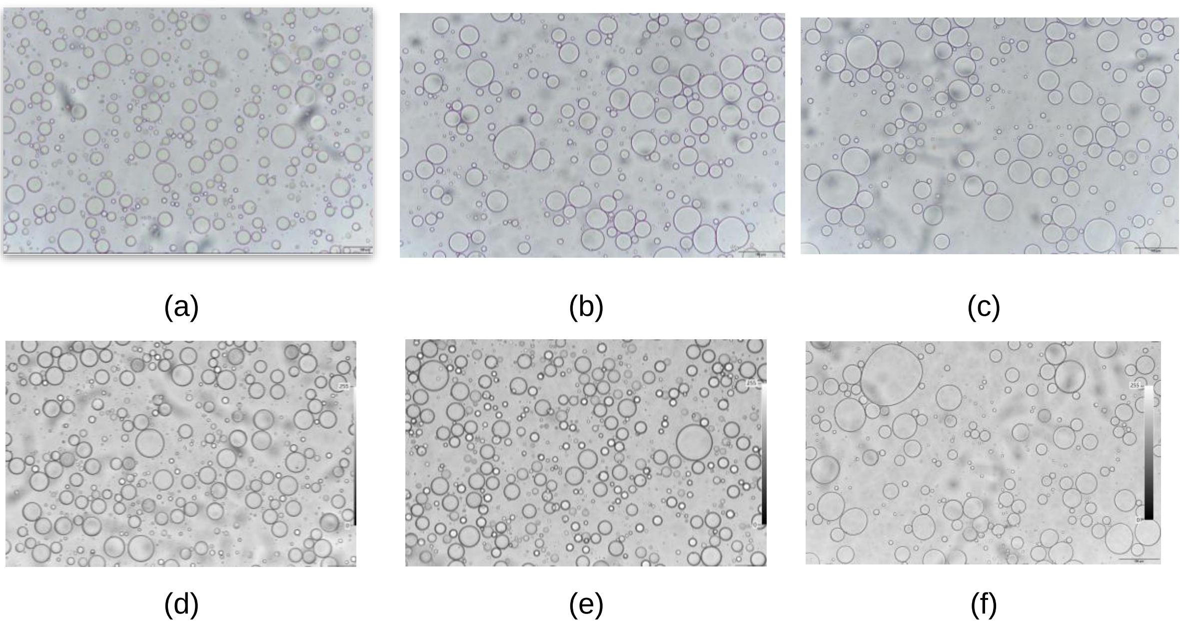
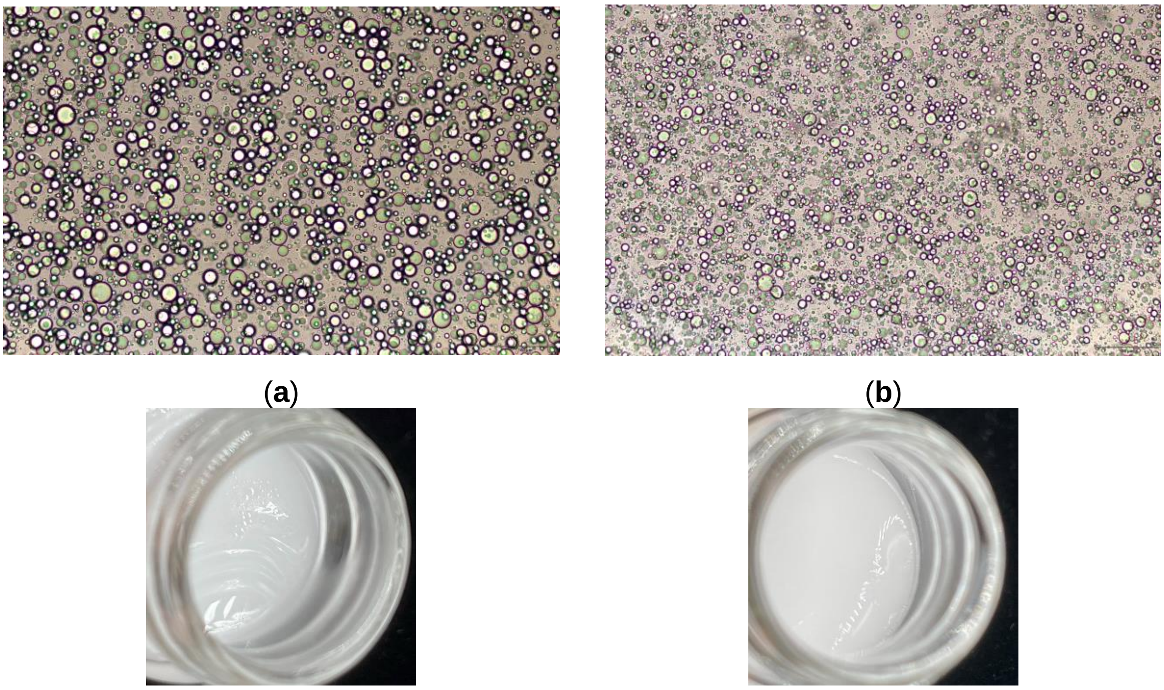



