**Rheology Performance Study Helped to Predict Long-Term Stability of Suspension System Using Rheometer**

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## Abstract

**Background**: We study rheology performance, yield stress of alkaline swellable emulsion polymer in cleansing formulation. The suspension capability with different polymer dosage is compared by using rheometer to predict the long-term stability. Additional of salt and back acid method also evaluated in predicting the rheology performance and long-term stability.

**Methods**: Alkaline swellable emulsion polymer (Acrylates Copolymer) in a cleansing formulation with surfactant mixture – anionic (SLES 11%TS) and zwitterionic (CAPB 3.45%TS) together with soft breakable beads and hard solid beads. Polymer with different dosage in the cleansing formulations were formulated to pH 6.3 – 6.8 and viscosity range adjusted with salt to 12,000 – 13,500cps (Brookfield® RV, DVII+ Viscometer (Brookfield AMETEK, Inc.) spindle #5@ 20 rpm, 25 °C). Rheology performance evaluated through Oscillation Amplitude, Oscillation Frequency and Flow Ramp test.

**Results**: The rheology study showed we can evaluate the cleansing formula suspension ability and helped predict product's long-term stability. Oscillation Amplitude test help identified LVE region, flow ramping identified the apparent yield stress provide good correlation between the rheological characteristics of the systems and the long-term stability prior to final full thermal stability. The study also indicate that the back-acid method further enhances the superior suspension through higher yield value obtained.

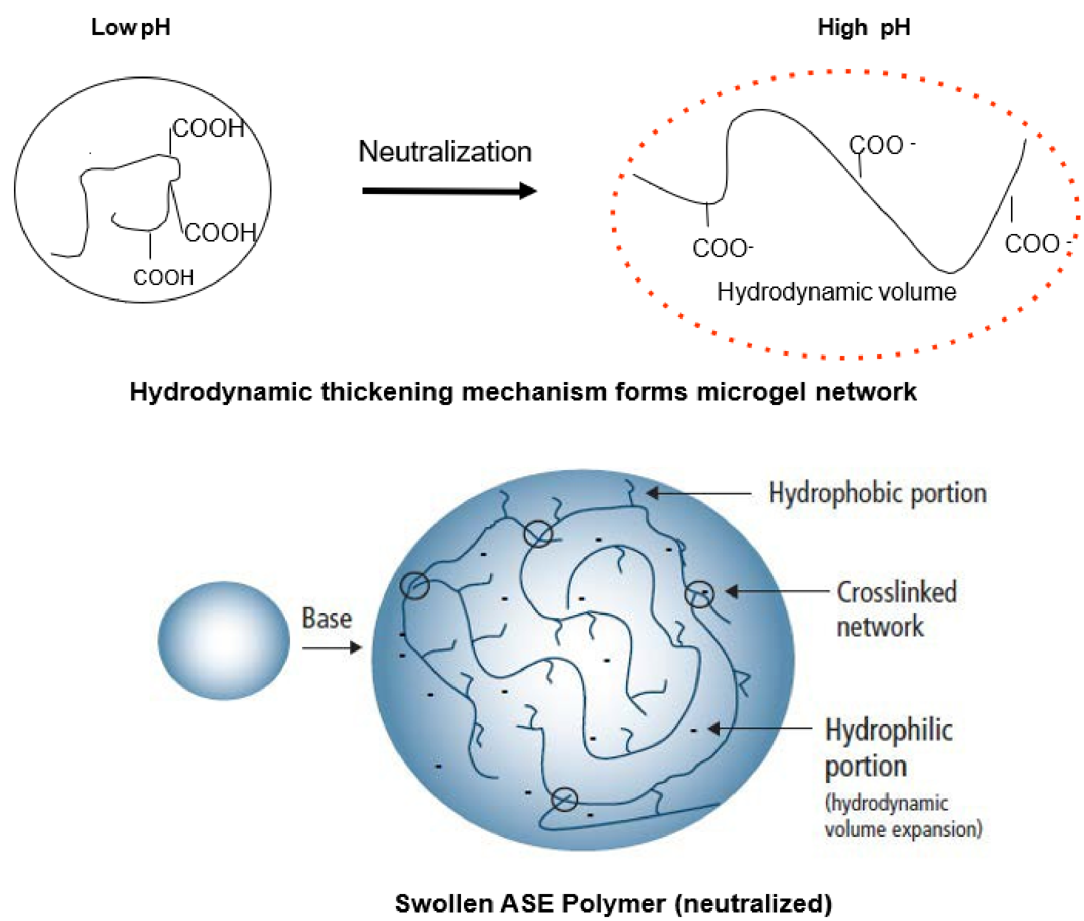
**Conclusion**: The rheometer analysis method showed it is a time saving screening method prior to final full thermal stability providing information on the LVE region, structure state, apparent yield stress of the polymer behavior in the cleansing system.

