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Fluid Loss Control in Water and Oil-Based Drilling Fluids using Amphipathic Star Shaped Polymer

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30% of this paper comes from “A novel star polymer for regulating fluid loss in oil-based mud under high temperature conditions,” published in Journal of Molecular Liquids, in November 2023.

Abstract

Methods, Procedures, Process: In this study, a class of new star homemade polymers was used as fluid loss control agents in either water or oil-based drilling fluids depending on its hydrophilic-lyophilic balance (HLB). The polymer was designed using hydrophilic and lyophilic monomer functionalities to create blocks with a tunable hydrophilic-lyophilic balance (HLB).

Results, Observations, Conclusions: Performance testing under high-temperature conditions was conducted using water or oil-based drilling fluids, and the results showed that the star copolymer was highly effective in reducing fluid loss and generating a thin filter cake. The study also showed that the star polymer is beneficial for enhancing the low-end rheology without obviously increase of the plastic viscosity. For oil-based mud, the emulsion stability outperforms other commercial fluid loss control products-based muds due to the amphipathic nature of the star polymer.

Novel/Additive Information: The polymer's star configuration and amphipathic nature offers superior fluid control abilities, without causing significant increases in the drilling mud's PV and AV. Additionally, it enhances the low-end rheology over a wide range of temperatures, thereby improving its ability to suspend cuttings. The findings of this research provide significant understanding for the advancement of fluid loss control additives in drilling fluids, thereby aiding the development of next-generation solutions for the drilling industry.

Introduction

Developing petroleum reservoirs is a costly endeavor, with drilling standing out as the most expensive phase(Lukawski et al. 2014). On the flip side, drilling fluid(Rana, Khan, and Saleh 2021; Sahu, Kumar, and Sangwai 2020) plays a crucial role in drilling operations by cooling the drill bit, elevating cuttings from the bottom hole to the surface, and managing subsurface pressure to ensure wellbore stability. This fluid, a complex mixture of solids, liquids, and gases, is categorized into different types based on the base fluids utilized. These types include water-based mud (WBM), oil-based mud (OBM), and foam drilling mud. Water-based mud(Dye et al. 2006; Ewy and Morton 2009; Gbadamosi et al. 2019; Mohanty et al. 2022; Mühlstedt et al. 2021; Fei Liu et al. 2022) is extensively employed in drilling due to its minimal environmental impact; however, in scenarios involving water-sensitive formations like shale or high-temperature reservoirs, oil-based mud becomes necessary. Comprising a blend of oil, water, and various additives such as emulsifiers(Celino et al. 2022; Y. Chen, Song, and Tan 2022), weighting agents, and viscosifiers (Ghavami et al. 2018), oil-based mud(Adewale and Ogunrinde 2010; Aston et al. 2002; Davies et al. 1984; Yan et al. 2023; Hajiabadi et al. 2021; Zhuang et al. 2017) serves as a viable alternative in specific drilling conditions.

Controlling fluid loss(Cao et al. 2017) is a critical element in oil-based mud drilling. Oil-based mud typically includes oil as the continuous phase, leading to potential high fluid loss and diminished drilling efficiency. To address this, additives like gilsonite(Guo et al. 2014; Pakdaman et al. 2020) are often integrated into oil-based muds due to their cost-effectiveness. However, the low chemical stability of gilsonite can render it unsuitable for use in high-temperature and high-pressure conditions. To overcome this challenge, gilsonite is frequently chemically treated to enhance its thermal stability and prevent degradation at elevated temperatures. Moreover, when gilsonite is added to oil-based muds without supplementary stabilizing additives, it tends to agglomerate, causing an undesirable increase in the plastic viscosity of drilling muds. The untreated gilsonite demonstrates low thermal stability and poor dispersibility in invert emulsions. Consequently, this has driven the development of second-generation fluid loss control additives based on linear polymers.

