



Effectiveness of two Tetrapolymers as Viscosifiers and Fluid Loss Reducers

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Authors' contributions

This research study is a joint effort of all the authors listed. Author RDN drafted the manuscript and carried out the laboratory experiments with the support of author APT. Author LZ initiated the idea, provided resources and supervised the work. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Aim: To synthesize and evaluate the effectiveness of two tetrapolymers as viscosifiers and filtration control agents in water-based drilling fluids for application in moderate saline and geothermal environment.

Study Design: Orthogonal design involving monomer feed ratio, monomer solid content, initiator dosage, reaction temperature and pH was used to establish optimum synthesis conditions.

Methodology: The tetrapolymers, TP1 and TP2, consisting of acrylamide-sodium 2-acrylamido-2-methylpropanesulfonate-sodium acrylate - N, N'-dimethyl acrylamide and acrylamide-sodium 2-acrylamido-2-methylpropanesulfonate-N-Vinyl-2-pyrrolidone-styrene were synthesized by free-radical polymerization. Monomeric compositions of the tetrapolymers were established by Fourier transform infrared spectroscopy. Rheological and filtration control properties were used as indicators to evaluate the effectiveness of the tetrapolymers in aqueous bentonite-based drilling fluids.

Results: TP1 provided superior viscosity build-up efficiency and fluid-loss control (9.0 cm³/30 min - 10.0 cm³/30 min) compared to TP2 fluid losses ranging from 11.5 cm³/30 min to 21.5 cm³/30 min in salt-free bentonite muds at temperatures between 120°C and 160°C. Comparatively, TP1 reduced fluid loss to 4.0 cm³/30 min -12.0 cm³/30 min whilst TP2 exerted less filtration control of 12.0 cm³/30 min -39.5 cm³/30 min in salt contaminated muds.

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Conclusion: Both tetrapolymers were considered suitable drilling mud additives with TP1 demonstrating excellent viscosity build-up efficiency and fluid-loss control at elevated temperatures. TP2, however, exhibited better salt tolerance in aqueous salt medium and bentonite-based muds.

Keywords: Tetrapolymer; drilling fluid; rheological property; filtration loss; salt tolerance; temperature resistance.

ABBREVIATIONS

TP1	: Tetrapolymer consisting of acrylamide, sodium 2-acrylamido-2-methylpropane sulfonate, sodium acrylate and N, N'-dimethyl acrylamide
TP2	: Tetrapolymer consisting of acrylamide, sodium 2-acrylamido-2-methylpropane sulfonate, N-Vinyl -2-pyrrolidone and styrene
NVP	: N-Vinyl -2-pyrrolidone
STY	: styrene
AMPS	: 2-Acrylamido-2-methylpropane sulfonic acid
DMAM	: N, N-dimethylacrylamide
AA	: acrylic acid
AM	: Acrylamide
TPM	: Tetrapolymer
KPAM	: Potassium polyacrylamide/acrylate
XCD	: Xanthan biopolymer
HPAM	: partially hydrolyzed polyacrylamide
SPNH	: sulfomethyl humate and phenolic resin
Φ_{600}	: Dial reading at 600rpm
Φ_{300}	: Dial reading at 300rpm
Φ_3	: Maximum dial reading at 3rpm
AV	: apparent viscosity
PV	: plastic viscosity
YP	: yield point
$G_{10"}$: gel strength at 10sec
$G_{10'}$: gel strength at 10min
FL	: filtrate loss
API	: American Petroleum Institute
AV	= $\frac{1}{2}\Phi_{600}$
PV	= $\Phi_{600} - \Phi_{300}$
YP	= AV-PV
G_{10}	= $\frac{1}{2}\Phi_3$
ppm	= mg/L

1. INTRODUCTION

Drilling of geothermal and deep oil wells with water-based muds has been problematic because of ineffective additives that fail to maintain stable rheologies and fluid-loss properties at elevated temperatures. The excessively high thermal conditions encountered in drilling of hot wells tend to cause premature breakdown of mud additives [1-3]. The problem is exacerbated in the presence of inorganic salts of sodium, calcium, and magnesium. Breakdown of water loss control agents causes a large increase in the fluid loss

accompanied by an increase in filter cake thickness. These conditions result in excessive drag, high-pressure surges, differential-pressure sticking, and reduction in production-zone permeability, and increases in shale sloughing [4-7]. It is therefore desirable to develop additives which will enable drilling fluids to retain their proper viscosity and fluid content over a broader range of conditions.

Bentonite clay has been used in most muds for viscosity and fluid loss control because it enhances excellent carrying capacity and suspension of cuttings if enough quantity is present in the mud. However, a major difficulty in formulating high-temperature water-based muds is that bentonite is affected by elevated temperatures, first gelling excessively and then becoming inert at extreme temperatures [8]. High chemical contamination, in combination with high temperature, has been reported to cause dehydration and flocculation of the bentonite, resulting in an increase in filtration rate. The addition of more solids or polymer was proposed as antidote to control filtrate loss [9].