**Keywords:** Suspension; Cleansing Formulation; Stability; Rheometer; Polymer; Surfactant

**Introduction**. A clear surfactant system is a common cleansing system. Aesthetic properties become important features of personal care products when formulators demand for better market positioning. Whereas consumers are more educated, treasure wellbeing lifestyle and demand not just a cleansing product but also eye-catching products with appealing sensory, texture and appearance. Incorporation of beads, mica, pearling agents, exfoliating abrasive agents into the clear surfactant system would readily make the product to be outstanding on the shelf and more pleasant to use.

To stabilize the insoluble particles, suspension and yield stress are crucial and key factors. A higher yield stress prevents the material to undergo sedimentation or aggregation. [1,2,3,4] Rheology modifiers like cross-linked acrylate copolymers (anionic acrylic acid emulsion polymer) are generally best candidates used in providing viscosity, superior suspension, and elegant flow to support aesthetic characteristics mentioned above. The lightly cross-linked acrylate copolymer is also known as alkaline swellable emulsion (ASE) polymer with INCI: Acrylates Copolymer (AC) that ionizes and expands into a three-dimensional network upon neutralization to pH 5-7 (this is due to the ionic charge repulsion between the carboxyl group, COO along the backbone of the polymer). [1,2]

**Picture 1: ASE polymer thickening mechanism**




However, it is time consuming for formulator to follow up stability of the suspension samples over time during the product development stage. It is important to have a quick and reliable method to assess and predict the long-term physical stability of the suspension systems with different rheology modifiers dosages and/or formulation processes. A reliable method will be helpful for the formulator in terms of time and cost saving during formulation development stage.

Rheology analysis method is reliable method to investigate yield stress to help further evaluate the cleansing formula performance in terms of predicting the long-term stability of suspension systems. [4,5,6,7] Rheology modifiers at different use levels and different formulation process (standard pH adjustment and back-acid) were tested using rheometer. Physical stability of the samples was monitored to evaluate the correlation between the rheology test results and standard inspection data. Different rheological techniques were investigated to optimize the methods.

We first conduct the Oscillation Amplitude test to first defined the limit of the linear viscoelastic region (LVE region). This is helpful to indicate the range of the strain value in which the test can be carried out without destroying the structure of the sample. The experiment continues with Oscillation Frequency test investigating the time-dependent deformation of the Acrylates Copolymer containing cleansing formulas provide further understand. This simulated in both short-term behavior (by rapid motion, i.e. at high frequencies like during application) and long-term behavior (by slow motion, i.e. at low frequencies like during at rest stability). [3] At last of the rheology experiment, we conduct flow ramping test with continuous shear rate from low to high. Through the shear rate ramping method to determine the apparent yield stress by fitting the rate curve with Bingham, Casson or Herschel-Bulkley models. [3,4]

The rheology test method also serves as an indication if the back-acid thickening has been applied correctly and hence provide good yield value, good suspension. Overall, this will be time saving in yield value/ suspension's long-term stability screening.

**Materials and Methods**.

*Materials*. Alginate agar based soft breakable beads (red colour), mannitol and cellulose and hydroxypropyl methylcellulose based none-breakable beads (sparkling yellow colour) were incorporated into Acrylates Copolymer (AC) cleansing formulation. Surfactant used are mixture of anionic (sodium laureth ether sulfate) and zwitterionic (cocamidopropyl betaine) with total solid 14.45%. Suspension performance with different dosage of acrylate copolymer and polymer rheology performance were investigated. Long-term stabilities of beads suspension were observed at 50°C.

*Methods. Cleansing Formula Preparation for Rheology Test.* We first prepare a cleansing formula with the surfactant mixture (11%TS SLES + 3.45%TS CAPB) and we post-add the premix mixture of water with different dosage of Acrylates Copolymer (1.5%TS, 1.75%TS, 2.25%TS, 2.5%TS, 2.75%TS) into respective model formula. Refers to Table 1 for formulation details. The final pH of the formula was neutralized to the pH range: pH6.3 –

pH6.8. While viscosity of the formula weas adjusted to the range of 12,000 – 13,500cps with additional of salt.

