IMPROVEMENT IN THERMO-CHEMICAL STABILITY OF NANOCOMPOSITE PREFORMED PARTICLE GELS FOR CONFORMANCE CONTROL IN HARSH OIL RESERVOIR CONDITIONS

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Gel treatment is one of the most promising technologies to improve conformance control in heterogeneous reservoirs. In this paper, new enhanced preformed particle gels (PPGs) are introduced for conformance control in high-temperature and high-salinity oil reservoirs. The thermo-chemical stability of this product is due to the incorporation of a new monomer, N,N-dimethyl acrylamide (DA), to the structure of the last well-known nanocomposite PPGs. Four species, N,N-dimethyl acrylamide, 2-acrylamido-2-methylpropane sulphonic sodium salt (AMPSNa), acrylamide (AM), and N-vinylpyrrolidone (NVP) monomers, were used to synthesize these PPGs via free radical cross-linking polymerization at room temperature using N,N-methylenebis (acrylamide) as a cross-linker. The mechanical properties of these new classes of PPGs were enhanced by adding the nano-clay montmorillonite Na^+. A temperature stability agent was also used to make these special PPGs compatible with high temperature and salinity reservoir conditions. A systematic study on PPGs preparation was conducted to improve PPGs stability for harsh reservoir conditions that exist in Persian Gulf oil reservoirs (a temperature of 145 °C and a water total dissolved solid of 225 000 mg/L). PPGs prepared with 0.30 g/g (30 wt%) of a 2:1:1:2 molar mass ratio of AM, DA, NVP, and AMPSNa could be completely stable for the mentioned conditions. Rheological behaviours of these PPGs were investigated and a mathematical model for prediction of storage modulus up to onset of elastic to viscous phase was presented. The results of this study reveal useful insights about the selection of appropriate material for successful conformance control in the heterogeneous reservoirs.

Keywords: PPG, conformance control, high salinity, rheological properties

INTRODUCTION

Improving water flooding sweep efficiency has been the subject of intensive scholarly studies during past years.[1–4] Since many oil reservoirs are not homogeneous in their geologic properties water injection can result in a very non-uniform displacement of the oil within the reservoir. It has been recognized that a substantial amount of oil remains in most reservoirs after secondary recovery due to poor reservoir sweep efficiency. The main cause of poor sweep efficiency has been identified as the existence of high permeability thief zones, resulting in early water breakthrough with high water cut in producing wells. Several approaches (mechanical isolation, polymer gels, etc.) have been proposed to treat water channelling and so reduce production water cut. High water cuts increase costs related to scale, corrosion, water/oil separation, and sometimes make a well unproductive and economically inefficient.[5,6] The annual cost of both treating and removing this water is estimated to be 40 000 000 000 U.S. dollars (USD) worldwide.[5,7]

Gel treatment is one of the most important methods to correct reservoir heterogeneity.[8–13] However, some gel conformance control methods have significant disadvantages: the bulk gel process usually requires high concentration of both polymer and cross-linker chemicals to make a strong gel, the gelation time and physical properties are difficult to predict, sequential injection of the gelant into the reservoir probably makes a chromatography separation in gelant composition, and most of them are not stable at more extreme reservoir conditions with high temperature.[14,15] In this regard, Reddy et al.[16] detailed the laboratory development of a natural acrylamide-based cross-linker system, which had no syneresis over a maximum 6-week period at 120 °C.

A more recent approach that does not have the above disadvantages is Preformed Particle Gels (PPGs) which are expandable and hydrophilic polymeric particles. PPGs are a powder product made up of a cross-linked polymer that will swell after floating in fresh or salt water. PPGs are added to the injection water for a period of time, and then followed by a normal water injection. PPGs are suitable for oil field application due to easily adjustable particle sizes ranging from micrometres to millimetres, swelling ability in brine, resistance to moderate saline environments, adjustable mechanical properties, and adjustable swelling ratios.[16–20]

Feng et al.[20] prepared two micro-gel samples by cross-linking an acrylamide-based terpolymer solution with a non-toxic zirconium cross-linker. The characteristics of these two micro-gel samples were determined by using different laboratory techniques in order to evaluate their performances for water shut off or profile control operations. Their mechanical and thermo-chemical stability were also assessed and both systems were stable up to a temperature of 70 °C and salinity of up to 100 mg/L. Coste et al.[19] also introduced new pre-gelled particles, which were stable at a temperature of 110 °C and salinity of 200 mg/L for 6 months.

