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Impact of Biodiesel on Diesel-Based Drilling Fluids: A Laboratory Evaluation

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Abstract

The oil and gas industry is continuously striving to reduce the environmental impact of its operations. In this pursuit biodiesel blended with diesel as base fluids were considered for use in diesel-based drilling fluids (DBDFs) to reduce the environmental impact of such drilling fluids.

Biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats designated B100 and meeting requirements of ASTM D 6751. Biodiesel comprises mainly of methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. Biodiesel is renewable and its low sulfur content produces low sulfur dioxide and sulfides emissions. The biodegradability rate of biodiesel is 98%; twice that of mineral diesel.

This paper provides examples of biodiesel - diesel blended DBDFs, using conventional chemical additives and illustrates the resultant properties.

The scope of work presented here is focused on rheology and chemical titrations, other drilling fluid parameters were not measured. Further investigations may be necessary to fully gauge the effects of biodiesel blended diesel as base fluids in DBDFs.

Introduction

To make diesel-based drilling fluids (DBDFs) more environmentally friendly, research was conducted on blending biodiesel with diesel. The aim of the research was to identify optimum formulations which could be used for drilling and also enhance the biodegradability of cuttings to reduce the overall environmental impact of the DBDFs. This study was undertaken to understand the overall effect and feasibility of using such base oil in land-based drilling operations.

The reason DBDFs were chosen was because they provide certain advantages when compared to more environmentally-friendly water-based drilling fluids (WBMs). These advantages include, excellent lubrication performance, shale inhibition, good wellbore stability, and higher thermal stability.

Presentation of Data and Results

The formulations represented in **Tables 1 to 8** are 1.44 specific gravity (SG) and built on a single blade Hamilton Beach mixer at 4000 rpm for 30 minutes. These samples were then sheared on a Silverson mixer at 6000 rpm to reach an internal fluid temperature of 135°F. All samples rheological properties and chemical titration measurements were done as per API *RP 13B-2*.

Formulations 1 and 2 were chosen to be representative for incumbent DBDFs whose parameters were tested accordingly to establish baseline for the further investigation of formulations containing biodiesel component in the base oil. The low- and high-alkalinity and salinity versions were based on historical data gathered in the field using incumbent DBDFs.

Table 1—Formulation 1 of 100% diesel, 20% by weight CaCl2 (low and high alkalinity versions).

Products, units	Low Alkalinity	High Alkalinity
Diesel, bbl	0.599	0.595
Biodiesel, bbl	0	0
Organophilic Clay, ppb	4.2	4.2
Lime, ppb	8.8	15.5
Emulsifier, ppb	5.9	5.9
Calcium Chloride ($CaCl_2$), ppb	13.78	13.69
Water, bbl	0.148	0.147
Fluid Loss Control (FLC)-1, ppb	2.8	2.8
FLC-2, ppb	3.5	3.5
Graphite blend, ppb	3.5	3.5
Calcium Carbonate ($CaCO_3$)-Sized, ppb	21	21
API Barite, ppb	186.2	181.1
API Evaluation Clay, ppb	35	35

The sample abbreviations used in **Fig. 1** (and all consecutive figures) are:

- BHR- before hot roll/Initial
- HR- after hot roll at 250°F
- SA1-static aged at 80°F for 96 hours
- SA2- static aged at 80°F for 192 hours

Formulation 1 (**Figs. 1 to 3**) rheological properties showed a lower 6 rpm reading with the higher alkalinity version when compared with its low alkalinity counterpart. After exposure to hot roll aging temperature a reduction in measured alkalinity (Pom) was observed.

Table 2— Formulation 2 of 100% diesel, 29% by weight $CaCl_2$ (low and high alkalinity versions).

Products, units	Low Alkalinity	High Alkalinity
Diesel, bbl	0.597	0.593
Biodiesel, bbl	0	0
Organophilic Clay, ppb	4.2	4.2
Lime, ppb	8.8	15.5
Emulsifier, ppb	5.9	5.9
Calcium Chloride (CaCl2), ppb	22.47	22.32
Water, bbl	0.146	0.145
Fluid Loss Control (FLC)-1, ppb	2.8	2.8
FLC-2, ppb	3.5	3.5
Graphite blend, ppb	3.5	3.5
Calcium Carbonate ($CaCO_3$)-Sized, ppb	21	21
API Barite, ppb	178.42	173.42
API Evaluation Clay, ppb	35	35

When Formulation 2 (**Figs. 4 to 6**) is compared to Formulation 1, it can be noted that the overall rheology of these fluids were higher and the decrease in measured alkalinity after heat exposure was higher in the low alkalinity version and similar in the high alkalinity version.

Table 3—Formulation 3 of 100% biodiesel, 20% by weight $CaCl_2$ (low and high alkalinity versions).

Products, units	Low Alkalinity	High Alkalinity
Diesel, bbl	0	0
Biodiesel, bbl	0.599	0.595
Organophilic Clay, ppb	4.2	4.2
Lime, ppb	8.8	15.5
Emulsifier, ppb	5.9	5.9
Calcium Chloride ($CaCl_2$), ppb	13.78	13.69
Water, bbl	0.148	0.147
Fluid Loss Control (FLC)-1, ppb	2.8	2.8
FLC-2, ppb	3.5	3.5
Graphite blend, ppb	3.5	3.5
Calcium Carbonate ($CaCO_3$)-Sized, ppb	21	21
API Barite, ppb	186.2	181.1
API Evaluation Clay, ppb	35	35

Formulation 3 (**Figs. 7 to 9**) represents the 100% biodiesel base oil which was a comparison to Formulation 1 showed extremely high rheology across all shear rates after hot rolling the fluid at 250°F. The 80°F rheology was immeasurable with the VG meter available at hand and the rheology at 150°F was higher when compared to Formulation 1. The alkalinity after hot roll and all subsequent samples was reduced to 0.

Table 4—Formulation 4 of 100% biodiesel, 29% by weight $CaCl_2$ (low and high alkalinity versions).

Products, units	Low Alkalinity	High Alkalinity
Diesel, bbl	0	0
Biodiesel, bbl	0.597	0.593
Organophilic Clay, ppb	4.2	4.2
Lime, ppb	8.8	15.5
Emulsifier, ppb	5.9	5.9
Calcium Chloride ($CaCl_2$), ppb	22.47	22.32
Water, bbl	0.148	0.147
Fluid Loss Control (FLC)-1, ppb	2.8	2.8
FLC-2, ppb	3.5	3.5
Graphite blend, ppb	3.5	3.5
Calcium Carbonate ($CaCO_3$)-Sized, ppb	21	21
API Barite, ppb	178.42	173.42
API Evaluation Clay, ppb	35	35

Formulation 4 (**Figs. 10 to 12**) when compared to Formulation 2 exhibited high rheological profile and no presence of alkalinity after hot rolling the fluid samples. This behavioral relationship was similar to Formulation 3 and 1 which were lower salinity counterparts of biodiesel and diesel base oil respectively.

Table 5—Formulation 5 of 90% diesel/10% biodiesel, 20% by weight $CaCl_2$ (low and high alkalinity versions).

Products, units	Low Alkalinity	High Alkalinity
Diesel, bbl	0.5391	0.5355
Biodiesel, bbl	0.0599	0.0595
Organophilic Clay, ppb	4.2	4.2
Lime, ppb	8.8	15.5
Emulsifier, ppb	5.9	5.9
Calcium Chloride ($CaCl_2$), ppb	13.78	13.69
Water, bbl	0.148	0.147
Fluid Loss Control (FLC)-1, ppb	2.8	2.8
FLC-2, ppb	3.5	3.5
Graphite blend, ppb	3.5	3.5
Calcium Carbonate ($CaCO_3$)-Sized, ppb	21	21
API Barite, ppb	186.2	181.1
API Evaluation Clay, ppb	35	35

Formulation 5 (**Figs. 13 to 15**) represents the 10% biodiesel

component of total base oil used and was used to evaluate performance as compared to Formulation 1. When you compare the two formulations it can be concluded that the rheological profile was higher than Formulation 1 but lower to its 100% biodiesel counterpart i.e. Formulation 3.

The alkalinity behavior in Formulation 5 was like that of Formulation 1 where measurement of the same was possible even after hot rolling the sample, however the initial measurements were comparatively lower than Formulation 1. The behavior of alkalinity seen in Formulation 5 was unlike that of Formulation 3 where alkalinity measurement reduced to 0 after hot roll aging.

Table 6—Formulation 6 of 90% diesel/10% biodiesel, 29% by weight $CaCl_2$ (low and high alkalinity versions).