**Table 1: Acrylates Copolymer Cleansing Formula**

| Ingredients | 0%TS AC | 1.5%TS AC | 1.75%TS AC | 2.25%TS AC | 2.5%TS AC | 2.75%TS AC |
|---|---|---|---|---|---|---|
| Deionized Water | 49.66 | 49.66 | 49.66 | 49.66 | 49.66 | 49.66 |
| Disodium EDTA | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| Glycerin | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 11%TS Sodium Laureth Ether Sulfate) | 15.71 | 15.71 | 15.71 | 15.71 | 15.71 | 15.71 |
| 3.45%TS Cocamidopropyl Betaine | 11.50 | 11.50 | 11.50 | 11.50 | 11.50 | 11.50 |
| Phenoxyethanol (and) Chlorphenesin (and) Aqua (and) Glycerin | 0.70 | 0.70 | 0.70 | 0.70 | 0.70 | 0.70 |
| Deionized Water | 20.33 | 15.78 | 15.03 | 13.48 | 12.75 | 12.00 |
| **Acrylates Copolymer** | **0.00** | **4.55** | **5.30** | **6.85** | **7.58** | **8.33** |
| **Total** | **100.00** | **100.00** | **100.00** | **100.00** | **100.00** | **100.00** |
| **Adjustment & specifications:** | | | | | | |
| 1) Neutralization with 18%NaOH (%) to pH 6.3-6.8 | qs | qs | qs | qs | qs | qs |
| pH aft 24hrs | 6.62 | 6.536 | 6.713 | 6.632 | 6.581 | 6.587 |
| Viscosity (cps) Brookfield® RV, DVII+, Spindle#4, 20rpm | 820 | 1,140 | 1,620 | 4,240 | 6,500 | 8,280 |
| 2) NaCl (adjustment to 12,000 - 13,500cps) | qs | qs | qs | qs | qs | qs |
| Viscosity (cps) Brookfield® RV, DVII+, Spindle#5, 20rpm | 12,600 | 12,440 | 12,400 | 13,020 | 12,180 | 12,040 |

*pH & Viscosity.* pH of respective cleansing formula was measured by Mettler Toledo pH meter. Viscosity was measured with Brookfield® RV, DVII+ Viscometer (Brookfield AMETEK, Inc.) spindle #5@ 20 rpm, 25 °C.

*Rheology.* Rheology experiments were conducted to study apparent yield stress and respective cleansing formula structure. A cone and plate geometry (stainless steel, 40 mm diameter, 1.018° angle) was used. Approximately 2 g of respective cleansing formula's sample was added onto the Peltier plate Aluminium. The sample's viscoelastic properties were assessed at 1 Hz at 25 °C between 0.01% to 500% strain amplitude to determine the linear viscoelastic region (LVER) by measuring the storage modulus G′ (associated with energy storage) and the loss modulus G″ (associated with loss of energy). The dynamic oscillation was measured from 0.01 to 100 Hz at a constant shear strain of 1% in the linear region at 25 °C. Apparent yield stress measured through fitting the rate curve with Bingham, Casson or Herschel-Bulkley models by ramping the sample from 0.1 – 1000 1/s shear rate in 300s and then ramping back down in another 300s at 25 °C.

*Cleansing Formula preparation for Back Acid Thickening Test.* A simple cleansing formula was prepared based on Table 2 with 2.5%TS of Acylates Copolymer. The sample was first neutralized to pH6.5 ±0.5. Continue with back acid thickening by adjusting pH to pH5.3 and pH4.7 respectively with 25% citric acid solution. We then evaluate how does back acid thickening method impact on the apparent yield stress from these 2 samples.

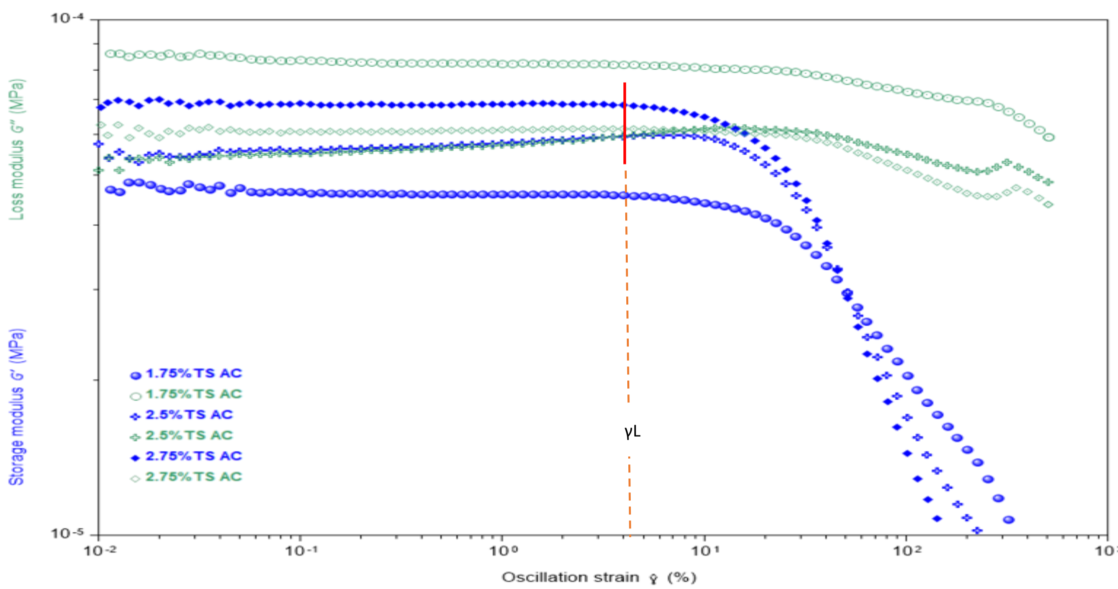
| **Ingredients** | **Back Acid to pH5.3** | **Back Acid to pH 4.7** |
|---|---|---|
| Deionized Water | 83.75 | 83.75 |
| Acrylates Copolymer (%TS) | 2.50 | 2.50 |
| Sodium Laureth Ether Sulfate (%TS) | 11.2 | 11.2 |
| Cocamidopropyl Betaine (%TS) | 2.30 | 2.30 |
| Sodium Benzoate (%TS) | 0.25 | 0.25 |
| 18% NaOH Solution (adjust to pH6.5 ±0.5) | | |
| **Total** | **100.00** | **100.00** |