Tailoring linear polymers(Fan Liu et al. 2016) with diverse structures and molecular weights allows them to be customized to meet specific requirements in drilling operations. This adaptability renders them a cost-effective and practical solution for addressing the challenges in drilling operations. Various studies have delved into the application of different linear polymer additives for managing filtration loss in Oil-Based Mud (OBM). In 2004, Stewart et al. (Stewart et al. 2004) suggested that incorporating around 2% by weight of a butadiene-styrene-butadiene block copolymer could effectively reduce filtration loss to below 0.2 mL/30min. Mettath et al. developed a quebracho-based product modified with amines(Mettath et al. 2011)v, demonstrating enhanced performance in controlling filtration loss in OBM, particularly under high-temperature conditions. Dias et al. (2015) utilized esterified starch as additives for regulating fluid loss in invert-emulsion drilling fluids. Additionally, Murphy and Bening introduced hydrogenated isoprene-styrene diblock copolymers(Dias, Souza, and Lucas 2015) to mitigate filtration loss in OBM, especially at temperatures exceeding 350 °F. However, a significant drawback of employing linear polymers to control fluid loss is the unintended increase in viscosity due to their high molecular weight. This has led to exploration in developing polymers with a more adaptable structure, capable of regulating fluid loss without significantly impacting the rheology or electrical emulsion stability of the oil-based mud (OBM).

In this study, a novel approach was taken to tackle the challenge at hand by introducing a new generation of amphoteric star polymers. Amphoteric star polymers(Luo et al. 2018) represent polymeric materials featuring a central core and multiple polymer arms extending outward. These polymers can be tailored to possess specific characteristics, including high molecular weight, a dense branching structure, and a substantial surface area. Experimental results indicated that the amphoteric star polymer formed aggregates, producing more stable emulsions in comparison to linear or gilsonite-type fluid additives. Moreover, the plastic viscosity of the drilling fluid containing the star polymer demonstrated minimal change, or even a decrease, under high-temperature conditions. Testing various mud systems with different densities and oils revealed that the mud system incorporating this star polymer yielded the thinnest filter cake and minimal fluid loss volume under elevated temperatures. These findings underscore the excellent fluid control and rheology profiles exhibited by the polymer developed in this study, making it well-suited for Oil-Based Mud (OBM) applications across a broad spectrum of densities and temperatures.

Materials and Methodology

Materials

Acrylic acid (AA, purity 99%), lauryl acrylate (LA, purity 90%), 2-(butylthiocarbonothioylthio) propanoic acid (BTPA, purity 95%), 2,2′-Azobis(2-methylpropionitrile) (AIBN, purity 98%), N,N′-methylenebis(acrylamide) (MBA, purity 99%), benzoyl peroxide (BPO) with 25% H_2O, tetrahydrofuran (THF, purity ≥99.9%), toluene (purity 99.8%), water (purity 99%), and ethanol (purity ≥99.5%) were procured from Sigma-Aldrich. All obtained reagents were used as received without the need for additional purification. The synthesis of the star polymer was conducted using an in-house method as shown in **Figure 1**.

Fourier-transform infrared spectroscopy (FT-IR)

Fourier-transform infrared spectroscopy (FT-IR) analysis was carried out using the Cary 630 FTIR Spectrometer from Agilent Technologies, and the subsequent data processing was executed using MicroLAb Expert, also from Agilent Technologies. The FT-IR test utilized the dry star polymer.

Thermal Gravimetric Analysis (TGA)

Thermogravimetric analyses (TGA) were conducted using a TA Thermogravimetric Analyzer (SDT Q600). The sample underwent heating from room temperature at a consistent rate of 10 °C/min, with air employed as the furnace gas, reaching temperatures up to 1000 °C.

Rheological behavior

The rheological characteristics of diverse mud systems were assessed using either the model 35 or model 77 rheometer from Fann Instrument Company. Rheology tests were conducted at various temperatures following a 16-hour hot rolling period at each temperature. The rheological data were obtained at different rotational speeds (600, 300, 200, 100, 6, and 3 rev/min), corresponding to shear rates of 1022, 511, 341, 170, 10, and 5 s^{-1}, respectively. The apparent viscosity (AV), plastic viscosity (PV), and yield point (YP) were calculated using the following equations.

$$AV = {}^{\theta_{600}}/_{2} \quad (mPa \cdot s) \tag{1}$$

$$PV = \theta_{600} - \theta_{300} \quad (mPa \cdot s) \tag{2}$$

$$YP = \theta_{300} - PV \quad (lb/100ft^2) \tag{3}$$

Where θ_{600} and θ_{300} represent the dial readings at rotational speeds of 600 rev/min and 300 rev/min, respectively. Gel strength refers to the shear stress measured at a low shear rate following shearing the mud system at a high shear rate and allowing it to set for a period. In this context, the gel strength was measured after 10 seconds and 10 minutes.