Water-soluble polymers are used extensively in various phases of drilling, completion, workover, and production of oil and gas wells [10-11]. Candidate polymers as drilling fluid additives should exhibit an increase in liquid viscosity at relatively low polymer concentration, and preferably at a minimal cost. Commercially, both partially hydrolyzed polyacrylamide (HPAM) and xanthan biopolymer are used in the oil industry. These traditional polymers rely on chain extension and physical entanglement of solvated chains for viscosity enhancement and filtration control. However, high shear rates cause breakage of the polymer backbone of HPAM, resulting in an irreversible decrease in viscosity [12]. Additionally, the viscosity of HPAM decreases rapidly as salinity or temperature increases [13-14]. In contrast to polyacrylamide, xanthan gum is a rigid polysaccharide that is neither readily shear-degraded nor sensitive to changes in salinity or concentration of divalent ions. However, it is expensive and susceptible to biodegradation. Solutions of both polymers exhibit decreasing viscosity as temperature is increased [12]. The treatment of high-yielding bentonite clay with high molecular weight polyacrylamide and polyacrylate or copolymers of vinyl carboxylates has been suggested to produce about the same viscosity as twice the amount of untreated bentonite [3,15].

Many synthetic polymers have been developed for application in the recovery of natural resources. The backbones of these polymers are composed of carbon-carbon bonds. Depolymerization of a synthetic polymer involves breaking the carbon-carbon bonds of the backbone which requires substantially large energy (of the order of 80 kcal/mol), and hence, synthetic polymers are not depolymerized under ordinary oilfield conditions except under extended use of several months [16].

This work focuses on synthesis and evaluation of two tetrapolymers with unique functional characteristics of thermal stability, hydrolytic resistance and salt tolerance to enhance viscosity and reduce fluid-loss in water-based drilling fluids.

2. EXPERIMENTAL SECTION

2.1 Materials and Synthesis

Materials including acrylamide (AM), acrylic acid (AA), N, N'-dimethyl acrylamide (DMAM), N-vinyl-2-pyrrolidone (NVP), styrene (STY), sodium metabisulfite, potassium persulfate,

sodium chloride and except acrylamido-2-methylpropane sulfonic acid (AMPS) were of analytical grade and used as received.

The tetrapolymers were synthesized in a three-neck flask equipped with a magnetic stirrer, nitrogen gas inlet tube and a thermostatic water bath by free radical polymerization in deionized water under nitrogen sparging using potassium persulphate-sodium metabisulphite redox initiation. Orthogonal design was used to optimize synthesis of the tetrapolymer using total monomer concentration, monomers feed ratios, pH, temperature and initiator dosage as variables.

2.1.1 Synthesis of TP1

Specified quantities of AA and AMPS were first dissolved in separate volumes of sufficiently low quantity of 0.5M NaCl, the pH was then adjusted to the desired value using 2MNaOH. Acrylamide was dissolved in a separate volume before being added to AMPS solution whilst DMAM was dissolved in AA solution after its pH was adjusted. The two solutions were mixed together and the pH finally adjusted to the desired value. The reactants system was then purged of oxygen for at least 20 minutes prior to initiation of the polymerization. Reaction was terminated when the reaction mixture became conspicuously viscous. The tetrapolymer was then isolated and purified using excess acetone.

2.1.2 Synthesis of TP2

Specified quantity of AMPS was first dissolved in sufficient volume of deionized water, the pH was then adjusted to the desired value using 2MNaOH. Acrylamide was dissolved in a separate volume before being added to AMPS solution whilst NPV was mixed with STY previously dissolved in ethanol. The two solutions were mixed together and the pH finally adjusted to the desired value. The reactants system was then purged of oxygen for at least 20 minutes prior to initiation of the polymerization. The tetrapolymer was then isolated and purified using excess acetone.

2.2 Characterization of TP1 and TP2

2.2.1 Fourier Transform-Infrared (FTIR) Spectra

The presence of the monomers in each tetrapolymer was established by Fourier Transform-Infrared (FTIR) spectroscopy. The sample was finely ground to powder and analyzed using NICOLET 6700 FT-IR spectrometer (Thermo Scientific SMART OMNI-SAMPLER, USA), recording the infrared spectra in the wave number range of 4,000-400cm⁻¹.

2.2.2 Intrinsic viscosity measurement

The intrinsic viscosity was determined using Brookfield DV-III Ultra programmable Rheometer (Brookfield Engineering Lab, Middleboro, USA) based on API RP 63 1990 procedure [17]. Different polymer concentrations were prepared in 3%NaCl and viscosity measured at 30rpm. Intrinsic viscosity was determined graphically using Huggins' and Kraemer's equations.

2.3 Effect of Salinity and Hardness on Solution Viscosities of Tetrapolymers

The apparent viscosities of polymer solutions were measured using Brookfield DV-III ultra rheometer (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA) at shear rate of 100 and 200rpm. Polymer solutions were prepared in different concentrations of NaCl, CaCl₂, MgCl₂, and NaCl:CaCl₂:MgCl₂(20:1:1). Salt tolerance was then evaluated by plots of polymer solution viscosities against salt concentrations as shown in Figs. 1-4.

2.4 Formulation and Test of Drilling Fluids

A stock base mud consisting of 500ml of tap water, 25g bentonite clay and 1.25g sodium carbonate per cup was prepared by mixing using electrically powered mechanical stirrer and allowed to age for at least 16 hours at ambient temperature. Test samples viz. DF-A, DF-B, DF-C, and DF-D were then prepared by mixing the base mud and functional additives, depending on the formulation recipe, and blending to uniformity using a multi-speed mixer. Mud samples were tested initially and after 16hours of hot-rolled aging according to American Petroleum Institute(API) procedure [18] and China Drilling Fluid Technical Handbook [19] for measurement of apparent viscosity, plastic viscosity, yield point, and gel strength using ZNN-D6 six-speed rotary viscometer (Qingdao Haitonghai Specialized instrument Factory). API fluid loss was determined at a pressure of 100psi using ZNS-A filter press tester. Test procedure after 16-hr aging involved cooling the drilling fluid to room temperature, stirring in a mixing cup using the multi-mixer for 5min and conducting the tests. Tests results are shown in Tables 2-5 and Figs. 5-8.