*Table 2: Cleansing Formula Prepared by Back Acid Thickening Method*

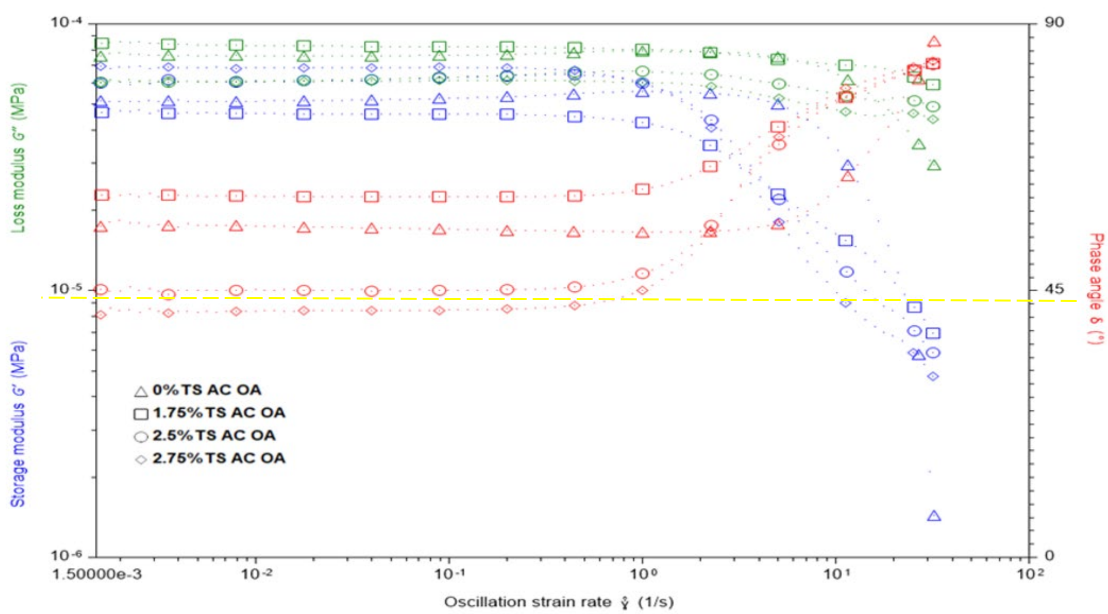
**Results**.

*Oscillation Amplitude Test.* Oscillation Amplitude test result showed (Figure 2(A)) when cleansing formula containing lower concentration of Acrylates Copolymer – 1.75%TS AC exhibits character of a viscoelastic liquid in the LVE range, G" > G'. Its viscous behavior dominates the elastic one and therefore exhibits as liquid character. When the Acrylates polymer concentration increased from 1.75%TS AC to 2.5%TS AC to 2.75%TS AC, the cleansing formula character of a liquid or fluid or sol (G" > G') become character of a gel or solid (G' > G"). At higher concentration, i.e 2.75%TS AC of Acrylates Copolymer, the cleansing formula elastic behavior dominates the viscous one and therefore exhibits certain rigidity.