Products, units	Low Alkalinity	High Alkalinity
Diesel, bbl	0.5373	0.5337
Biodiesel, bbl	0.0597	0.0593
Organophilic Clay, ppb	4.2	4.2
Lime, ppb	8.8	15.5
Emulsifier, ppb	5.9	5.9
Calcium Chloride ($CaCl_2$), ppb	22.47	22.32
Water, bbl	0.146	0.145
Fluid Loss Control (FLC)-1, ppb	2.8	2.8
FLC-2, ppb	3.5	3.5
Graphite blend, ppb	3.5	3.5
Calcium Carbonate ($CaCO_3$)-Sized, ppb	21	21
API Barite, ppb	178.42	173.42
API Evaluation Clay, ppb	35	35

Formulation 6 (**Figs. 16 to 18**) represents the 10% biodiesel addition analog for Formulation 2 were we can observe higher overall rheology for Formulation 6. Additionally, higher alkalinity samples exhibited a higher viscosity profile regarding high shear rate viscosities and lower viscosity profile on low shear rate viscosities when compared with low alkalinity versions.

The initial alkalinities measured on Formulation 6 were lower than Formulation 2 but after hot roll the behavior was comparable.

Table 7—Formulation 7 of 85% Diesel/15% Biodiesel, 20% by weight $CaCl_2$ (low and high alkalinity versions).

Products, units	Low Alkalinity	High Alkalinity
Diesel, bbl	0.5092	0.5058
Biodiesel, bbl	0.0899	0.0893
Organophilic Clay, ppb	4.2	4.2
Lime, ppb	8.8	15.5
Emulsifier, ppb	5.9	5.9
Calcium Chloride ($CaCl_2$), ppb	13.78	13.69
Water, bbl	0.148	0.147
Fluid Loss Control (FLC)-1, ppb	2.8	2.8
FLC-2, ppb	3.5	3.5
Graphite blend, ppb	3.5	3.5
Calcium Carbonate ($CaCO_3$)-Sized, ppb	21	21
API Barite, ppb	186.2	181.1
API Evaluation Clay, ppb	35	35

Formulation 7 (**Figs. 19 to 21**) represents the 15% biodiesel addition analog of Formulation 1. The behavior exhibited by Formulation 7 was a higher rheological profile when compared to Formulation 1, and when compared with Formulation 5 (10% biodiesel) showed a lower profile on the lower alkalinity version only. The higher alkalinity version of Formulation 7 exhibited higher rheological profile when compared to Formulation 5 and Formulation 1.

The decrease in alkalinity as observed in Formulation 7 was comparable to Formulation 1 on the lower alkalinity version. However, when the high alkalinity version is compared to the similar analog of Formulation 1 we can observe that the alkalinity measured is reduced to 0, a behavior observed in Formulation 3 (100% biodiesel).

Table 8—Formulation 8 of 85% diesel/15% biodiesel, 29% by weight $CaCl_2$ (low and high alkalinity versions).

Products, units	Low Alkalinity	High Alkalinity
Diesel, bbl	0.5075	0.5041
Biodiesel, bbl	0.0896	0.089
Organophilic Clay, ppb	4.2	4.2
Lime, ppb	8.8	15.5
Emulsifier, ppb	5.9	5.9
Calcium Chloride (CaCl2), ppb	22.47	22.32
Water, bbl	0.146	0.145
Fluid Loss Control (FLC)-1, ppb	2.8	2.8
FLC-2, ppb	3.5	3.5
Graphite blend, ppb	3.5	3.5
Calcium Carbonate ($CaCO_3$)-Sized, ppb	21	21
API Barite, ppb	178.42	173.42
API Evaluation Clay, ppb	35	35

Formulation 8 (**Figs. 22 to 24**) represents the 15% biodiesel analog of Formulation 2 which showed higher rheological profile when compared to Formulation 2. The behavior of decrease in alkalinity measurements after hot rolling the fluid sample and eventually reducing to 0, was comparable to Formulation 4 (100% biodiesel).

The study lead to observations regarding the unique behavior of biodiesel blended fluids to changes in alkalinity, rheology and the impact of application of heat (i.e., hot roll). It is evident that the rheological profiles as observed at 80°F is higher and in some cases, is unreasonably thick in nature when compared to DBDFs. This could lead to potential problems with storage of such fluids under ambient temperature conditions under low or no shear for extended periods of time.

Maintaining alkalinity control of the fluids with biodiesel is difficult and additions of lime lead to higher rheological profiles observed. Exposing these fluids to heat results in a reduction of overall measured alkalinity (Pom) and most certainly followed by an increased rheological profile. This would indicate that the feasibility of mixing biodiesel with diesel should be carefully considered and its impact on drilling operations kept in mind before they are considered for application.

Conclusions

1) High pH environment created by addition of lime results in the mono alkyl-esters to hydrolyze into fatty acids and alcohol. The fatty acids then react with free calcium ions resulting into calcium grease leading to high rheology profiles
2) Exposure to heat reduces alkalinity
3) Alkalinity decreases with increase in amount of biodiesel in the base fluid
4) Formulations which show alkalinity values of 0.5 or lower exhibit higher rheology when compared to those which show more alkalinity
5) The rheological profiles of the blended drilling fluids when checked at 150°F were vastly different from its behavior at 80°F
6) Increasing the biodiesel content lead to increase in rheology

Acknowledgments

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References

1. API RP 13B-2, Fifth Edition April 2014.
2. Wang M., Sun M., Shang H., Fan S., Liu M., Liu F., SPE 155578 "Biodiesel-based Drilling Fluids"

Appendices

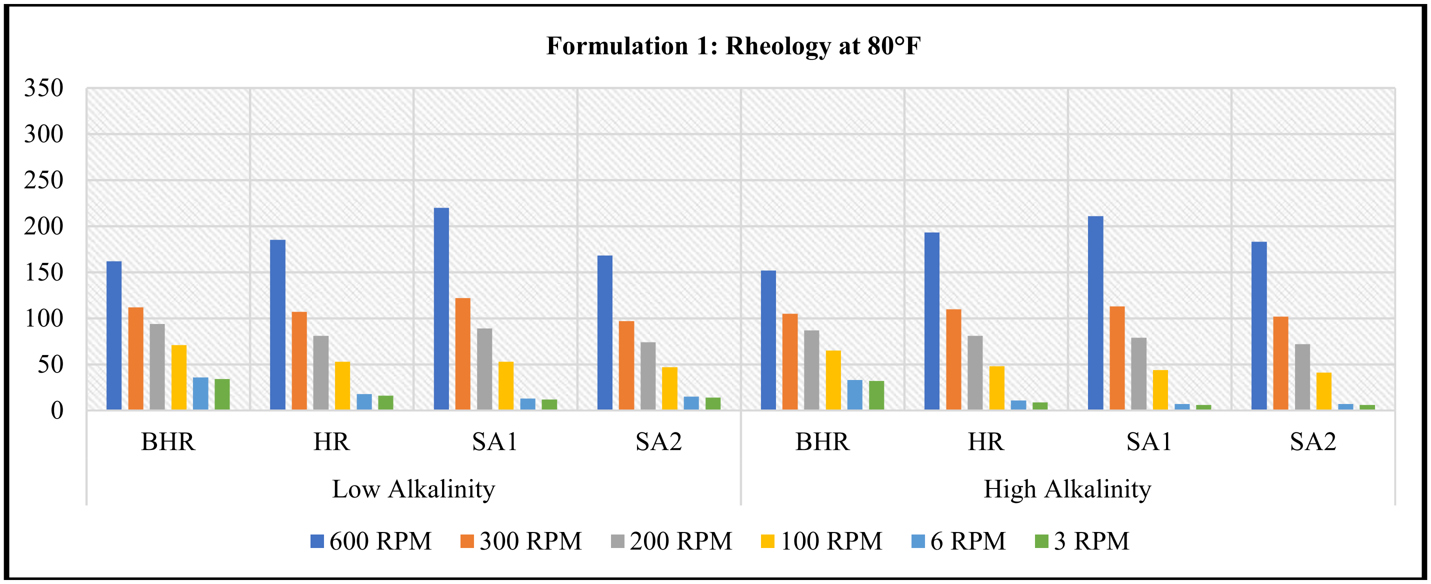

Fig. 1—Formulation 1 depicting lower 6 rpm readings for the high alkalinity compared to the low alkalinity versions.