3. RESULTS AND DISCUSSION

3.1 Optimized synthesis of Tetrapolymers

Based upon the values of relative viscosity in Table 1, optimum conditions for the synthesis of the TP1 tetrapolymer was achieved at monomer molar ratio of AA :DMAM:AM:AMPS to 22:11:45:22, respectively using total monomer concentration of 2.2M (22.95wt/v%) and initiator dosage of 0.5wt% at reaction temperature of 45°C and pH of 8.0, after a reaction time of 3 hours.

3.2 Characterization of TP1 and TP2

Comparative analysis of FTIR spectra of tetrapolymers with some known spectra of homopolymers and copolymers of the monomers confirmed the presence of the four monomers. Peak at 1662.72cm⁻¹ was attributed to carbonyl stretching from AM, DMAM and AMPS. Carboxylate asymmetric stretching at 1573.33 cm⁻¹ and symmetric stretching at 1404.36 cm⁻¹ were notably assigned to AA. Peak bands at 1189.85cm⁻¹ and 1044.12 cm⁻¹ were respectively, associated with asymmetric and symmetric stretching of sulfonate group of AMPS whilst amide characteristic peak at 1452.18 cm⁻¹ was assigned to -CN- from AM, DMAM and AMPS. Rocking of C-H bond of methyl group of DMAM and AMPS appeared at 1363.89 cm⁻¹. The composition of TP1 as AM-AA-AMPS-DMAM tetrapolymer was therefore validated.

Presence of the monomers in TP2 was established using a similar procedure as stated above. Strong peak at 1661.41cm⁻¹ was attributed to carbonyl stretching from AM, AMPS and NVP. Bands at 1187.35cm⁻¹ and 1042.45 cm⁻¹ indicated asymmetric and symmetric

stretching of sulfonate group of AMPS. Amide characteristic peak of -CN- at 1447.32 cm^{-1} was assigned to AM and AMPS. Peak at 1550.35 cm^{-1} suggested stretching vibrations of the carbons in the aromatic ring of STY, supported by band at 836.35 cm^{-1} and 799.35 cm^{-1} . The structural composition of TP2 as AM-AMPS-NVP-STY tetrapolymer was therefore confirmed.

The intrinsic viscosity of the TP1 and TP2 were obtained as 5.0dL/g and 3.2dL/g, respectively.

Table 1. Experimental design factors for synthesis of Tetrapolymer

Tetrapolymer composition (Mole % ratio)	total moles (mol/100 cm^3)	Temp ($^{\circ}\text{C}$)	pH	Initiator dosage (wt%)	Relative viscosity (η_{rel})
AA:DMAM:AM:AMPS					
20:12:48:20	0.2	40	7.5	0.4	6.7
22:11:45:22	0.22	45	8.0	0.5	25.0
24:10:42:24	0.24	50	8.5	0.6	7.8
26:9:39:26	0.26	55	9.0	0.7	9.8
28:8:36:28	0.28	60	9.5	0.8	14.3
AM: AMPS:NVP:STY					
46:40:10:4	0.16	40	7.5	0.4	5.6
50:35:11:4	0.18	45	8.0	0.5	6.8
53:35:12:5	0.2	50	8.5	0.6	7.8
57:25:13:5	0.22	55	9.0	0.7	6.4
60:20:14:6	0.24	60	9.5	0.8	7.7
64:15:15:6	0.26	65	10	0.9	6.8

TP2 was optimally synthesised using monomer molar ratio of AM:AMPS:NVP:STY to 53:35:12:5, respectively, at total monomer concentration of 2.0M (23.68 wt/v%), initiator dosage of 0.6wt%, reaction temperature of 50 $^{\circ}\text{C}$ and pH of 8.5, after 3 hours

3.3 Effect of Salinity and Hardness on Solution Viscosities of TP1 and TP2

The tetrapolymers were soluble in all concentrations of salt tested without precipitation or flocculation. Their high solubility could be attributed to their strong hydrophilicity arising from the carboxylate or sulfonate groups in addition to the hydrogen bonding between the water molecules and amide groups. Figs. 1-4 illustrate the characteristic patterns of each tetrapolymer in $\leq 20.0\%$ NaCl, $\leq 2.0\%$ CaCl_2 , $\leq 2.0\%$ MgCl_2 , and 11.0% NaCl/ CaCl_2 / MgCl_2 aqueous salt solutions. TP1 showed initial decline in viscosity followed by relative stability as concentration of electrolytes increased. The initial viscosity loss could be attributed to shielding effect of ionic groups, which reduces repulsion and causes polymer chain folding in aqueous salt solution. TP2, however, demonstrated higher salt tolerance compared to TP1. The relatively higher viscosity enhancing potential of the tetrapolymers, particularly, TP1 is attributable to its larger hydrodynamic volume in aqueous medium in addition to its greater ionic charges which creates stronger electrical repulsion between the molecular chains and cause more molecular stretching. The stronger salt resistance of TP2 resulted from the presence of the aromatic ring of styrene and pyrrolidone ring structure which provided higher rigidity and steric hindrance in the aqueous salt media and thus minimized polymer chain folding. Observably, Fig. 4 illustrates anti-aging stability of both tetrapolymers at 80 $^{\circ}\text{C}$ in 110,000ppm (11.0% NaCl/ CaCl_2 / MgCl_2) salt solution for the aging period of 10days.