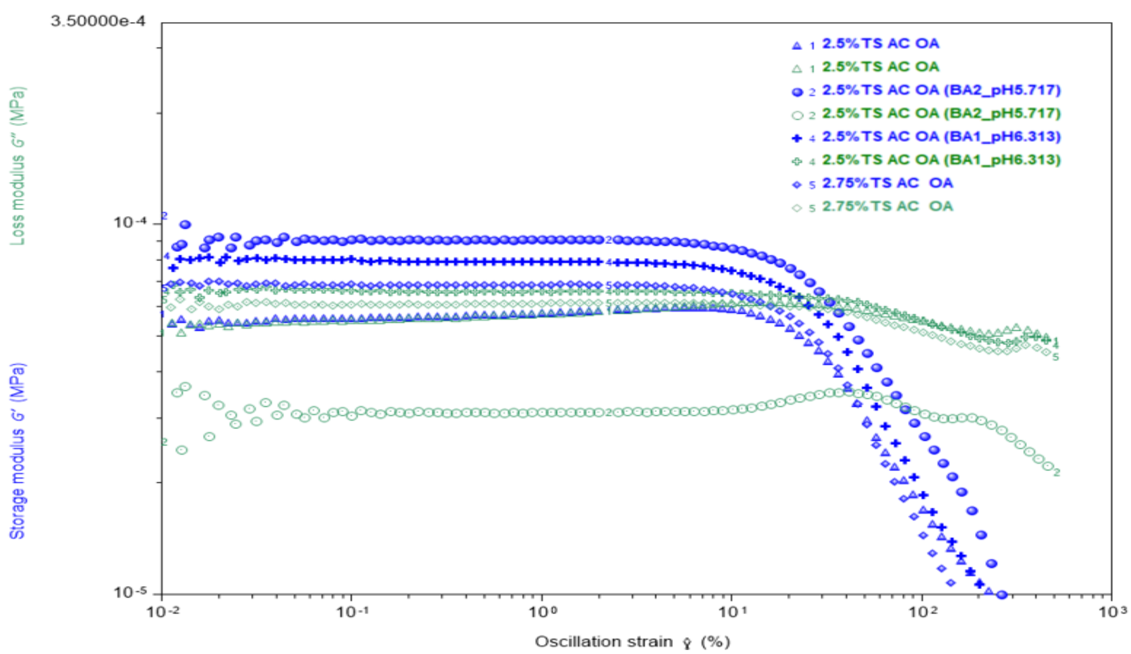
Figure 2(B) showed 2.75%TS AC showing low-viscosity flow behavior at medium and high shear rates with G' > G" in the LVE region has indicates gel-like consistency in the low-shear rate range. When at rest, for this kind of structure, "semi-solid matters" or viscoelastic solids, a certain firmness and stability can be expected even if they show a weak gel structure only. 2.75%TS AC sample showed phase angle of 45° > δ > 0° with G' > G", this again verify 2.75%TS AC sample has the behavior of viscoelastic gel or solid. Whereas 2.5%TS AC sample showed δ closed or equal to 45° with G' = G" indicates the sample has viscoelastic behavior showing 50/50 ratio of the viscous and elastic portion. While the sample with much lower Acrylates Copolymer (1.75%TS AC) and no polymer has showed phase angel range of 90° > δ > 45° with G" > G' saying that they are having character of viscoelastic liquid.




(A)




(B)




(C)

*Figure 2(A) – Strain amplitude sweep of different Acrylates Copolymer concentration showing when concentration of Acrylates Copolymer increased change character of a viscoelastic liquid in the LVE range, i.e. G" > G' to gel-like character in the LVE range, i.e. G' > G" (with the limiting γL)*
*Figure 2(B) – Influence of Acrylates Copolymer concentration on phase angle and its behavior.*
*Figure 2(C) – Influence of back acid thickening on the linear viscoelastic region of cleansing formulas containing different concentration of Acrylates Copolymer.*

Figure 2(C) showed influence of back acid thickening on the LVE range of the cleansing formula containing different Acrylates Copolymer concentration. Both the samples (1)2.5%TS AC (BA1_pH6.313) and (2)2.5%TS AC (BA2_pH5.717) have first been neutralized to pH6.3 – pH6.8 with 18% NaOH solution as described in methods. Then decreasing the pH with 25% citric acid solution to pH6.313 and pH5.717 respectively. The strain amplitude sweep showed both samples (1)2.5%TS AC (BA1_pH6.313) and (2)2.5%TS AC (BA2_pH5.717) showed character of gel-like in LVE range, G' > G". this indicates both these samples exbibits a better gel strain as compared to the samples without going through the back acid thickening. They are sample 2.5%TS AC & 2.75%TS AC. This will be further elaborate in the flow ramping and yield stress session.