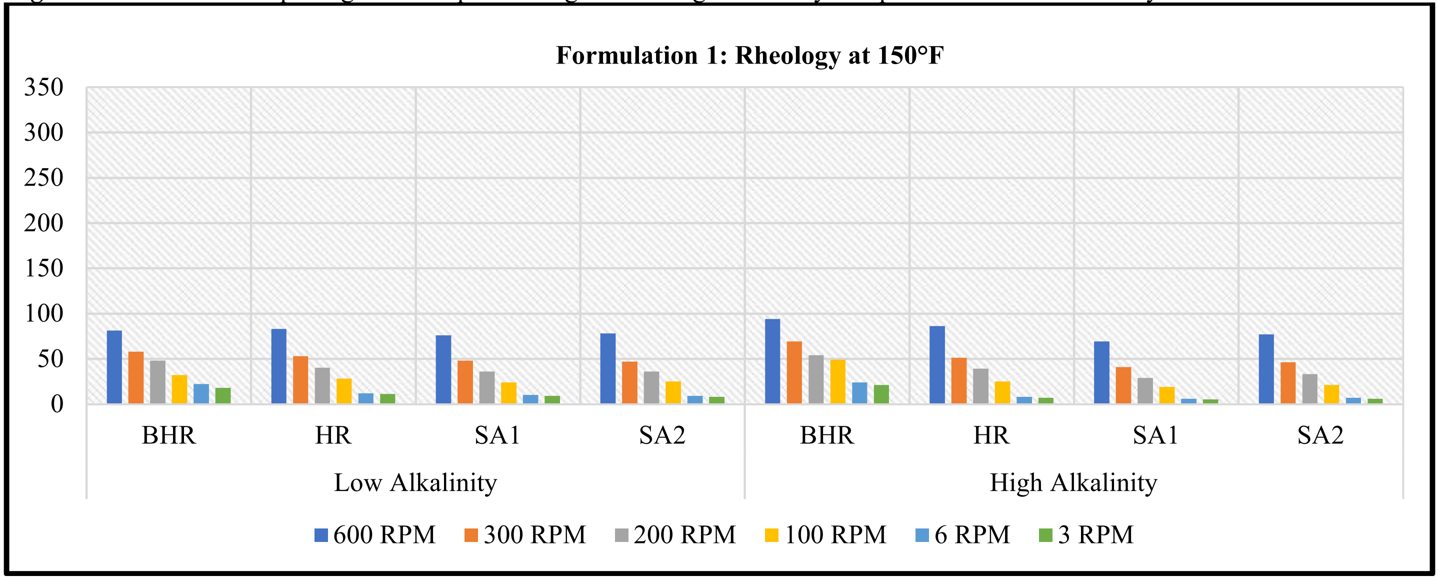

Fig. 2—Formulation 1 depicting lower 6 rpm readings for high alkalinity when compared to low alkalinity versions.

Fig. 3—Formulations 1 changes in Pom (measured); the heat exposure reduces alkalinity.

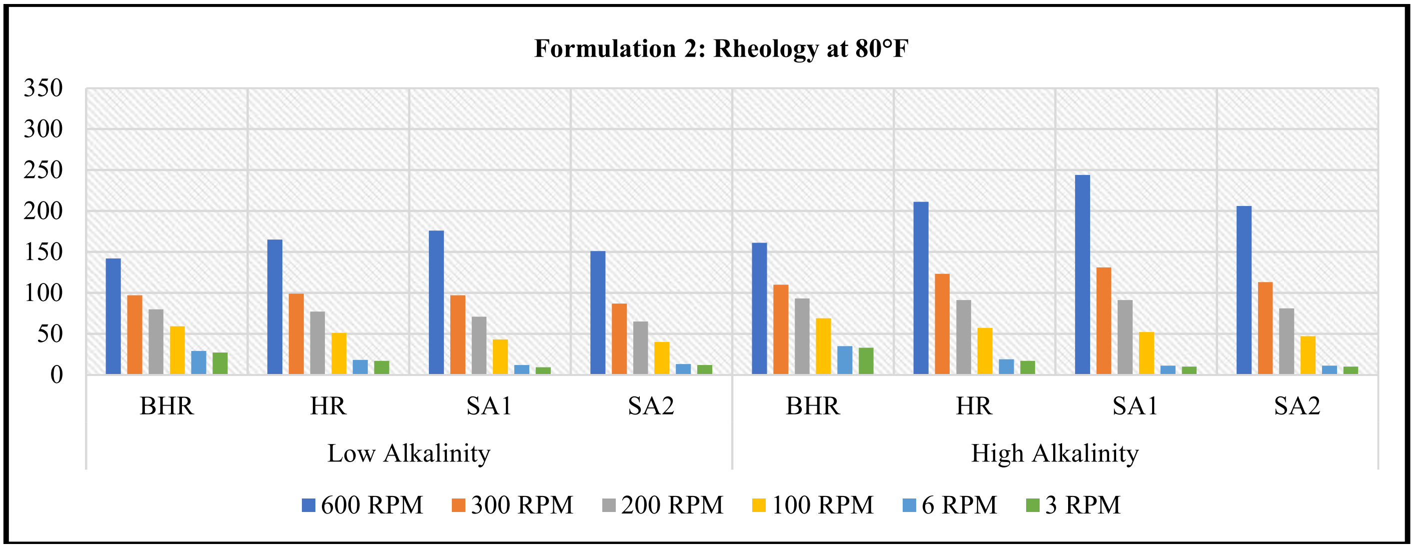

Fig. 4—Formulation 2 is a high alkalinity sample that is thicker than the Formulation 1 high alkalinity sample (Fig. 1).

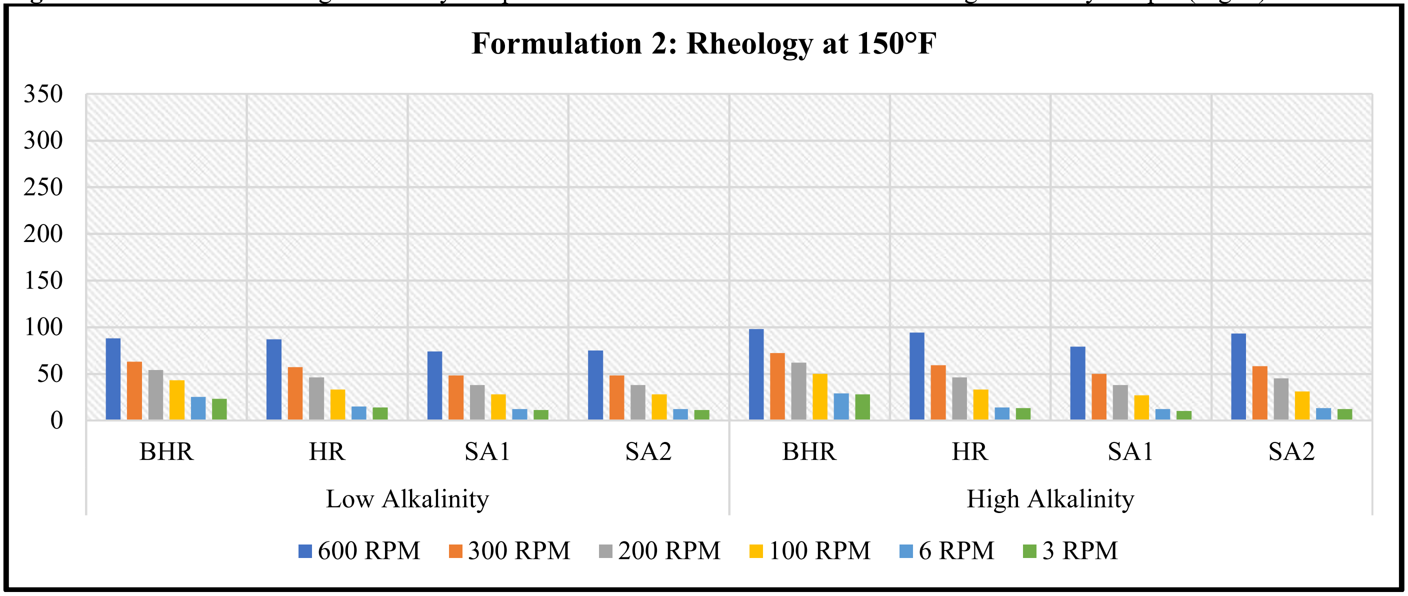

Fig. 5—Formulation 2 has a thicker rheology when compared to Formulation 1 (Fig. 2).

Fig. 6—Formulation 2 shows changes in Pom (measured); a higher rate of reduction in alkalinity after heat exposure in a low alkalinity environment when compared to Formulation 1 (Fig. 3).