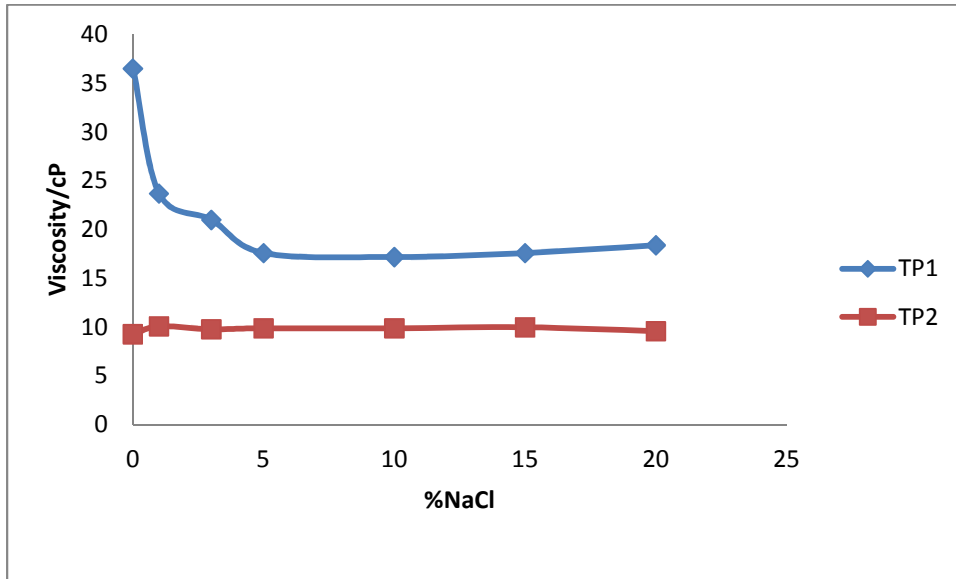


Fig. 1. Effect of NaCl on the viscosities of tetrapolymers at 40°C and shear rate of 200rpm

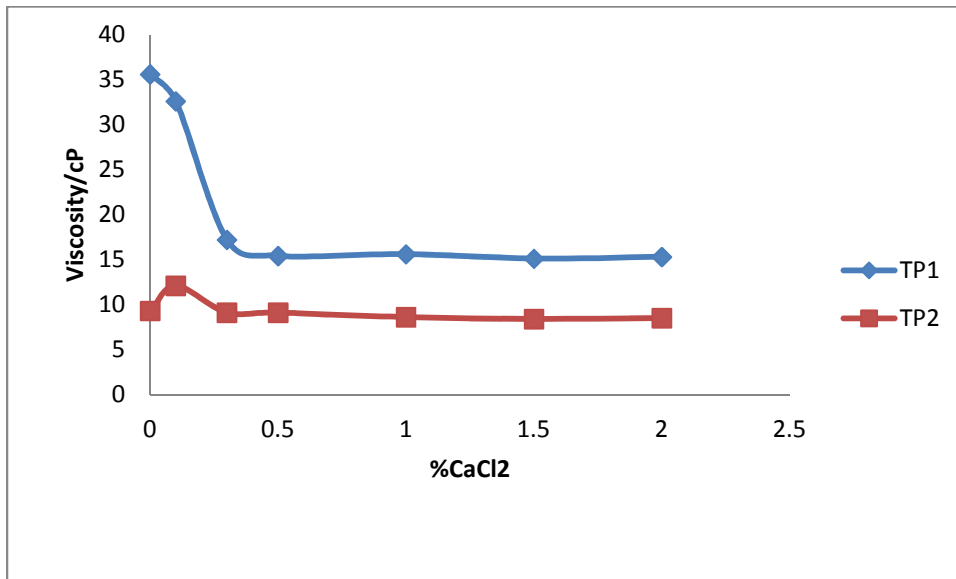


Fig. 2. Effect of CaCl₂ on the viscosities of tetrapolymers at 40°C and shear rate of 200rpm

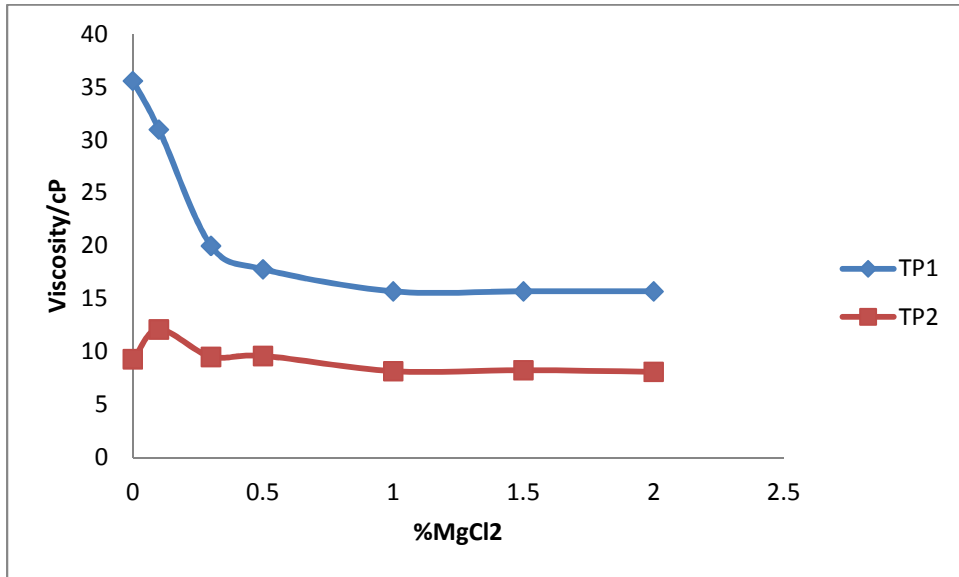


Fig. 3. Effect of MgCl₂ on the viscosities of tetrapolymers at 40°C and shear rate of 200rpm