Filtration Loss

The fluid loss measurement was conducted using the high-temperature high-pressure filter press. The HTHP tests were conducted at 350 °F at a different pressure of 500 psi for 30 mins. The volume of fluid loss after 30 mins was recorded and the thickness of filter cake was measured.

Results and discussions

Polymer synthesis

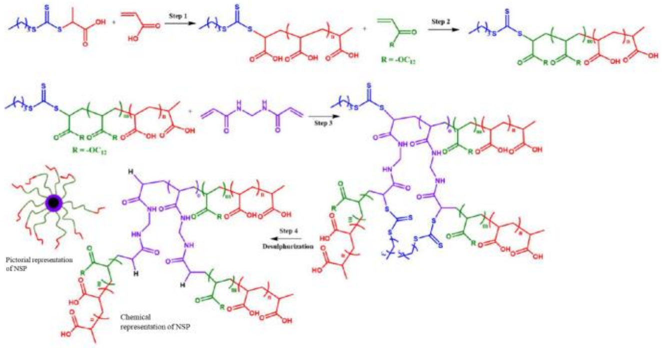


Figure 1 Steps for polymer synthesis

Figure 1 illustrates the one-pot synthesis of a block star polymer, incorporating hydrophilic acrylic acid and lipophilic lauryl acrylate, along with the crosslinker methylene bisacrylamide. The synthesis involved three monomers: (A) acrylic acid (AA), (B) lauryl acrylate (LA), and (C) methylene bisacrylamide (MBA). The process for creating the final star polymer is outlined in several steps, employing a one-pot-three step addition approach. The schematic depiction of the star polymer synthesis process is presented in Error! Reference source not found.

Fourier-transform infrared spectroscopy (FT-IR)

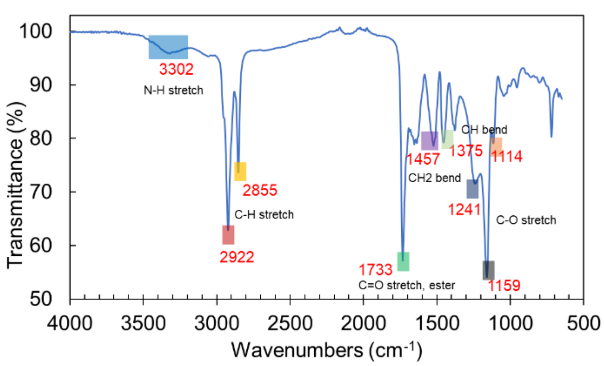


Figure 2 FT-IR spectra of NSP (MBA-c-PAA-b-PLA)

Based on Figure 2, the broad adsorption band at 3302 cm-1 corresponds to the N-H stretching(Lu et al. 2018) vibration of the amide group. The absorption band at 2922 cm-1 and 2855 cm-1 corresponds to asymmetric(Rodrigues et al. 2019) and symmetric(Lando et al. 2017) stretching of C-H, the absorption bands at 1733 cm-1 correspond to ester carbonyl group C=O stretch(Dzulkefly et al. 2010), the absorption band at 1457 cm-1 is CH2 in-plane bending mode(Cai, Lv, and Feng 2013). 1375 cm-1 corresponds to C-H bending(Carrillo et al. 2004), and the absorption band at 1241 cm-1, 1159 cm-1, 1114 cm-1 is due to the C-O stretching vibration of the ester(Cai, Lv, and Feng 2013; Smith 2018; Kurrey et al. 2020).

Thermal Gravimetric Analysis (TGA)

According to the information provided in **Figure 3**, the polymer experiences an initial mass loss at temperatures up to 225°C. This initial decline is associated with the evaporation of the solvent that is trapped within the dry polymer. It implies that the solvent used in dissolving the polymer during synthesis remains confined within the polymer structure even after the drying phase. Upon heating the polymer, the solvent evaporates, leading to the observed initial mass loss.

