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

Liew, Chiew Ngan[1]; Chen, Ye[1]; Yao, Ge[1]; Jin Susie[2]; Xia Siron[2]; Xin Liu[2]
1 Lubrizol Life Science, Lubrizol Southeast Asia (Pte) Ltd. 44 Tanjong Penjuru 609032, Singapore
2 Lubrizol Specialty Chemicals Manufacturing (Shanghai) Co., Ltd, 300 Shu Hui Road, Songjiang District, Shanghai 201611, China

Introduction:

A clear surfactant system is a common cleansing system. Incorporation of beads, mica, and etc. into the clear cleansing system would readily make the product to be outstanding on the shelf. 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 acrylates copolymer (anionic acrylic acid emulsion polymer) are generally best candidates used in providing viscosity, superior suspension, and elegant flow to support aesthetic characteristics mentioned above.

In this study, we evaluate the lightly cross-linked acrylates copolymer (alkaline swellable emulsion, ASE polymer) rheology performance, yield stress in a clear 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. Overall, this will be time saving in yield value/ suspension's long-term stability screening.

Materials & Methods:

Rheology Experiments: -
Geometry: Cone and plate geometry (stainless steel, 40 mm diameter, 1.018° angle)
Sample size: Approximately 2 g of respective cleansing formula's sample per test
Stage: Peltier plate Aluminium
Oscillation Amplitude method: 1 Hz at 25 °C between 0.01% to 500% strain amplitude
Dynamic oscillation method: From 0.01 to 100 Hz at a constant shear strain of 1% in the linear region at 25 °C.
Apparent yield stress: From 0.1 – 1000 1/s shear rate in 300s and vise versa in another 300s at 25 °C.

Red Beads: Alginate agar based soft breakable beads
Yellow Beads: Mannitol and cellulose based none-breakable beads

Table 1 & ***Table 2*** are formulations that prepared for rheology experiments.

Table 1: Acrylates Copolymer Cleansing Formulas

Ingredients	0%TS AC	1.5%TS AC	1.75%TS AC	2.25%TS AC	2.5%TS AC	2.75%TS AC
Deionised 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
Deionised 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

Table 2: Cleansing Formula Prepared by Back Acid Thickening Method

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) then perform back acid		
Total	**100.00**	**100.00**

Results & Discussion:

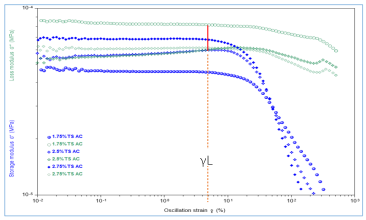


Figure 1(A) – Strain amplitude sweep of different Acrylates Copolymer concentration showing when concentration of Acrylates Copolymer increased change character of a viscoelastic liquid in the LVE range, i.e. G" > G' to gel-like character in the LVE range, i.e. G' > G" (with the limiting yL)

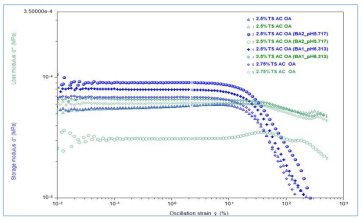
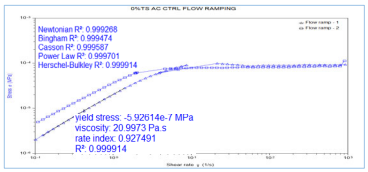


Figure 1(B) – Influence of back acid thickening on the linear viscoelastic region of cleansing formulas containing different concentration of Acrylates Copolymer.

Figure 1(A) shows 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. 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 1(B) shows both back acid samples (1)2.5%TS AC (BA1_pH6.313) and (2)2.5%TS AC (BA2_pH5.717) exhibit character of gel-like in LVE range, G' > G" indicates both samples has better gel strain as compared to the samples without going through the back acid thickening.



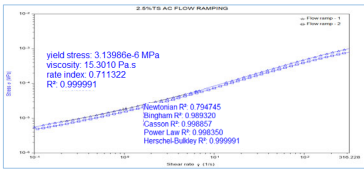


Figure 2(A) – Flow ramping curves for 0%TS AC (control) and **Figure 2(B)** – Flow ramping curves for 2.5%TS of Acrylates Copolymer.

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 2(A) & 2(B)**, we have calculated the apparent yield stress, Pa based on the Herschel/ Bulkley model with the best R2. Control has no polymer and no apparent yield value as predicted. Based on this experiment, the apparent yield value increase with correlation of higher dosage of Acrylates Copolymer in used. Hence as prediction, apparent yield value is dose dependent.

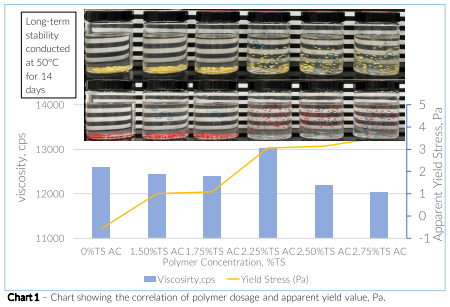


Chart 1 – Chart showing the correlation of polymer dosage and apparent yield value, Pa.

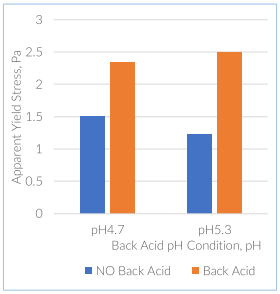


Chart 2 – Influence of back acid thickening.

Chart 1 shows result of physical long-term stability that conducted at 50°C, both red beads and yellow beads 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 up to 28 days at 50°C.

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

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.

Chart 2 shows the correct back acid thickening contributing to higher apparent yield stress, Pa. In order to ensure correct back acid thickening, 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.

Conclusions:

Acrylates Copolymer is an effective rheology modifier providing good yield value, suspension, clarity and it is dose dependent.
Back Acid mechanism further increase the apparent yield stress hence providing better suspension capability, better stability.
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, rheology performance study is time saving in yield value/ suspension's long-term stability screening.

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