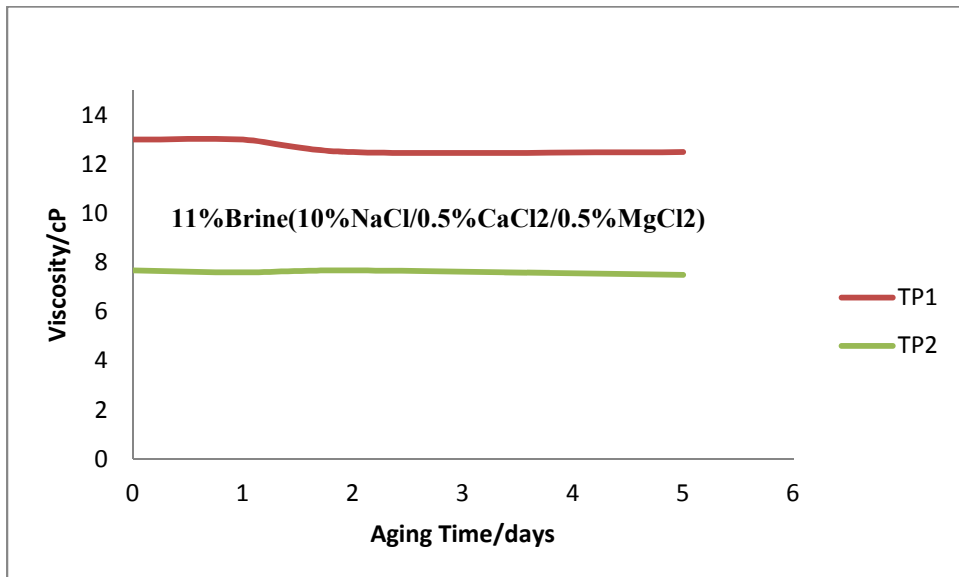


Fig. 4. Effect of aging time on stability of tetrapolymers in 110,000ppm brine at 80°C and shear rate of 100rpm

3.4 Rheological and Fluid Loss Control Properties

3.4.1 Thermal stability of polymer-incorporated Muds

Referring to Figs. 5-8 and Table 2, apparent viscosities of both TP1 and TP2 incorporated-mud formulation DF-A samples before and after hot-aging were fairly high and stable with average values of about 50 cP and 28.5 cP, respectively, up to 150°C. Viscosity of TP1-mud, however, dropped by almost 36 % (to 32cP) whilst that of TP2-mud reduced by 12% compared to KPAM-mud with a viscosity loss of 81% at 160°C. Both tetrapolymers, thus, demonstrated superior thermal stability as mud additives than KPAM at 160°C. Corresponding plastic viscosity of TP1 increased to a peak value at 150°C and declined at 160°C whilst that of TP2 increased from 12cP to a fairly constant value of 23cP after heat treatment. Yield points of TP1-mud and TP2-mud decreased gradually from 28cP to 6cP and 8cP to 3cP, respectively, after heat treatment. The blank completely lost its yield point and gel strength after hot-aging at 120°C whilst KPAM-mud showed a yield point of unity and zero gel strength after hot-aging at 160°C. Comparatively, tetrapolymer TP1 effectively reduced filtration loss to favourably low values (9.0 cm³/30 min -10.5 cm³/30 min) whilst TP2 kept fluid loss within 11.5 cm³/30 min -21.5 cm³/30 min in mud formulation DF-A before and after 120°C - 160°C hot-aging as depicted in Fig. 8. The blank exhibited excessively high filtration loss of 107cm³/30min after hot-aging at 120°C. The detrimentally high fluid loss in the blank could be attributed to dehydration and flocculation of the bentonite clay whilst TP1 and TP2 favourably stabilized the bentonite clay in the polymer-incorporated muds resulting in improved control of fluid losses.

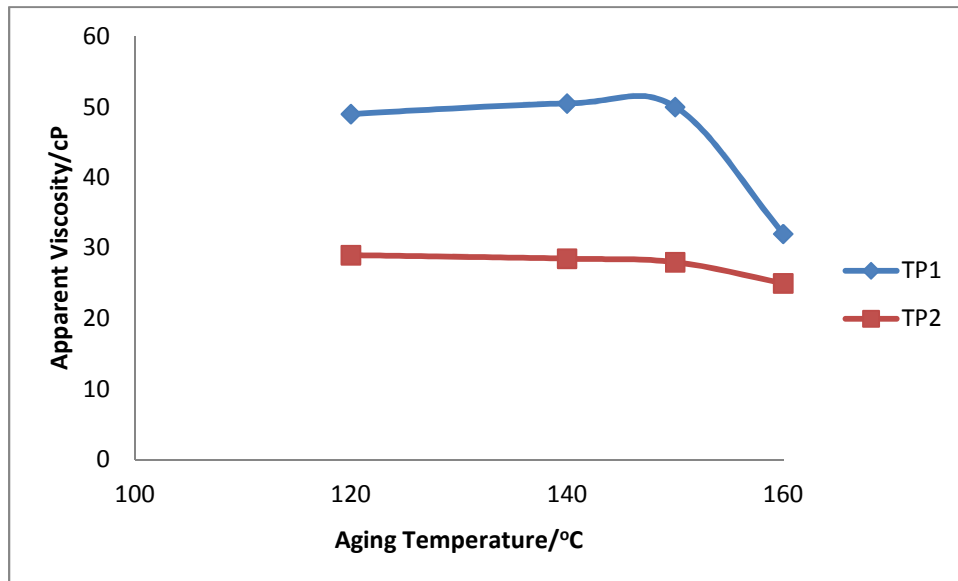


Fig. 5. Effect of Tetrapolymer additive on rheological properties at elevated temperatures