*Oscillation Frequency Test.*

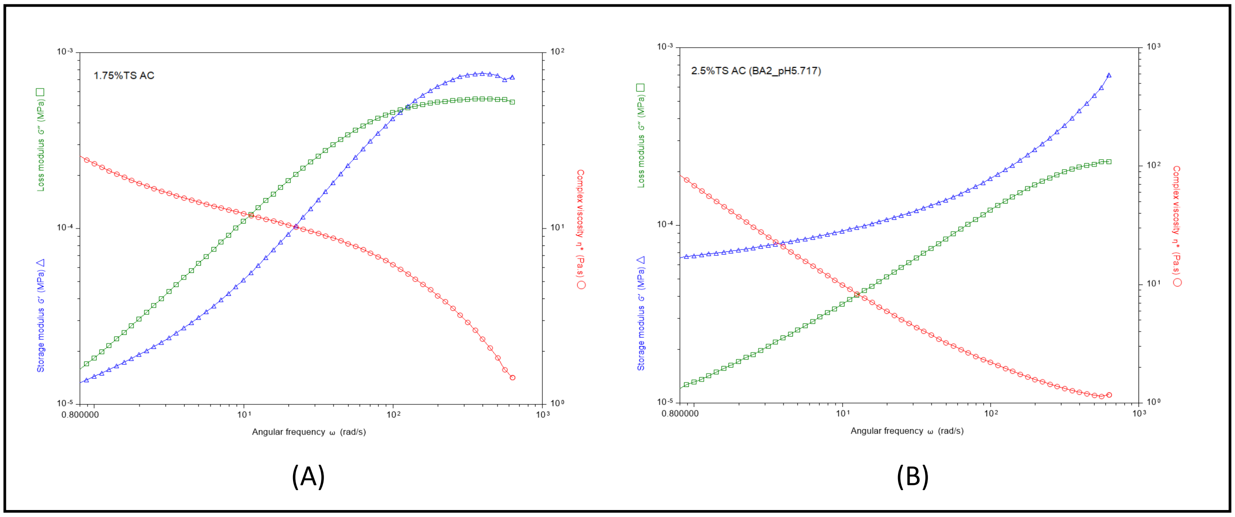



*Figure 3(A) & (B) – Frequency sweeps evaluation in cleansing formula containing 1.75%TS Acrylates Copolymer and 2.5%TS Acrylates Copolymer with back acid thickening to pH5.717.*

Frequency sweep test Figure 3(A) showed the lightly cross-linked Acrylates Copolymer molecule with loss modulus, G" > storage modulus, G', the |η*|-function approximates to the plateau value of the zero-shear viscosity, indicating the behavior of a viscoelastic liquid at rest. The phenomenon observed in the frequency sweeps for 1.75%TS AC, again match the finding in amplitude sweeps referring to the LVE range G" > G' and phase angle of 90° > δ > 45° with G" > G' saying that sample 1.75%TS AC is having character of viscoelastic liquid. Figure 3(B) showed the lightly cross-linked Acrylates Copolymer loss modulus G' > storage modulus, G", the |η*|-function slopes up to "infinitely high" value, indicates the "gel-like state" and therefore stability at rest.

*Flow Ramping & Apparent Yield Stress.* Based on flow ramping test, we have adopted the curve fitting method based on best fit curve analysis from the rheometer software where it is adapted to the available measuring points of the curve. The curve fitting is carried out using one of the various model functions, e.i. according to Bingham, Casson or Herschel/ Bulkley models. Referring to Figure 4(A)-(F), we have generated the apparent yield stress, Pa based on the Herschel/ Bulkley model with the best $R^2$.