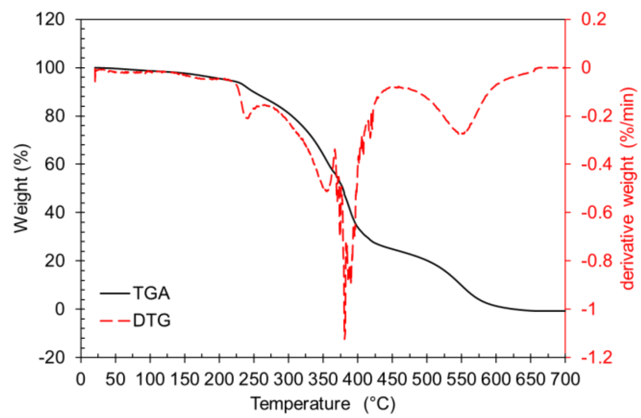


Figure 3 TGA curve for NSP (PAA-b-PLA)

Nevertheless, beyond 225°C, a consistent mass loss is observed in the polymer, primarily attributable to its degradation (Moharram and Khafagi 2006; Daugaard, Jankova, and Hvilsted 2014). The heating process initiates the breakdown of polymer chains, resulting in the release of fragments and subsequent mass loss. The study highlights two prominent degradation peaks in the polymer, occurring at 380°C and 550°C. Despite degradation at higher temperatures, the findings indicate that NSP exhibits notable thermal stability up to 225°C. This suggests the polymer's ability to withstand elevated temperatures without significant degradation, making it a desirable material for high-temperature drilling applications.

Rheology and fluid loss of diesel-based or synthetic oil-based mud

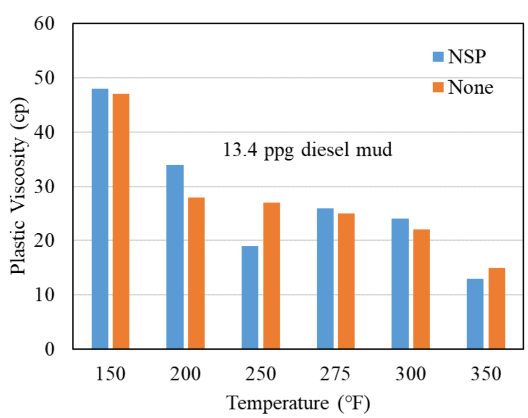
In this research, various materials were utilized, encompassing diesel, Organoclay (a rheology modifier), lime (a primary emulsifier), a wetting agent, DI water, calcium chloride-saturated brine, NSP, the linear polymer Pliolite, natural gilsonite, barite, and Rev dust. **Table 1** and **Table 2** present the mud formulations with two distinct densities (10.5 and 13.4 lbm/gal), utilizing diesel and as the oil phases.

Table 1 Oil-based mud formulation with a density of 13.4 ppg using diesel

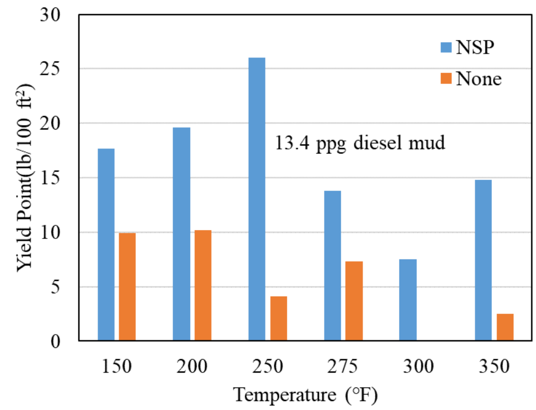
Fluid formulations (lb/bbl)	NSP	Linear polymer	Gilsonite based	No FLA
Diesel	178.3	178.3	178.3	178.3
Organoclay	4	4	4	4
Rheology modifier	2	2	2	2
Lime	10	10	10	10
Primary emulsifier	10	10	10	10
Wetting agent	5	5	5	5
DI water	18.58	18.58	18.58	18.58
Calcium Chloride saturated brine	53.27	53.27	53.27	53.27
NSP	3.6	-	-	-
Linear polymer	-	4	-	-
Gilsonite based	-	-	4	-
Barite	280	280	280	280
Rev Dust	50	50	50	50
Density, lbm/gal	13.4	13.4	13.4	13.4
Aging conditions	Rolling	Rolling	Rolling	Rolling
Aging period, hr	16	16	16	16