**Figure 4**. Microstructure image of ASMC simple emulsion with electrolytes: (a) No electrolytes; (b) 0.2% wt. NaCl in emulsion; (c) 0.5% wt. NaCl in emulsion; (d) 0.2% wt. Dipotassium Glycyrrhizate in simple emulsion; (d) 0.5% wt. Dipotassium Glycyrrhizate in simple emulsion; (e) 1.0%wt. Dipotassium Glycyrrhizate in simple emulsion.

*ASMC emulsion with co-stabilizer*

ASMC demonstrates strong emulsion stabilizing capability, outstanding emollient compatibility, emulsifying emollient without polarity limitation. However, when stabilize low polarity emollient at limit dosage, ASMC simple emulsion meet the challenge from freeze-thaw test and 50 °C stability. In the simple emulsion according **Table 1** formula, with emollient set as 5% and 10%(wt.) 318, , the oil accumulation has been observed after 5 freeze-thaw cycles as shown in **Figure 5**. In 50 °C stability tracking, a viscosity increase has been observed, which is shown in **Figure 6**. After 1 month stock in 50 ºC, viscosity varies from 4,060 mPa·s to 7,220mPa·s, with 43% growth rate in 5%(wt.) 318 contained emulsion. When oil dosage is set at 10% (wt.), the viscosity changes from 5,180 mPa·s to 8,520 mPa·s, growth rate reaches 39%. Dramatically viscosity fluctuation may cause texture change. Hence, stabilizing the viscosity behavior within acceptable range shall be came into notice.



(**a**) (**b**)

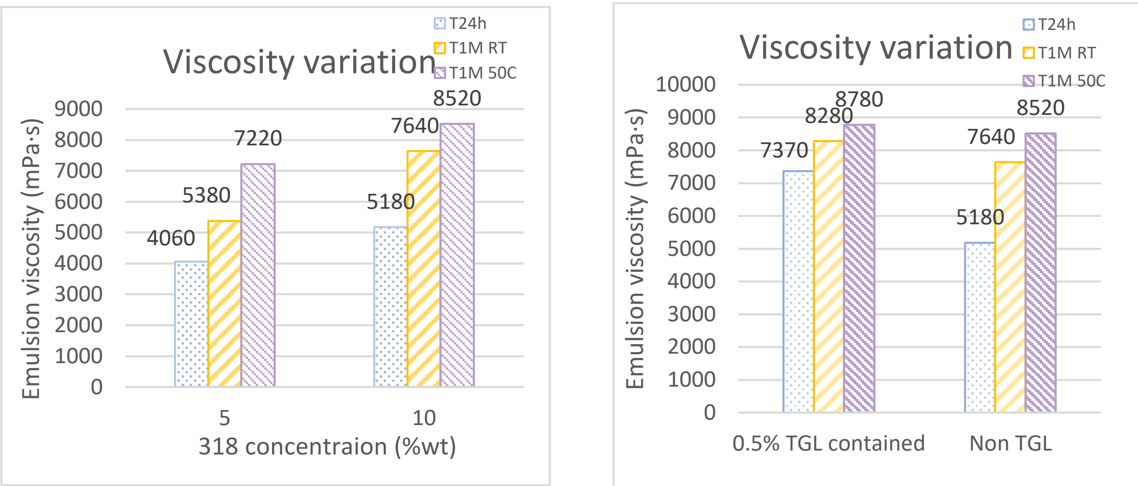
(c) (d)

**Figure 5**. 10% (wt.) 318 contained ASMC emulsion with and without 0.5% (wt.)TGL; (a) 10% (wt.) 318 ASCM emulsion microstructure; (b) 10% (wt.) 318 ASCM emulsion with 0.5% (wt.) TGL microstructure; (c ) 10% (wt.) 318 ASCM emulsion aspect after 5 freeze-thaw cycles; (d) 10% (wt.) 318 ASCM emulsion with 0.5% (wt.) TGL aspect after 5 freeze-thaw cycles.