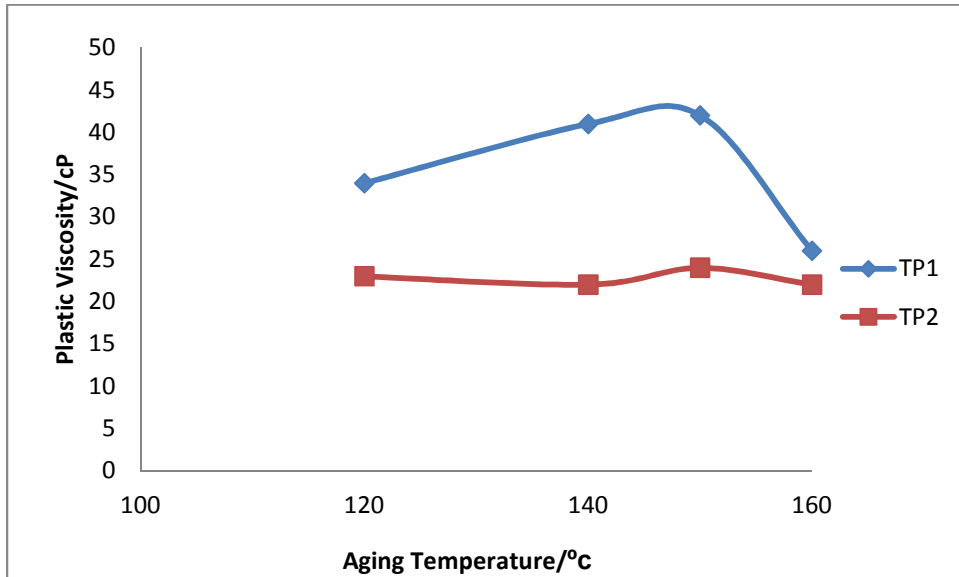


Fig. 6. Effect of Tetrapolymer additive on rheological properties at elevated temperatures

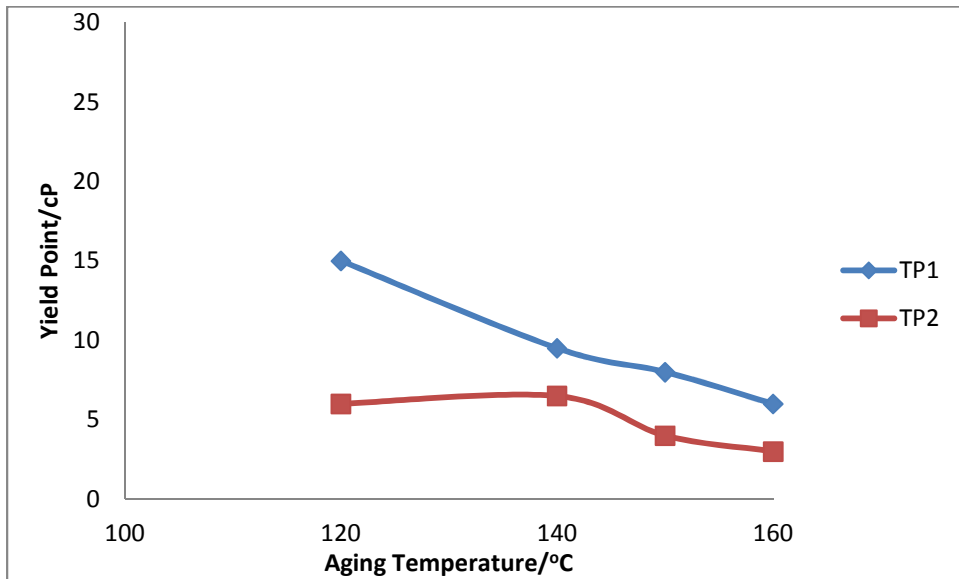


Fig. 7. Effect of Tetrapolymer additive on rheological properties at elevated temperatures

Table 2. Thermal Effect on Mud Properties

Mud formulation DF- A	Additive Quantity	
	Blank	Polymer -mud
Water	500cm ³	500cm ³
Bentonite clay	25g	25g
Na ₂ CO ₃	1.25g	1.25g
Polymer	-	4.0g

Parameter	Mud properties @ ambient temp				Mud properties after hot-rolled aging									
	Blank	TP1	TP2	KPAM	HR @ 120°C		HR@140°C		HR@150°C		HR @ 160°C			
					Blank	TP1	TP2	TP1	TP2	TP1	TP2	KPAM	TP1	TP2
Apparent Viscosity (AV), cP	11.3	52	31	52.5	10	49	29	50.5	28.5	50	28	10	32	25
Plastic Viscosity (PV), cP	3.5	24	12	30	10	34	23	41	22	42	24	9	26	22
Yield point (YP), cP	7.8	28	8	22.5	0	15	6	9.5	6.5	8	4	1	6	3
10 Sec gel (G10 ^{''}), cP	7	9.5	8.5	6.5	0	2	2.0	1	1.5	1	1.0	0	0.5	0.5
10 min gel (G10 [']), cP	9.5	19.5	11.5	11	0	3	2.5	1.5	2.5	1.5	1.5	0	0.75	0.5
API Fluid loss, cm ³ /30min	24	10	11.5	*NC	107	10.5	12.5	10	14	9.5	19.5	11	9.0	21.5