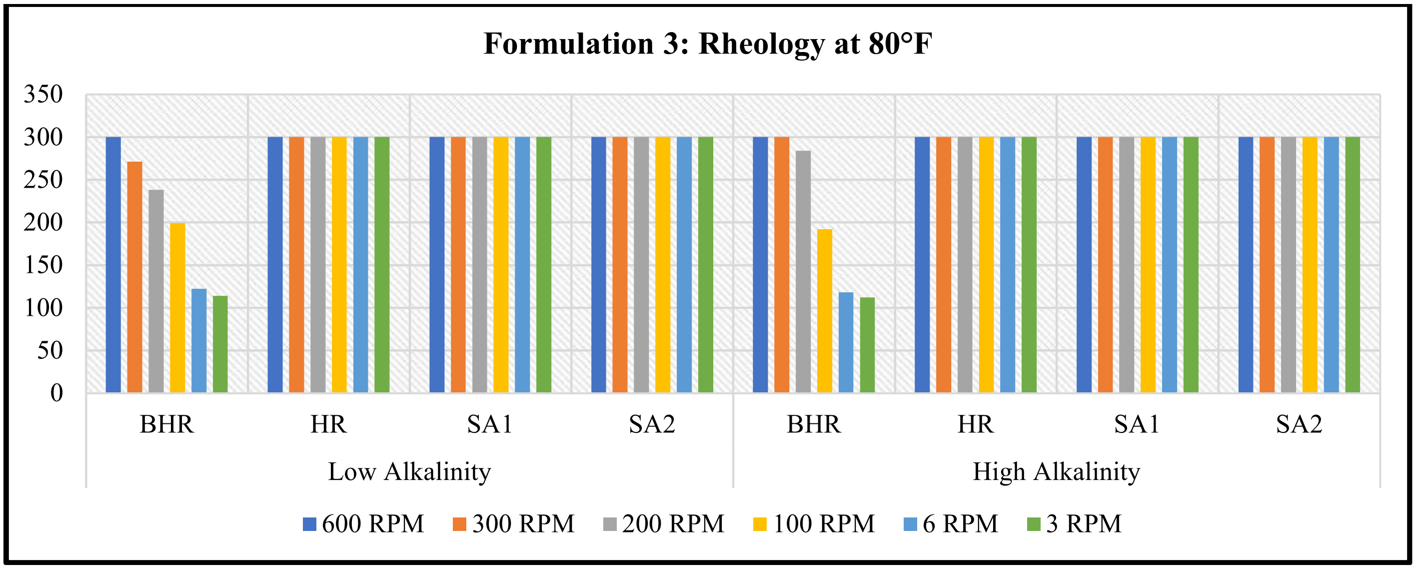

Fig. 7—Formulation 3[1] displays an overall thicker rheology when compared to Formulation 1 (Fig. 1).

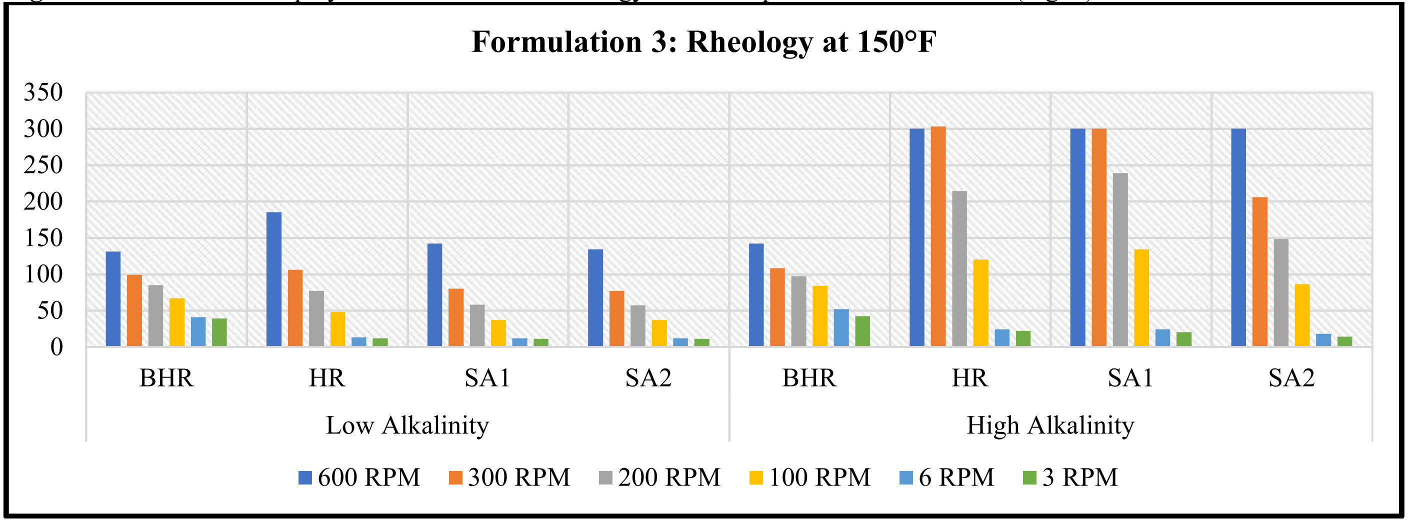

Fig. 8— Formulation 3[1] has a thicker rheology with higher alkalinity compared to Formulation 1

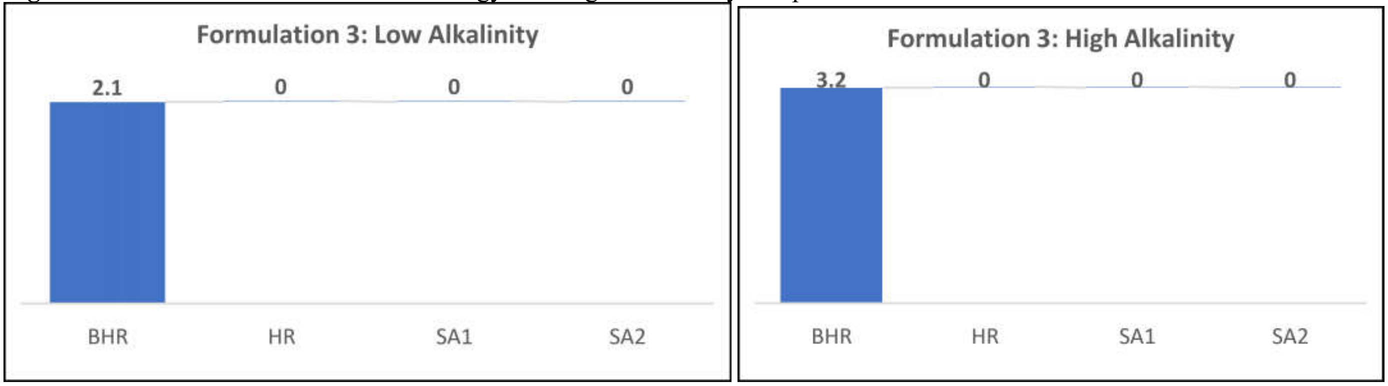

Fig. 9—Formulation 3 shows changes in Pom (measured); a reduction in alkalinity after exposure to heat and initial alkalinity lower when compared to Formulation 1 (Fig. 3).

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[1] All rheological values which were out of scale for the rheometer have been represented as 300 on the figures

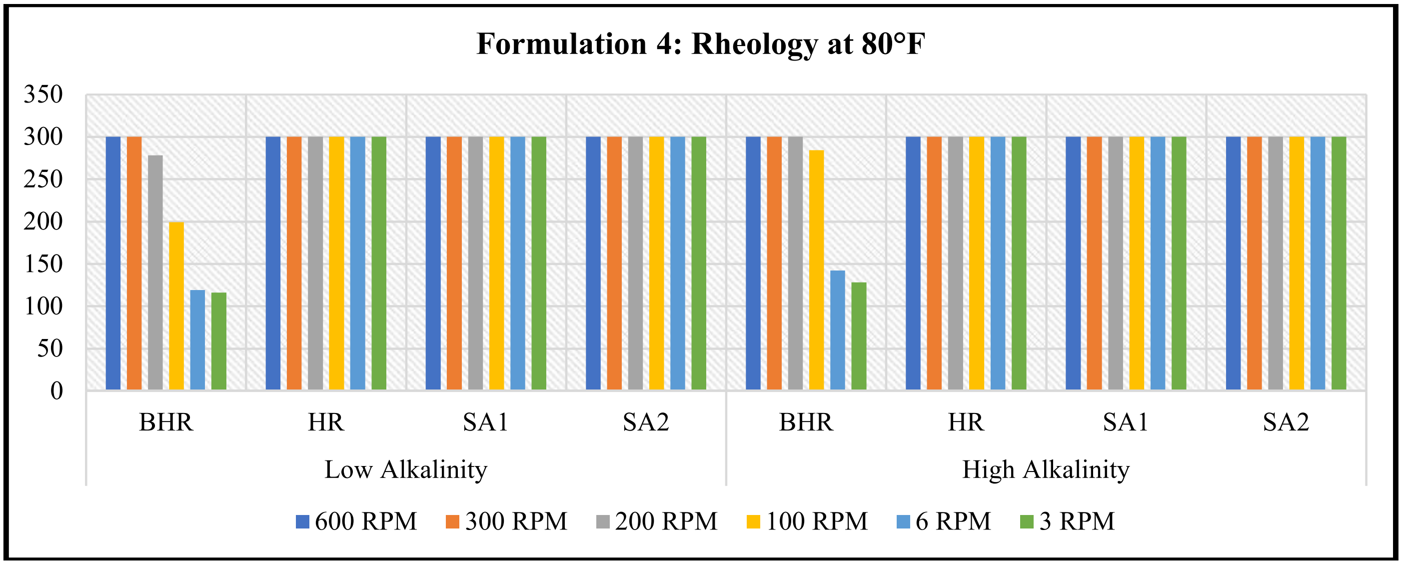


Fig. 10—Formulation 4[1] showed overall thicker rheology when compared to Formulation 2 (Fig. 4).