Table 2 Oil-based mud formulation with a density of 10.5 ppg using diesel

Fluid formulations (lb/bbl)	NSP	Linear polymer	Gilsonite based	No FLA
Diesel	203.5	203.5	203.5	203.5
Organoclay	4	4	4	4
Rheology modifier	2	2	2	2
Lime	10	10	10	10
Primary emulsifier	10	10	10	10
Wetting agent	5	5	5	5
DI water	21.5	21.5	21.5	21.5
Calcium Chloride saturated brine	61	61	61	61
NSP	4	-	-	-
Linear polymer	-	4	-	-
Gilsonite based	-	-	4	-
Barite	120	120	120	120
Rev Dust	50	50	50	50
Density, lbm/gal	10.5	10.5	10.5	10.5
Aging conditions	Rolling	Rolling	Rolling	Rolling
Aging period, hr	16	16	16	16



(a)



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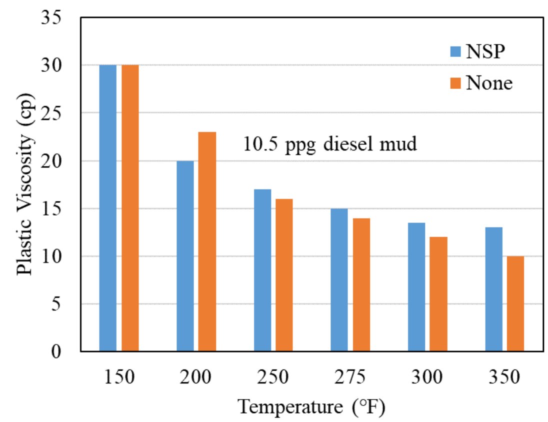

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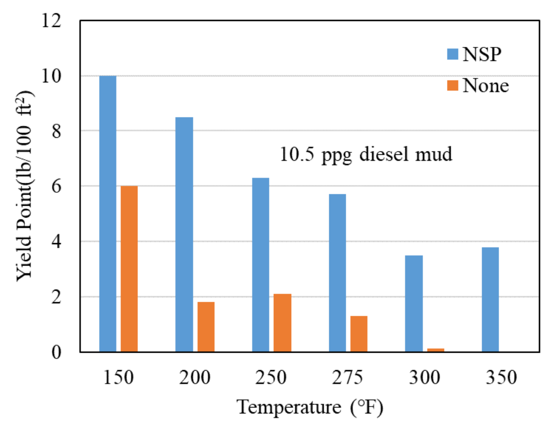


(d)

Figure 4 Rheology of diesel mud for (a) plastic viscosity (13.4 ppg); (b) yield point (13.4 ppg); (c) plastic viscosity (10.5 ppg); (d) yield point (10.5 ppg) with Fann 77 at different temperatures at 10, 000 psi.

Figure 4 depicts the rheology outcomes of mud samples at varying temperatures (150, 200, 250, 275, 300, 350 °F). Notably, at 250 °F and 350 °F, the plastic viscosity (PV) values for the NSP-based mud system were lower than those for the mud without any fluid loss additive. In contrast, the yield point of the NSP-based mud exceeded that of the control sample, reaching a maximum of 25 lb/100 ft2 at 250 °F and 15 lb/100 ft2 at 350 °F. The NSP mud system exhibited improved yield point performance compared to the mud system without a fluid control additive at all tested temperatures, indicating enhanced cutting suspension capability.

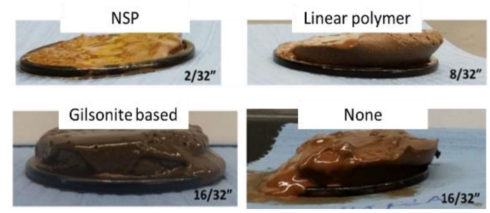
For the 10.5 lbm/gal mud, the presence of NSP led to slightly higher plastic viscosity up to a temperature of 350 °F. However, the yield point of the NSP-based mud significantly surpassed that of the mud without any fluid control additive across all investigated temperatures. These results suggest that NSP demonstrates superior suspending capability (Fayad et al. 2021; Y. Chen et al. 2021) compared to oil-based mud (OBM) lacking NSP, particularly at elevated temperatures.