**Table 5**. ASMC oil in water emulsion with 40% emollient

| Phase | Ingredient Name | Weight % |
|---|---|---|
| A | Deionized Water | To 100 |
| | Phenoxyethanol (and) Ethylhexyl Glycerin (PEHG) | 0.50 |
| | Glycerin | 5.00 |
| | Acrylates/Steareth-20 Methacrylate Copolymer (ASMC) | 1.50 |
| B | Sodium Hydroxide | To pH 6-6.5 |

| | | |
|---|---|---|
| C | Isopropyl Isostearate (IPIT) | 10.00 |
| | Neopentyl Glycol Diethylhexanoate (NGDO) | 26.00 |
| | Butyrospermum Parkii Butter | 4.00 |
| | Caprylic/Capric Triglyceride (and) Hydrogenated Poly(C6-20 Olefin) (and) HDI/Trimethylol Hexyllactone Crosspolymer (CHHT) | 0/0.3 |
| D | Disodium EDTA | 0.1 |

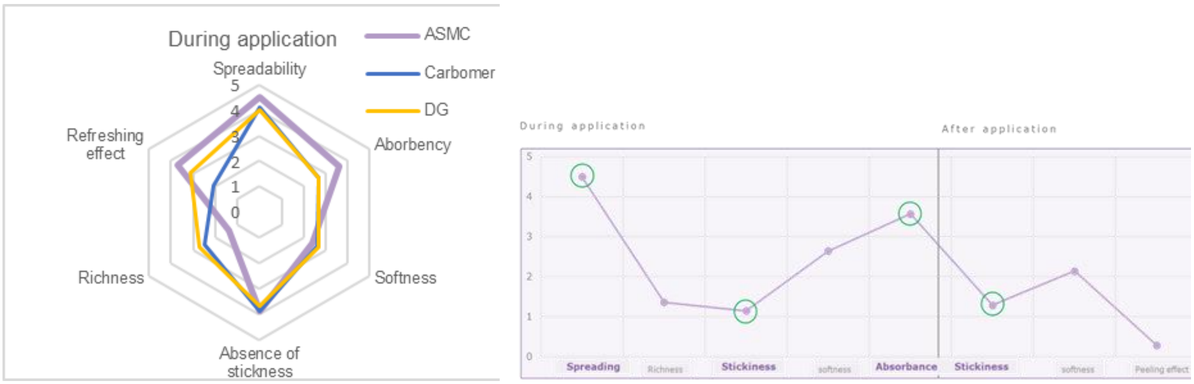



(**a**) (**b**)

**Figure 6**. ASMC emulsion viscosity behavior under stability tracking. (a) ASCM simple emulsion with low dosage of 318; (b) 10% 318 ASCM emulsion with & without 0.5% TGL

*Watery and fresh sensory*

A sensory study was conducted to evaluate the sensory properties of ASMC. Emulsion formulations are designed as in **Table 1.** ASMC simple emulsion, ASMC combine with 0.15% Carbomer made simple emulsion and ASMC combine with 0.375% DG made simple emulsion. Carbomer a cross-linked homopolymer that provides stabilization and texture, and DG is a polysaccharide that acts as a stabilizer. Carbomer and DG were picked out for comparison due to their widespread use in formulation. The sensory comparation and mapping is illustrated in **Figure 7.** Sensory comparation among ASMC simple emulsion and ASMC simple emulsion contains Carbomer or DG are shown in **Figure 7** (a). During application, ASMC simple emulsion shows extraordinary spread-ability, refreshing effect and absorbency. As ASMC owns linear molecular structure, the emulsion breaks down quickly during application on the skin, resulting in faster absorbency and spread ability. Introducing DG or Carbomer into simple emulsion can strength the polymer network, resulting in stabilizing emulsion interface, postpone emulsion breakout or hydrogel collapse. Hence, emulsion added DG or Carbomer show less fast spread-ability, freshness and absorbency. DG is a polysaccharide, which contribute in better richness results, Carbomer contained samples show similar results as it also leverage more effort to collapse emulsion structure. ASMC leaves non-sickness, a characteristic shared across all three samples. Once the ASMC formulation is absorbed, it leaves the skin smooth and free of residue, with no signs of peeling or stickiness as shown in **Figure 7** (b).




(a) (b)

**Figure 7.** Sensory profile for ASMC, Carbomer and DG emulsion; Sensory journey of ASMC simple emulsion

## 4. Discussion

In this study, the Acrylates/steareth-20 methacrylate copolymer (ASMC)is a hydrophobically-modified alkali swellable emulsion polymer with 30% total solids, without crosslink. The performance of ASMC as an emulsion stabilizer is assessed via designed oil-in-water emulsion without emulsifier. As a hydrophobic modified acrylate polymer, hydrophobic portion of ASMC reduces interfacial tension of water and oil, stabilizing oil droplets in continuous water phase. Hydrophilic portion (equatorial plan formed by hydroxyl groups) is swollen in the water phase and thickens the continuous phase to prevent oil droplets coalescence [2].