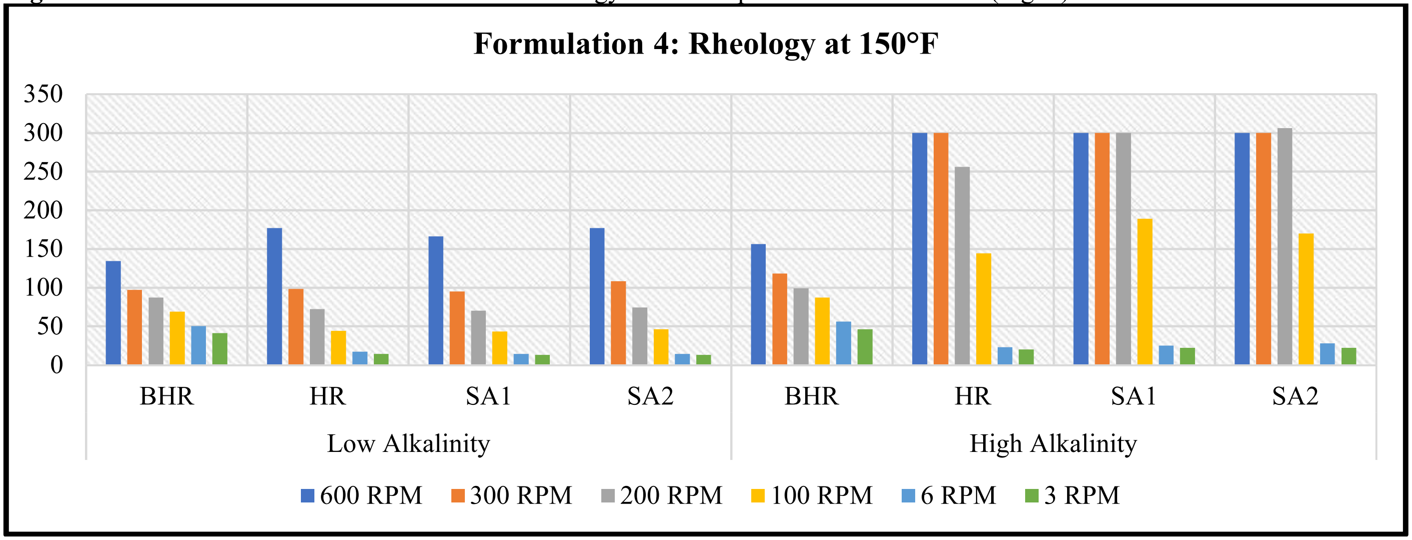


Fig. 11—Formulation 4[1] showed thicker rheology when compared to Formulation 2 (Fig. 5).

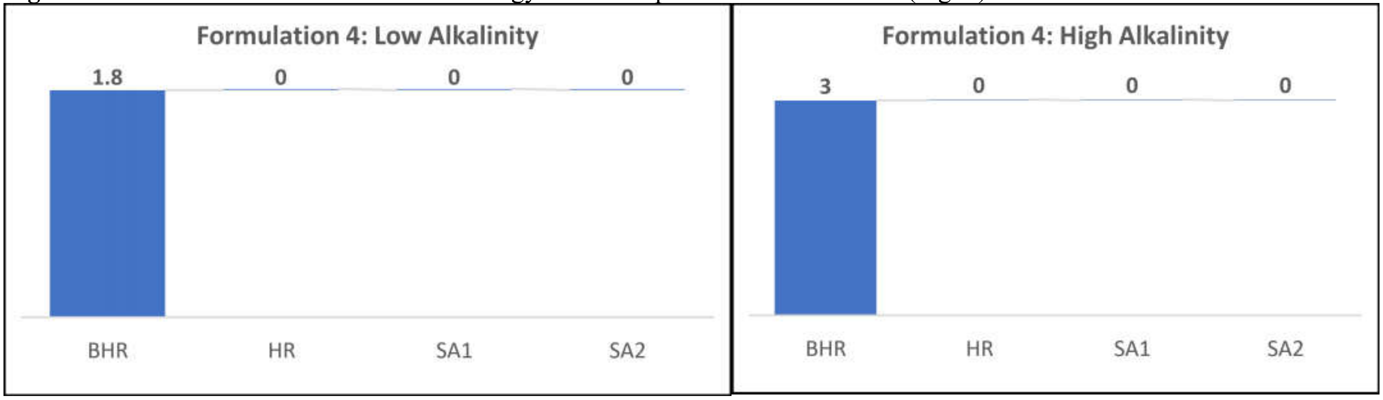


Fig. 12—Formulation 4 shows changes in Pom (measured); there were lower initial alkalinities when compared to Formulation 2 (Fig. 6).

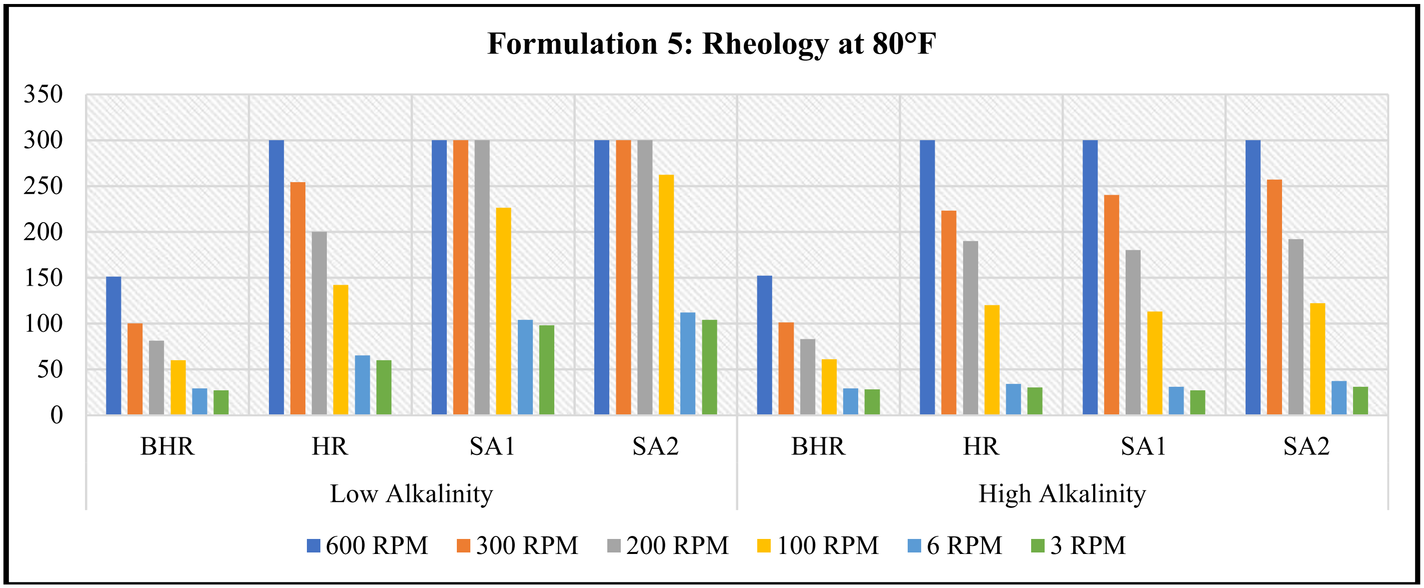


Fig. 13—Formulation 5[1] showed higher rheology than Formulation 1 (Fig. 1) and lower rheology than Formulation 3 (Fig. 7).