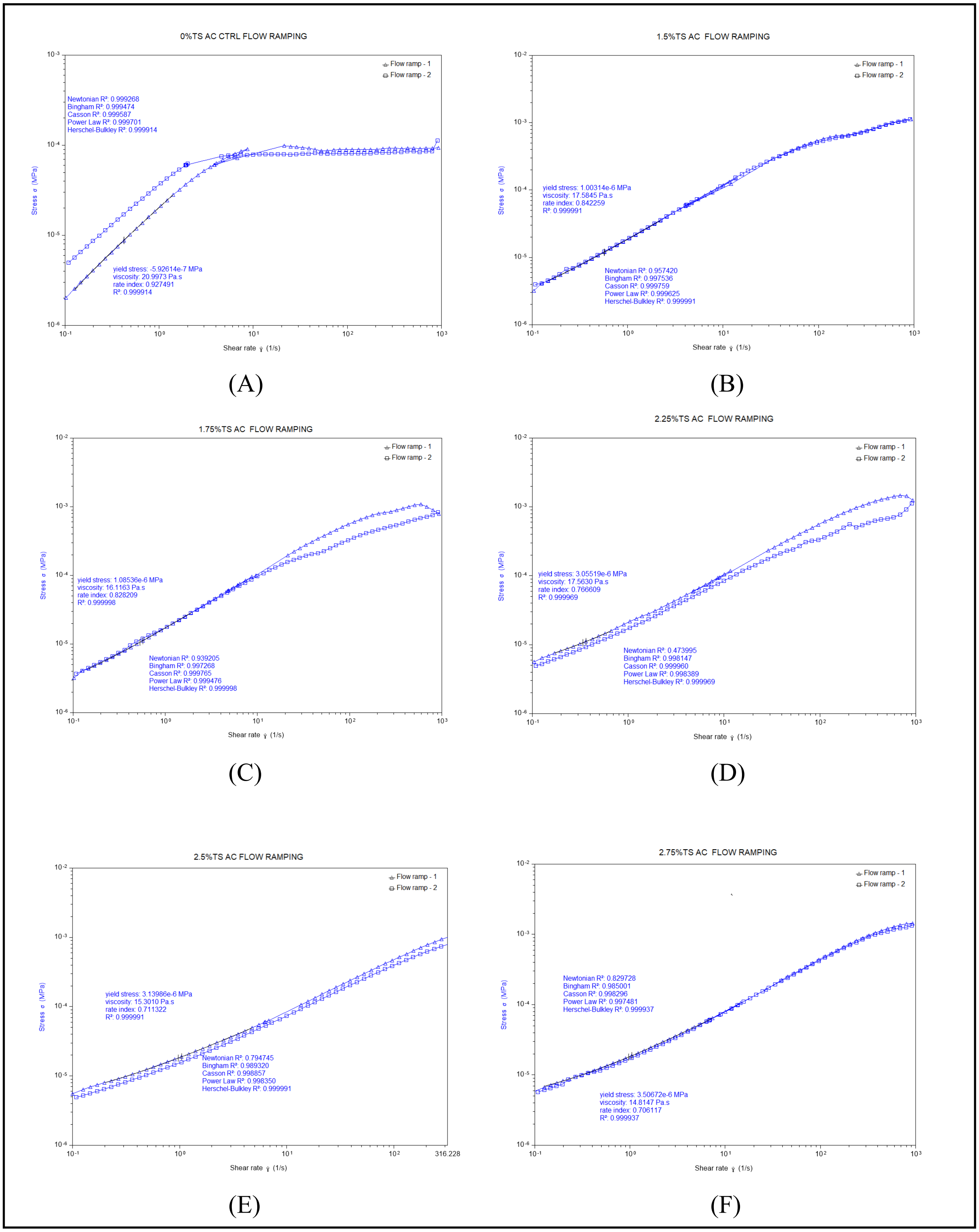



*Figure 4(A)-(F) – Flow ramping curves for different concentration of Acrylates Copolymer.*

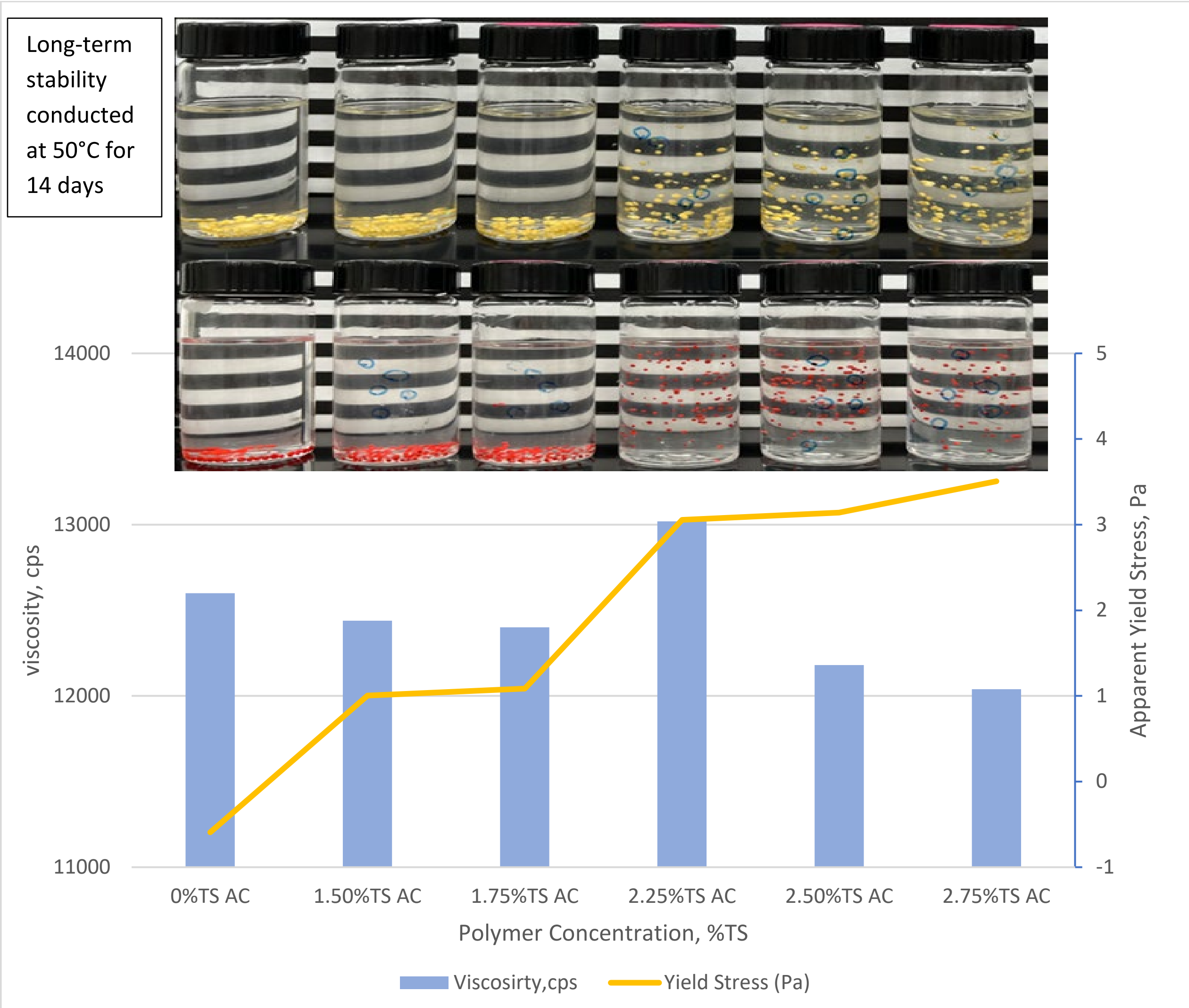



*Chart 1 – Chart showing the correlation of polymer dosage and apparent yield value, Pa.*

We then plotted Chart 1 with apparent yield stress, Pa ($Y_2$-axis) against different polymer concentration (%TS) in the x-axis. Chart 1 has showed apparent yield value has no direct relation with viscosity, cps but correlate with the dosage of Acrylates Copolymer in uses. The higher the %TS of Acylates Copolymer in used help contributing to a higher apparent yield stress, Pa and expecting to provide better suspension ability and long-term product stability.