Table 3 API HTHP fluid loss measurement of 13.4 ppg OBM with diesel at 350°F

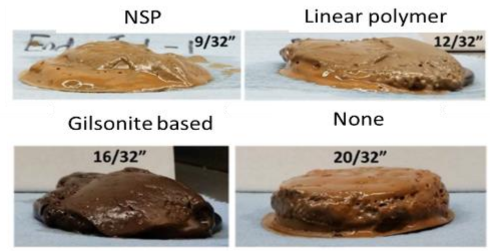
Fluid loss control additive	Fluid loss volume (mL)	Filter cake thickness
NSP	<1	2/32”
Linear polymer	2.2	8/32”
Gilsonite based	8.2	16/32”
None	2.8	16/32”

Table 4 API HTHP fluid loss measurement of 10.5 ppg OBM with diesel at 350°F

Fluid loss control additive	Fluid loss volume (mL)	Filter cake thickness
NSP	3.6	9/32”
Linear polymer	2.6	12/32”
Gilsonite based	4.0	16/32”
None	6.4	20/32”



(a)



(b)

Figure 5 Filter cake of different polymers based OBM with diesel(a)13.4 ppg mud; (b)10.5 ppg mud

Table 3 presents the fluid loss measurements of a 13.4 lbm/gal mud system using different fluid control additives. Notably, the NSP mud system exhibits minimal fluid loss, measuring less than 1 mL, and showcases the thinnest filter cake (2/32") compared to other investigated fluid loss control additives, as depicted in **Figure 5**.

In Table 4, focusing on a 10.5 lbm/gal mud system, the linear polymer emerges as the most effective in terms of fluid loss volume. Both NSP and gilsonite-based additives exhibit fluid loss volumes ranging from 3.6 to 4.0 mL, slightly outperforming the mud system without fluid control additives. However, NSP stands out by significantly reducing the filter cake thickness from 20/32" to 9/32" when compared to the control mud system. These results emphasize that the configuration and amphipathic nature of NSP particles play a crucial role in regulating fluid loss, especially at elevated temperatures.

This phenomenon aligns with previous research. For instance, Chen et al. (Y. Chen et al. 2021) reported a hyper-cross-linked polymer synthesized from poly (maleic anhydride-alt-1-octadecene) (PMAO) cross-linked with amine, serving as a fluid loss control agent for diesel-based OBM. The hyper-cross-linked polymer (ACP) particles, being amphipathic, can be dispersed in the oil phase, reducing OBM fluid loss by 90% at 450 °F. However, significant increases in apparent viscosity and plastic viscosity for their mud systems suggest challenges arising from the linear nature of the long polymer chains. Similarly, Chen et al. (F. Chen et al. 2023) reported slightly amphiphilic poly (acrylamide-co-divinylbenzene) (PACD) microspheres, dispersed in diesel oil phase, reducing API fluid loss at 356 °F to 7.5 mL with 0.56wt% addition, compared to around 29 mL for conventional oxidized asphalt in a 7.4 lbm/gal OBM system. The low fluid loss of OBM with PACD is attributed to its ductile property under HTHP conditions and its amphipathic affinity to both oil and water. This amphipathic affinity stabilizes emulsions in OBM, aiding emulsion droplets in plugging holes and voids during the API HTHP fluid loss test.

Conclusions

In summary, this study introduces the synthesis and characterization of a novel star polymer (NSP) derived from the crosslinking of poly(acrylic acid)-block-poly(lauryl acrylate) with methylene bisacrylamide. Thorough analyses using TGA and FTIR confirmed the NSP's thermal stability and the presence of desired functional groups. Moreover, when dispersed in diesel oil, the NSP exhibited distinct advantages in rheology and fluid loss tests. Rheological data indicated that the NSP significantly improved low-end rheology and yield point, enhancing the suspension performance of oil-based mud (OBM), particularly at elevated temperatures. Additionally, the amphipathic nature of micron-sized NSP particles facilitated adsorption at the water-oil interface, leading to improved emulsion stability. This stabilized emulsion proved beneficial in enhancing fluid loss performance, as the emulsion droplets effectively sealed holes and voids during the API HTHP fluid loss test.

These findings pave the way for further research in polymer-based additives for oil-based muds. The unique properties of NSP, including thermal stability, rheological enhancement, fluid loss control, and emulsion stabilization, offer promising applications in oil-based drilling fluids. Future investigations can delve into optimizing the synthesis process, employing additional characterization techniques, and exploring NSP's performance under diverse drilling conditions. Furthermore, the impact of NSP concentration, particle size, and other formulation parameters on its effectiveness in specific oilfield applications can be explored for further refinement.

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