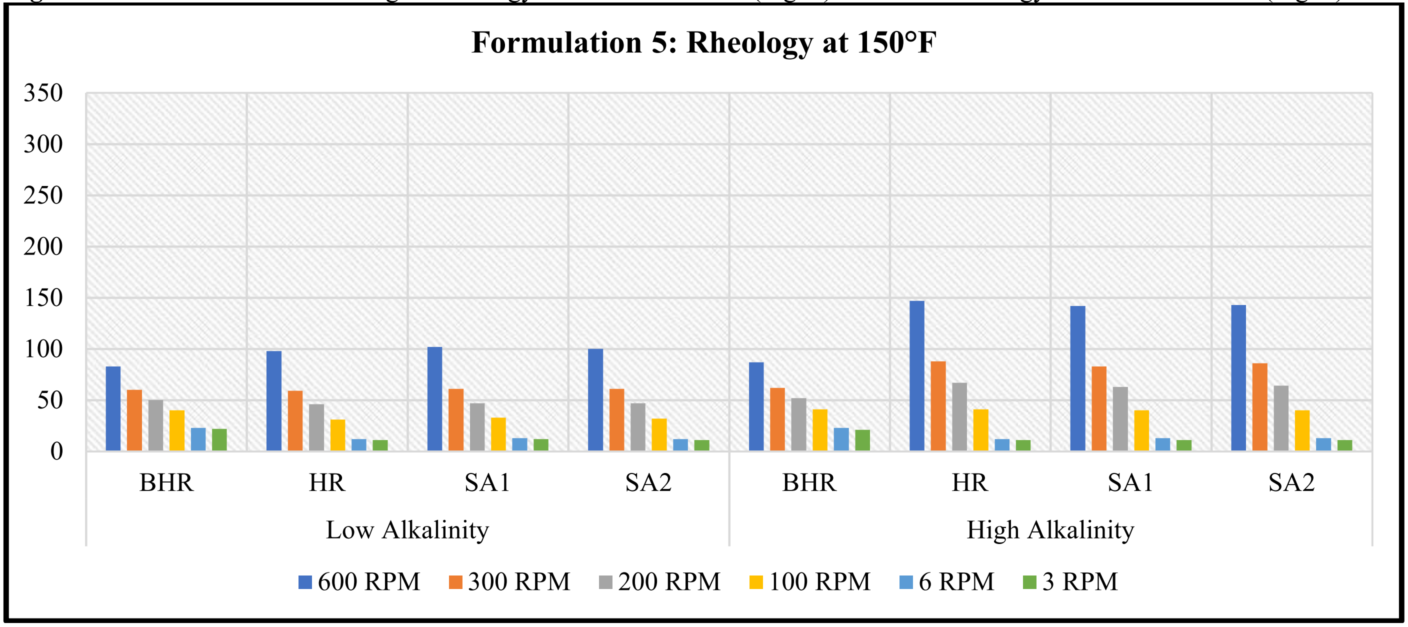


Fig. 14—Formulation 5 showed higher rheology than Formulation 1 (Fig. 2) and lower rheology than Formulation 3 (Fig. 8).

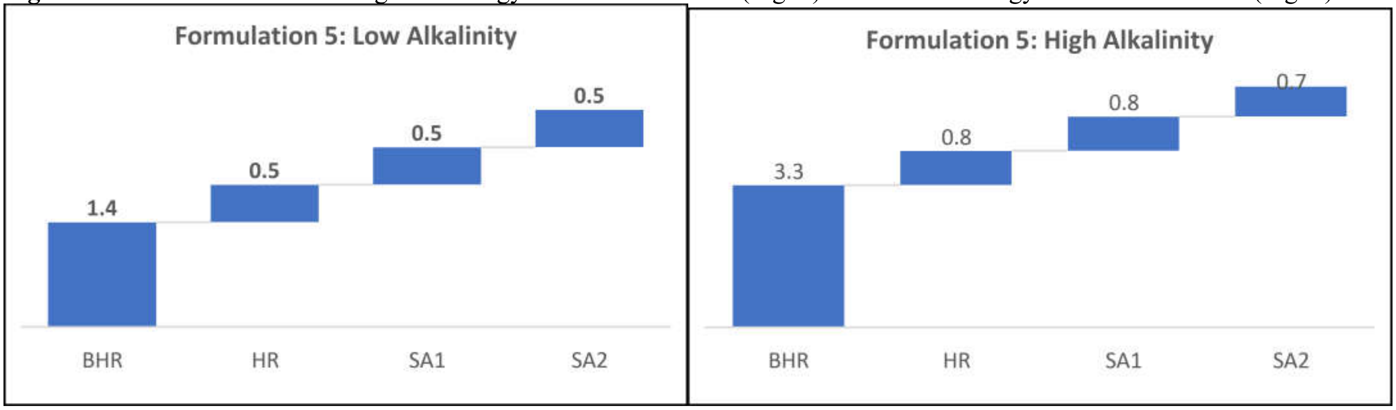


Fig. 15—Formulation 5 showed changes in Pom (measured); the Pom decreases with heat exposure, but there is the presence of alkalinity after aging that was not observed in Formulation 3 (Fig. 9).

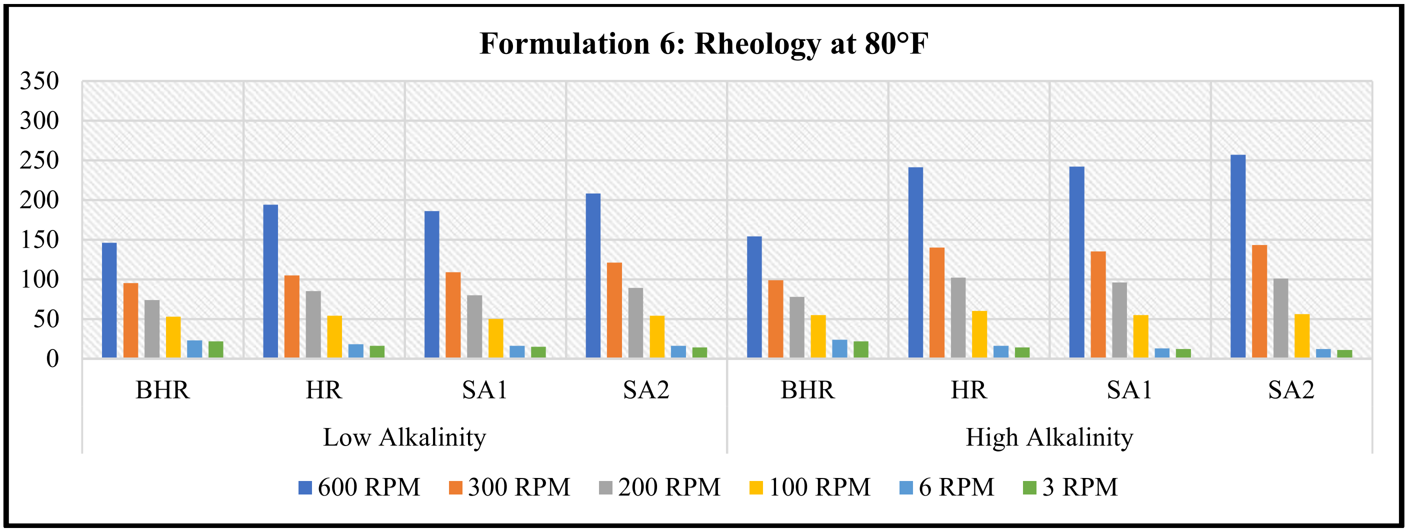


Fig. 16—Formulation 6 showed lower rheology when compared to Formulation 5 (Fig. 13).

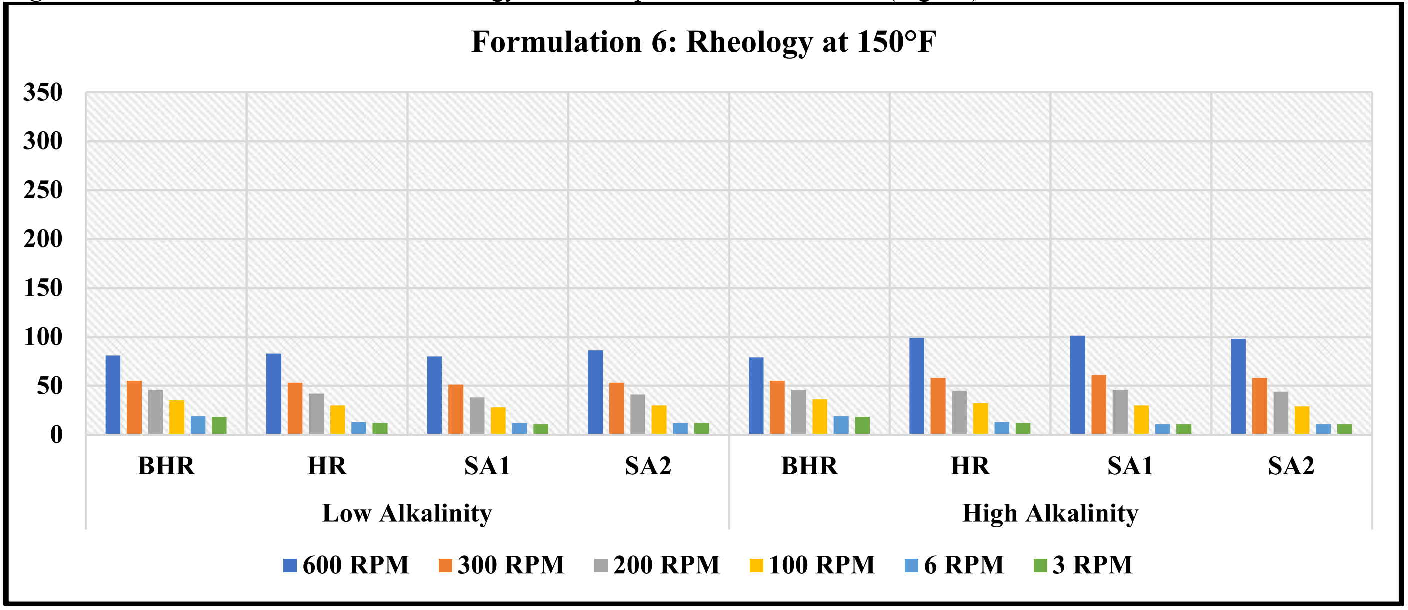


Fig. 17—Formulation 6 showed lower rheology when compared to Formulation 5 (Fig. 14).