*NC: No control

Ambient temperature:28.0±0.5°C

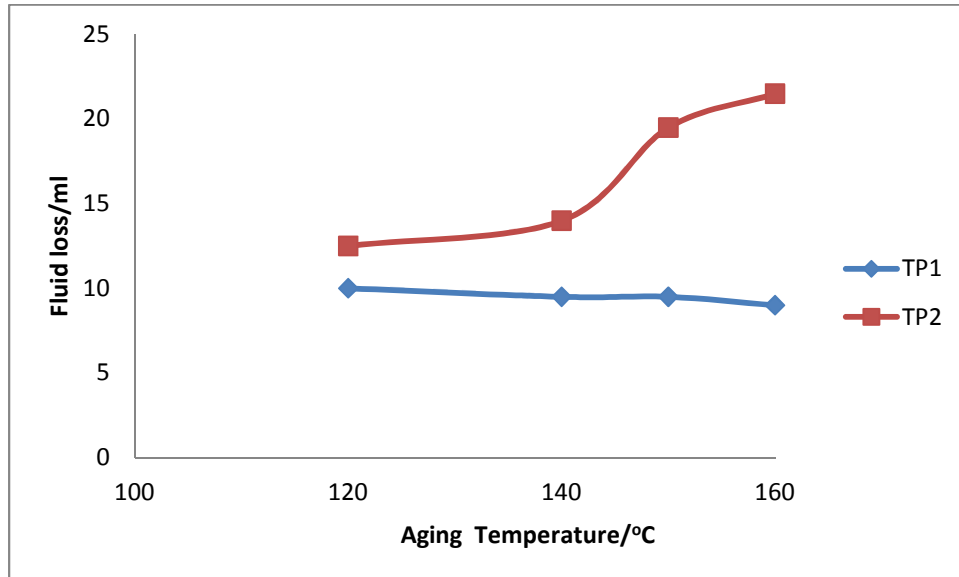


Fig. 8. Effect of Tetrapolymer additive on fluid loss at elevated temperatures

3.4.2 Tolerance to salt contaminated mud at Elevated Temperatures

Tetrapolymers TP1 and TP2 improved rheological properties and fluid loss control in the salt contaminated mud (fluid DF-B) as shown in Table 3. The apparent viscosities of TP1 and TP2 muds increased from 77.5cP to 85cP and 31.5cP to 36cP, respectively, whilst plastic viscosities correspondingly increased from 15cP to 42cP and 20cP to 21cP after hot-aging at 120°C in the presence of 5% NaCl. The yield points of TP1 and TP2 muds also changed from 62.5cP to 43cP and 11.5cP to 15cP. Compared to corresponding values of 84cP to 86cP, 16cP to 64cP and about two-third reduction of yield point (67cP to 22cP) for KPAM after hot-aging. The tetrapolymer TP1 evidently maintained better filtration control (6.0 to 6.5 cm³/30min) and rheological properties and therefore exhibited superior anti-aging performance than both KPAM and the blank whilst TP2 retained rheological properties but showed less effectiveness in fluid loss control. The blank, however, suffered severe loss of filtration control from 42.0 to 71.0 cm³/30min and indicated poor viscosity retention after hot-aging.

Drilling mud formulation DF-C as indicated in Table 4 had similar composition to DF-B except for slight reduction in polymer concentration and increase in aging temperature. Addition of TP1, KPAM or xantham biopolymer in the muds, demonstrated considerable improvement in rheological properties and filtration control as expected. Whilst KPAM apparently showed higher effectiveness in reduction of filtration loss, the tetrapolymer manifested fairly higher dual-functional efficiency in filtration control and viscosity retention after aging at 150°C.

With no extra fluid loss control agent present in fluid DF-D, the tetrapolymer TP1 effected and maintained a much lower filtration loss of 4.5 cm³/30min before and after 120°C hot-aging compared to the blank filtration loss of 82cm³/30min. The addition of 0.8% of the tetrapolymer resulted in almost seven-fold increase in fluid viscosity in the combined presence of 5% NaCl-0.25% CaCl₂-0.25% MgCl₂. Revealing that the both monovalent and

divalent ions would have insignificant influence on the performance of salt contaminated mud when fortified with the tetrapolymer TP1. In the blank mud, the high chemical contamination coupled with high temperature caused dehydration and flocculation of the bentonite, resulting in a much higher filtration rate, in spite of the higher solid content.

Table 3. Properties of brine Contaminated Mud at Ambient Temperature and 120°C

Mud formulation DF-B	Additive quantity	
	Blank	Polymer-mud
Water	500cm ³	500cm ³
Bentonite clay	25g	25g
Na ₂ CO ₃	1.25g	1.25g
SPNH	7.5g	7.5g
Lignite	7.5g	7.5g
NaCl	25g	25g
Barite	100g	100g
Polymer	-	4.0g

Parameter	Mud properties @ ambient temp			Mud properties after hot-rolled aging @ 120°C for 16 hr			
	TP1	TP2	KPAM	Blank	TP1	TP2	KPAM
Apparent Viscosity (AV), cP	77.5	31.5	84	13	85	36	86
Plastic Viscosity (PV), cP	15	20	16	6	42	21	64
Yield point (YP), cP	62.5	11.5	67	7	43	15	22
10 Sec gel (G10''), cP	49	10.5	55.5	5	21	9.5	15
10 min gel (G10'), cP	52.5	13.0	57.5	5.5	22.5	11.5	20
API Filtrate loss, cm ³ /30min	6.0	12.0	6.5	71.0	6.5	39.5	7.5