As illustrated in **Figure 1**, the particle size is impacted by emollient. Dimethicone (5cSt) droplets are more obvious than others, as ASMC cannot emulsify the silicone oil; as a non-crosslink polymer, ASMC cannot suspend Dimethicone at such high dosage, which dominates the emulsion phase separation in freeze-thaw test and hot temperature. 318 emulsion shows most tighten and uniform droplets, CATCN CN and NGDO droplets are similar, more obvious than 318 one, but smaller than DIS and DIA ones. Droplets size is driven by emollient structures [2]; as 318 carbon chains possess 18 carbons, which is close to ASMC hydrophobic chain, the emulsification efficacy is better than others. NGDO and CATC CN one possess around 12-16 carbons, and their droplets size are bigger than 318. DIS carbon chain contains 10 carbons, which is longer than DIA 6 carbon chain, thus, DIA shows bigger droplets than DIS one.

In **Figure 2**, 318 contained emulsion at 5% and 10% (wt.) failed in freeze-thaw test and at 50 °C, although 318 carbon chain is more compatible with ASMC hydrophobic chain, but in extreme condition with low dosage, oil polarity shall play an important role to stabilize the water/oil interface. With limited oil dosage, the Ostwald Ripening shall be easily conducted due to high interface tension between water and oil phase [3]. At low use level of oil, limited steric hindrance will accelerate emulsion instable process. By optimizing emollient polarity, the control of the interface tension via increasing emollient polarity would benefit in stabilizing emollient, even at low use level.

ASMC shows better electrolytes tolerance in $K^+$ system as seen in **Figure 3** and **Figure 4**, thanks to $K^+$ possessing a smaller hydrated radius, which is smaller than $Na^+$. Smaller hydrated radius indicates looser water molecule organization, whose effect as less interference with emulsion hydration layers, provide better stability in ASMC simple emulsion [4].

The polyacrylate maintains an extended chain conformation in solution due to electrostatic repulsion between charged groups, leading to high viscosity. When electrolytes (e.g., $Na^+$, $K^+$) are added into system, counterions screen the charges on the polymer chain, reducing electrostatic repulsion, which cause the chains collapse from an extended to a coiled state, decreasing hydrodynamic radius and viscosity. Electrolytes also leave an impact on emulsion as high concentration of salt competes with surfactants, dehydrating the emulsion stabilizer hydrophilic groups, resulting in destabilizing emulsion [2]. ASMC stabilization of the oil droplets relies on the hydrophobic chain, which anchor in the oil/water interface [5]. However, with limited amount of low polarity oil, the hydroponic connection is not strong enough to conquer the challenge from freeze-thaw, the interface is broken out during water phase and oil phase freeze and melting procedure [6]. TGL is a soluble emollient with HLB 11.3, TGL hydrophilic part contributes to stabilizing the oil/water interface, strengthening the emulsion structure [7], which is proved by microstructure (**Figure 5**) with smaller particle size and better stability performance. 5SCC is an efficient oil thickener, which contributes to strengthening the oil water interface, optimizing emulsion stability, especially after freeze-thaw test, by solidating the oil phase, adjusting oil rheology behavior in freeze-thaw test, preventing oil release from inner phase, and inhibiting bulk slip along with package wall.

## 5. Conclusion

This study targets evaluating ASMC polymer capability in stabilizing O/W emulsions. According to the results of the study, ASMC is an efficient rheology modifier in stabilizing simple emulsions from low to high oil dosage, delivering thin lotion, soft cream and bounce cream textures via adjusting emollient concentration. As an emulsion stabilizer, ASMC exhibits excellent compatibility with low, medium, and high polarity oil, but ASMC shows limited emulsification power with Dimethicone. ASMC is a perfect solution for electrolyte contained systems, as ASMC can manage the system's viscosity, aspect, and stability for electrolytes contained emulsion structure. Although low polarity oil at low use level challenges ASMC simple emulsion stability, small quantities of a co-stabilizer can solve the problem. Even in high oil loading system, ASMC simple emulsion leverages good emulsion stability, but co-stabilizers strengthen the emulsion structure to conquer the potential issue from extreme environment. ASMC made emulsion deliver ultra fresh and watery sensory, which can be easily perceived by consumers.

## 6. References

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