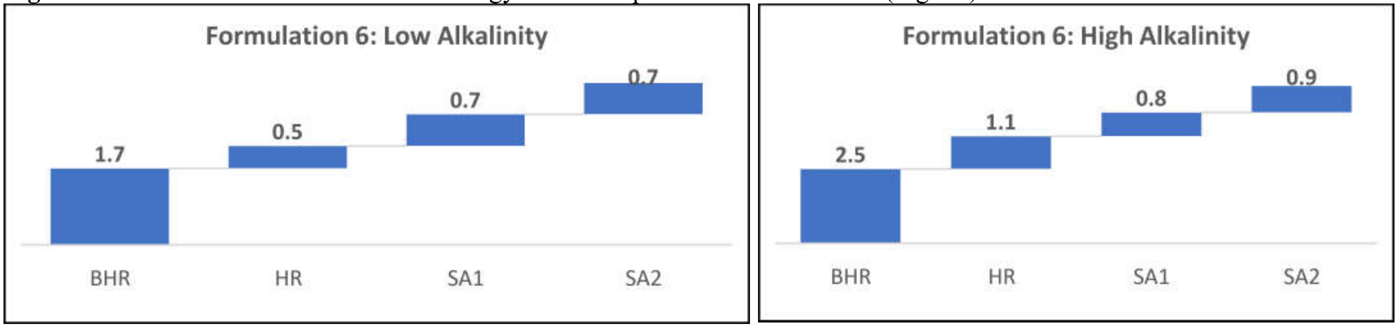


Fig. 18—Formulation 6 showed changes in Pom (measured); there are similar trends after aging between Formulations 5 and 6 (Fig. 15).

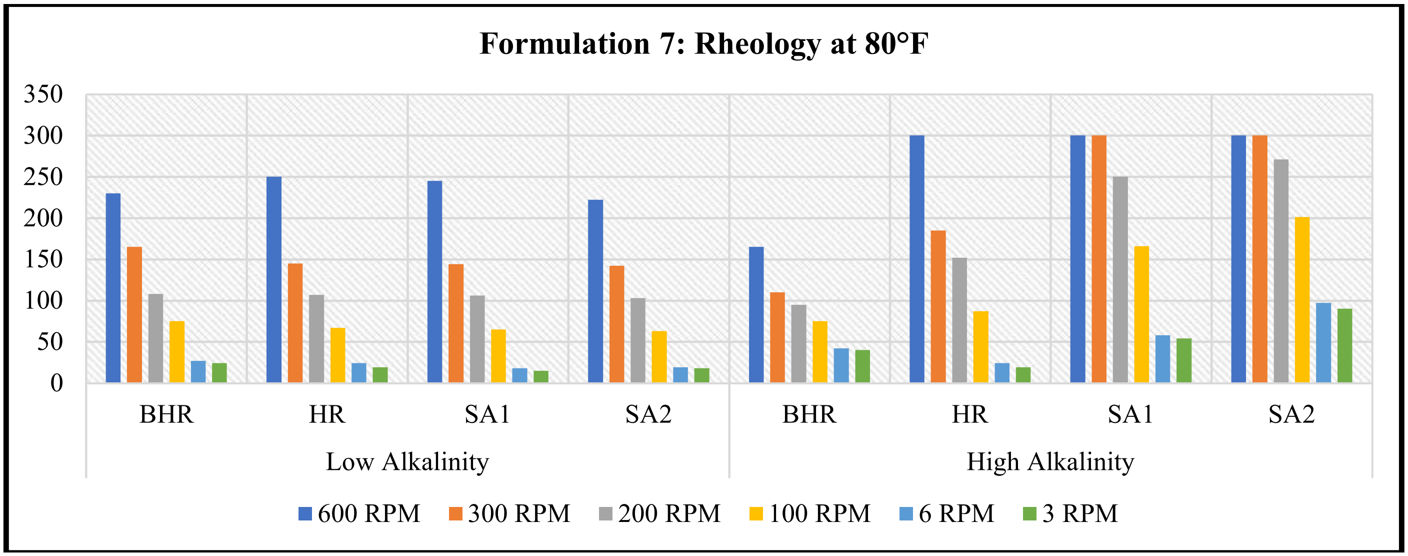

Formulation 7: Rheology at 80°F

Fig. 19—Formulation 7[1] showed higher rheology with the high alkalinity version when compared to Formulation 5 (Fig. 13).

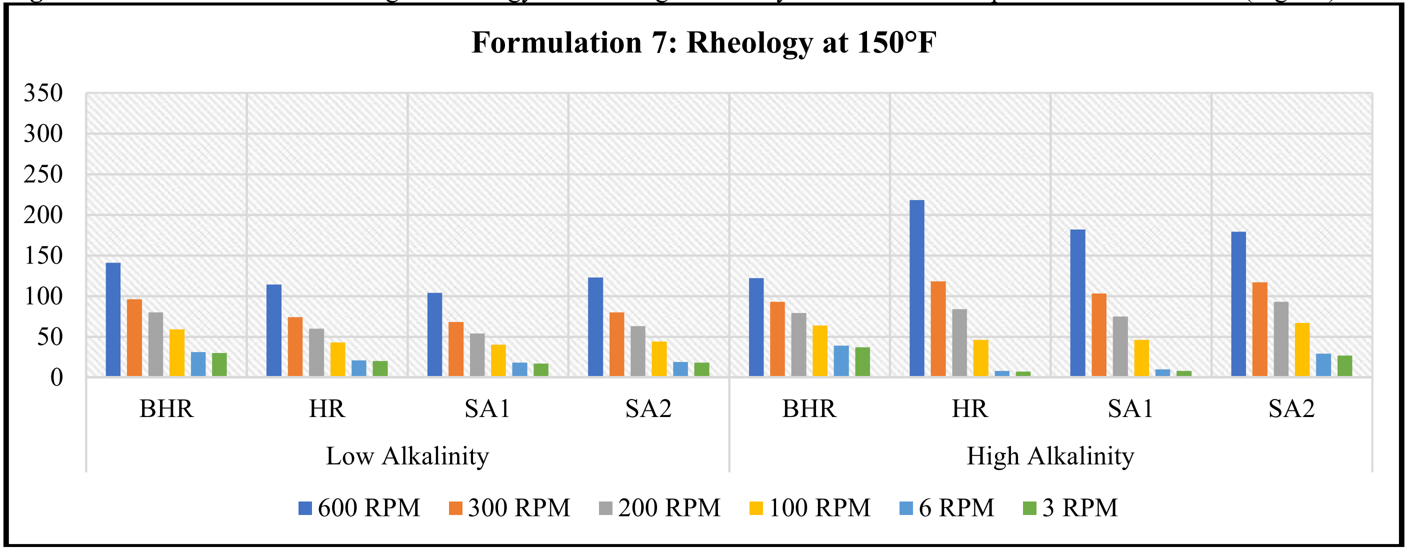
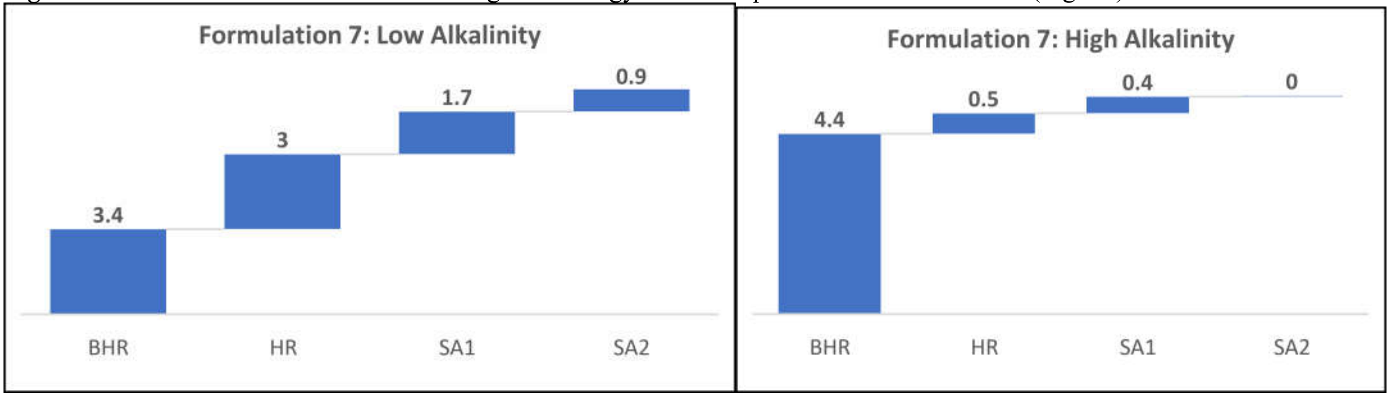

Formulation 7: Rheology at 150°F

Fig. 20—Formulation 7 showed an overall higher rheology when compared with Formulation 5 (Fig. 14).