Table 4. Properties of brine Contaminated Mud at Ambient Temperature and 150°C

Mud formulation DF-C	Blank	Polymer-mud	
	Water	500cm ³	500cm ³
Bentonite clay	25g	25g	
Na ₂ CO ₃	1.25g	1.25g	
SPNH	7.5g	7.5g	
Lignite	7.5g	7.5g	
NaCl	25g	25g	
Barite	100g	100g	
Polymer	-	3.0g	

Parameter	Mud properties after hot-rolled aging @ 150°C for 16 hr					
	Blank	XCD	Blank	TP1	KPAM	XCD
Apparent Viscosity (AV), cP	16.5	75	12	62	54	55
Plastic Viscosity (PV), cP	7	13	11	51	42	29
Yield point (YP), cP	9.5	62	1	11	12	26
10 Sec gel (G10''), cP	8.5	33.0	0.5	3.5	6	8.5
10 min gel (G10'), cP	10	33.5	1.0	4.0	7	10
API Filtrate loss, cm ³ /30min	42	6.0	82.0	12.0	11.0	15.0

3.4.3 Functional properties and performance of tetrapolymer TP1 and TP2

The improvement of rheological properties of the four mud systems following the addition of the tetrapolymers is attributed to their ionic character, water solubility and structural

hydrophilicity. These functional properties of the tetrapolymers apparently resulted in electrostatic interactions between polymer molecules and charged clay particles, interpolymer association of ionic molecules and further through hydrogen bonding between vicinal polymer and water molecules. The electrical repulsion between polymer molecular chains causes molecular stretching, in addition to the ionic interactions with clay particles resulting in a large hydrodynamic volume in the presence of the water and consequently, enhancing the apparent viscosity, plastic viscosity, yield point, and gel strength of the muds. The relatively high viscosity build-up efficiency of the tetrapolymer suggests that the drill mud would offer sufficient resistance to reduce slip velocity of the cuttings and effectively suspend cuttings during drilling operations.

The main chain or backbone of a polymer plays a key role in thermal stability. Structurally, the incorporation of the large AMPS side group together with acrylamide-based dimethyl group into the TP1 and benzylic or cyclic structure into TP2 effectively improved their thermal and hydrolytic resistance and thus enhanced their superior rheological functionality at elevated temperatures compared to KPAM and the blank.

Filtration losses in all TP1-muds before and after heat treatment between 120°C-150°C were favourably lower than that of TP2. This could be partly attributed to the higher ionic character of TP1 arising from both the sulfonate and acrylate groups with greater synergetic interactions with clay molecules and inter polymer molecules compared to TP2. The filtration control is effected through adsorption on the drill solids and interaction with the clay particles. The tetrapolymer functions as a protective colloid or enhances the colloidal properties of the drilling fluid with the solids in the mud forming a thin low permeability filter cake resulting in drastic reduction of the amount of fluid permeating into the pore spaces. This would potentially maintain hole integrity, protect water sensitive shales, minimize formation damage and reduce log analysis problems.

Table 5. Effect of Salt on TP1–mud at 120°C

Mud formulation DF-D	Blank	Polymer-mud	
Water	500cm ³	500cm ³	
Bentonite clay	30g	30g	
Na ₂ CO ₃	1.5g	1.5g	
NaCl	25g	25g	
MgCl ₂	1.25g	1.25g	
CaCl ₂	1.25g	1.25g	
Barite	100g	100g	
TP1	-	4.0g	
		Mud properties @ ambient temperature	Mud properties after hot- rolled aging @ 120°C for 16 hr
Parameter	Blank	TP1-mud	TP1-mud
Apparent Viscosity (AV), cP	12.0	88.0	85
Plastic Viscosity (PV), cP	6.0	23.0	74
Yield point (YP), cP	6.0	65.0	9
10 Sec gel (G10 ^{''}), cP	4.5	37.5	3.5
10 min gel (G10 [']), cP	5.0	39.5	5
API Filtrate loss, cm ³ /30min	85.5	4.5	4.5

4. CONCLUSION

Both acrylamide-sodium 2-acrylamido-2-methylpropanesulfonate-sodium acrylate - N, N'-dimethyl acrylamide terpolymer (TP1) and acrylamide-sodium 2-acrylamido-2-methylpropanesulfonate-N-Vinyl-2-pyrrolidone-styrene tetrapolymer (TP2) stabilized the bentonite-based drilling muds by providing good temperature resistance and anti-aging performance. Tetrapolymer TP1 exhibited superior viscosity build-up efficiency and fluid-loss control ($9.0 \text{ cm}^3 / 30 - 10.0 \text{ cm}^3 / 30 \text{ min}$) compared to TP2 fluid losses of $11.5 \text{ cm}^3 / 30 - 21.5 \text{ cm}^3 / 30 \text{ min}$) under similar conditions. TP1 would therefore find useful application as an excellent viscosity builder and fluid-loss reducer in bentonite and salt contaminated muds at elevated temperatures up to 160°C . Tetrapolymer TP2 demonstrated higher salt tolerance in $\leq 20.0\% \text{ NaCl}$, $\leq 2.0\% \text{ CaCl}_2$ and $\leq 2.0\% \text{ MgCl}_2$ aqueous media than TP1 and would be more suitable for enhanced oil recovery, in addition to its suitability in providing thermal and saline stability to bentonite-based drilling muds. The two tetrapolymers could also be versatile drilling-mud polymeric additives suitable to function in different systems of salt-free clay muds and salt contaminated water based muds.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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