Based on result of physical long-term stability that conducted at 50°C, both (1) alginate agar based soft breakable beads (red colour), (2) mannitol and cellulose and hydroxypropyl methylcellulose based none-breakable beads (sparkling yellow colour) are well suspended in the cleansing formula that containing 2.25%TS AC, 2.5%TS AC & 2.75%TS AC up to 14days and the long-term stability continues.

Whereas for cleansing formula that has 0%TS AC, 1.5%TS AC and 1.75%TS AC failed to suspend both type of beads and observed right after 1 hour for cleansing formula that act as control and after 24hours for cleansing formula with 1.5%TS AC & 1.75%TS AC.

This phenomenon matches the prediction from amplitude and frequency sweeps where sample 1.75%TS AC had showed character of viscoelastic liquid indicates sample without consistent chemical network. Vise versa, the cleansing formula with higher Acrylates Copolymer (2.5%TS AC) exhibits the structured gel-like state with better gel strain for enhancing better suspension stability.

*Back Acid Thickening.* The correct back acid thickening has showed contributing to apparent yield stress, Pa. We shall first neutralize the cleansing formula to pH6.3 – 6.8 with alkaline and then adjust to reduce to acidic pH. Back acid thickening can be used to further increase the efficiency of the polymer in formulation and/or to formulate products at more acidic pH.

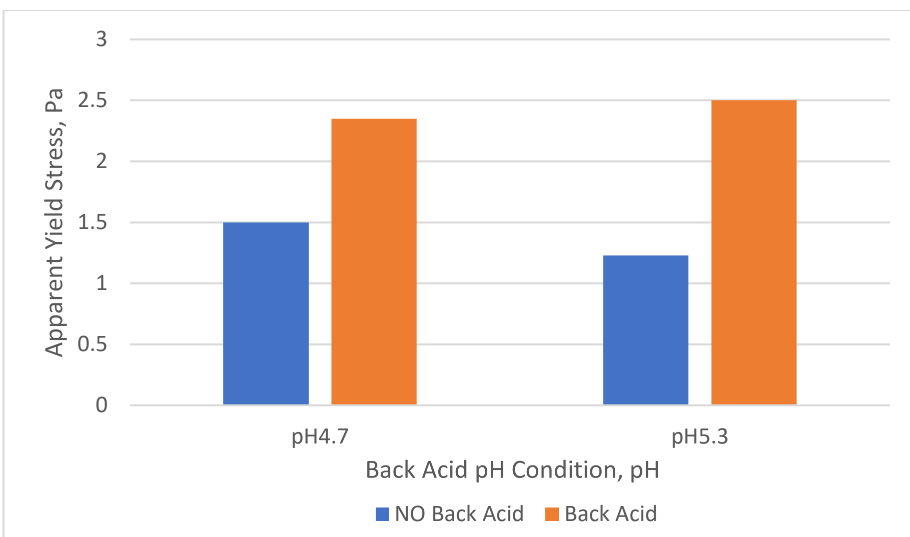



*Chart 2 – Influence of back acid thickening.*

**Discussion.** Oscillation Amplitude is useful method in understand the Arylates Copolymer structural character. Based on the method and results, we can identify the sample that has high possibility to be stable for good suspension performance where sample exhibits more structural gel or solid behavior with Storage modulus G' > loss modulus G" in the LVE range. Phase angle is another important parameter to evaluate to further identify and help verify the polymer structural behavior.

Frequency Sweep has showed information on the behavior and inner structure of polymer as well as on the long-term stability of dispersion.

Flow ramping that adopted to ramp from low to high ramp helps defined the apparent yield stress and again this helps us to cross check the structural character and the apparent yield stress, suggesting the performance of suspension.

**Conclusion**.

The rheology performance study via amplitude sweeps, frequency sweeps and flow ramping method helped to predict long-term stability of suspension system using rheometer.

The rheology test method also serves as an indication if the back-acid mechanism has been applied correctly and hence provide further apparent yield stress, good suspension. Overall, this will be time saving in yield value/ suspension's long-term stability screening.

**Acknowledgments.** Contributions from anyone who does not meet the criteria for authorship should be listed, with permission from the contributor. Financial and material support should also be mentioned.

**Conflict of Interest Statement**. It is the responsibility of the corresponding author to ensure that any conflict of interest of any of the authors is disclosed. A declaration must be made, if there is no conflict of interest, write NONE.

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