Formulation 7: Low Alkalinity

Formulation 7: High Alkalinity

Fig. 21—Formulation 7 showed changes in Pom (measured); the alkalinity reduced to 0 on the high alkalinity sample. A similar behavior was seen in Formulation 3 (Fig. 15).

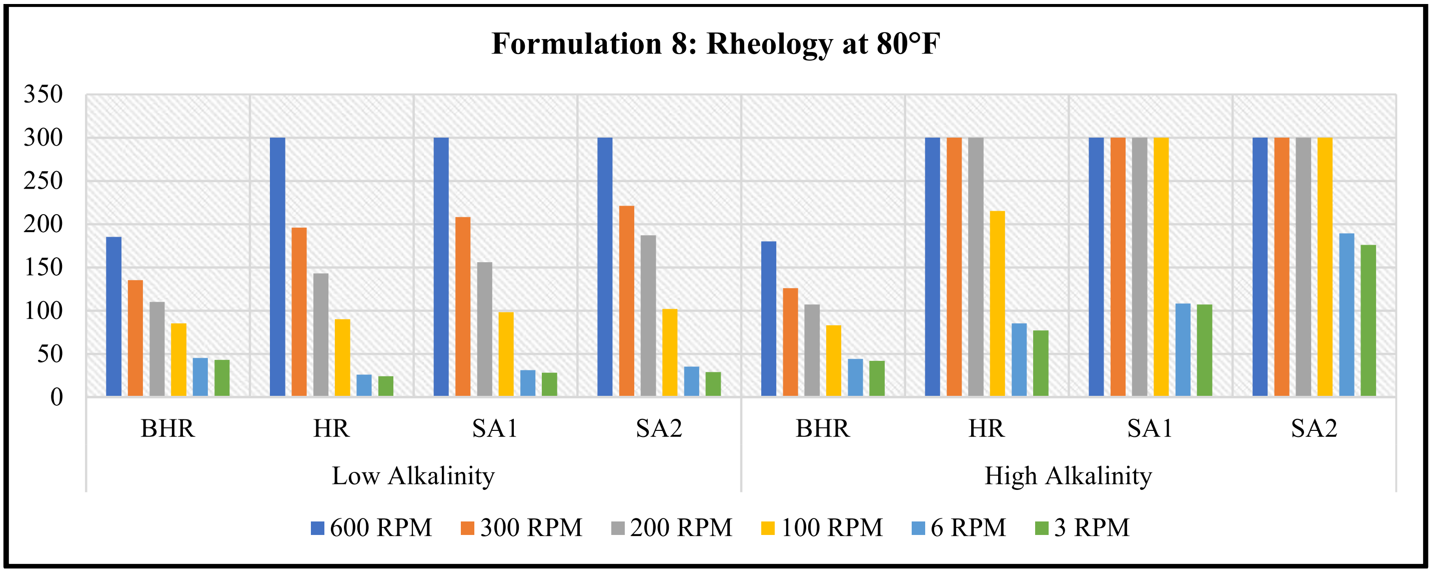


Fig. 22—Formulation 8[1] exhibited a higher rheology when compared to Formulation 6 (Fig. 16).

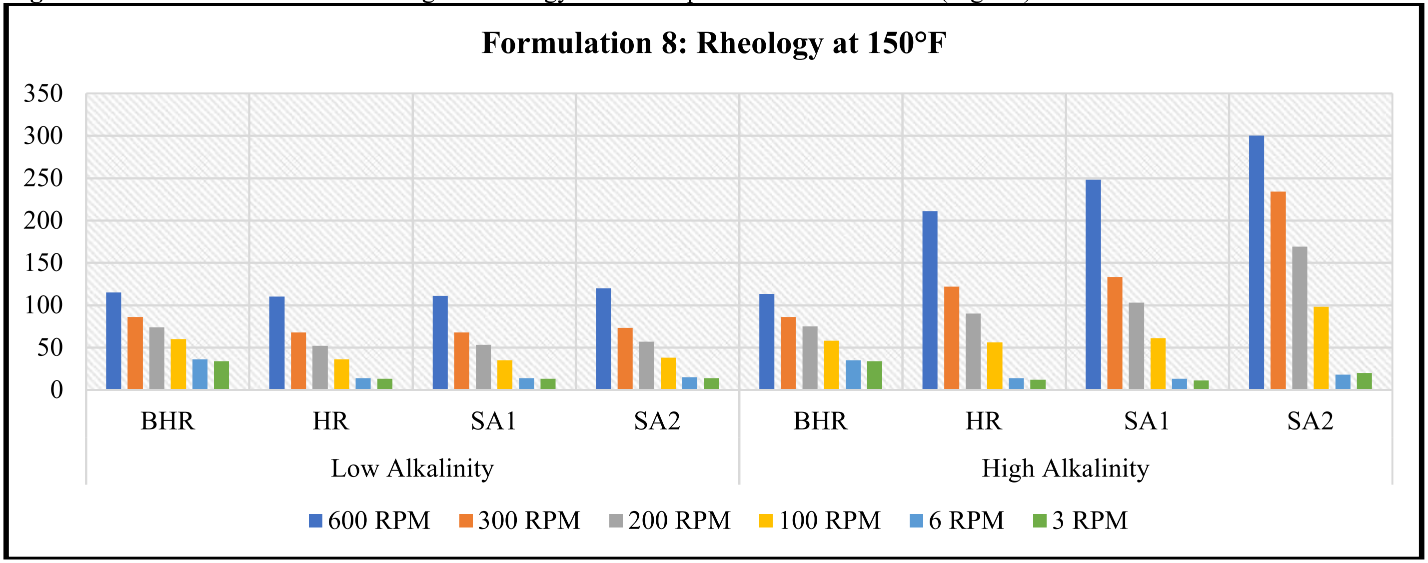


Fig. 23—Formulation 8[1] exhibited a higher rheology when compared to Formulation 6 (Fig. 17).

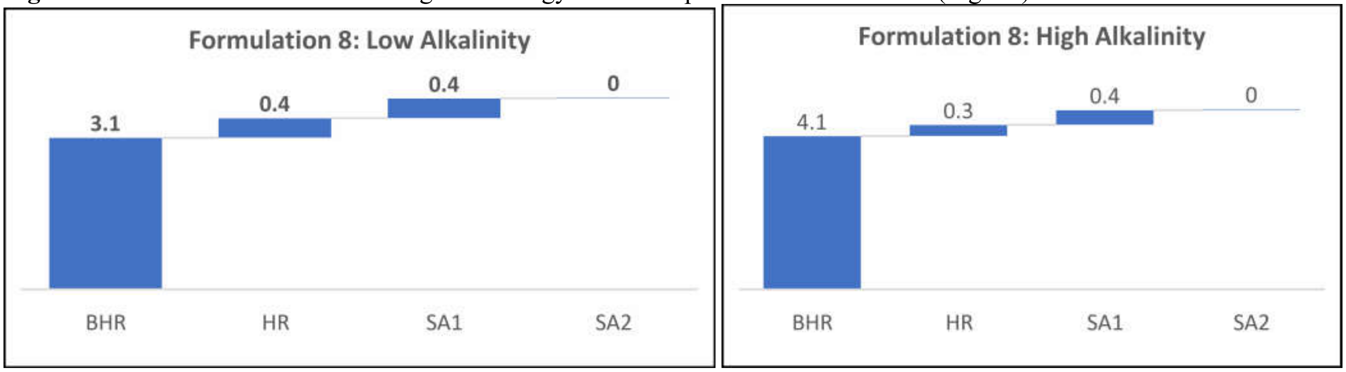


Fig. 24—Formulation 8 showed changes in Pom (measured); the alkalinity reduced to 0 in both versions when compared to Formulation 7 (Fig. 21).