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PPGs have been applied in about 4000 wells in China to reduce fluid channelling in both water and polymer flooding.[21] The success of any chemical treatment strongly depends on the oil field characteristics.[22] Because of differences in temperature, mineral composition, hardness, pH, and water salinity among oil fields, PPGs applied in specific oil fields may not be suitable for other reservoirs.

Most PPGs-based treatments have been successfully applied in mature fields, but there have been very few experimental reports on understanding the effects of functional groups and reservoir conditions on PPGs thermo-chemical stability.[18] Water expulsion will reduce the volume of the particle gel in reservoirs with high temperature, salinity, and hardness due to gel syneresis and hydrolysis of the amide groups and posterior ionic cross-linking with metal cations in the water.[13] High salinity brine used to prepare the PPGs results in a lower swelling ratio, and higher swollen particle strength. It is well known that fully swollen PPGs exhibit shear-thinning or pseudo-plastic behaviour and follow a power law model.[14,19] Molecular structure degradation due to the thermal effect is also common.[23] Therefore, the goal of this study is to synthesize enhanced PPGs, which could withstand a wide range of oil reservoir conditions.

One of the most extreme reservoirs in the Persian Gulf with regards to salinity and temperature was selected as a candidate for this investigation. Since there are few reports on synthesizing PPGs for treating oil reservoirs under extreme conditions like those in the Persian Gulf, several parameters such as type and concentration of monomers, pH, salinity, and temperature were investigated in this work to better understand the performance of these newly produced PPGs and to improve the structure of existing commercial PPGs for use in enhanced oil recovery from reservoirs with harsh conditions. One of the benefits of our newly developed PPGs is that they can withstand temperatures of up to 145 °C and water salinities of up to a TDS of 225 000 mg/L. Additionally, a new model was proposed that combines the effects of intrinsic properties of proposed PPGs to their elastic phase storage modulus.

MATERIALS AND METHODS

Chemicals

The chemicals used to prepare the PPGs are listed in Table 1.

Synthesis of the PPGs

PPGs were prepared by free-radical polymerization of monomers at room temperature (27 °C) in distilled water, using N,N-methylenebis (acrylamide) (MBA) as a cross-linking agent and sodium persulphate as an initiator. An additive such as ammonium chloride, N,N, N',N' tetramethylethylenediamine, or the nano-clay montmorillonite Na^+ was used as a swelling, catalyst, and mechanical properties modifier. All the syntheses were performed in distilled water at different mass percentages of acrylamide (AM), N,N-dimethyl acrylamide (DA), 2-acrylamido-2-methylpropane sulphonic sodium salt (AMPSNa), and N-vinylpyrrolidone (NVP). The polymerization recipes are listed in Table 2. The manufacturing process is as follows.

Nano-clay montmorillonite Na^+ was added to the required amount of distilled water followed by placing the mixer in an ultrasonic bath for 4 h under continuous irradiation. Then specific amounts of AM and NVP monomers were weighed, and sprinkled gently into the dispersed clay solution while stirring the solution followed by adding DA and AMPSNa monomer and specific temperature stability agent. Stirring was continued for 1 h until all the monomers were completely dispersed. The weighed MBA were poured into the solution followed by adding ammonium chloride while strong stirring and nitrogen purging were used. After stirring for 40 min, specific amounts of sodium persulphate and the N,N,N',N'-tetramethylethylenediamine catalyst were added and then nitrogen purging was stopped. The exothermic polymerization reaction began almost immediately, and hydrogel formation was observed within 20 min. Two types of PPGs were obtained, one by cutting resulting gel into small pieces and then drying it in an oven at 55 °C under vacuum condition for 24 h, and the other by pouring the gelant into moulds (with dimensions of 0.08 cm × 1 cm × 1 cm) to form completely polymerized films. The films were then dried in an oven at 55 °C under vacuum for 24 h.

Experimental Approach

Chemical compositions of test waters are reported in Table 3. Based on the recipes shown in Table 2, 26 PPG samples were synthesized. For each sample, a weighed amount of dry PPG powder (Wd) was gently sprinkled into a 50 mL test tube already filled with different target test water at room temperature. Interface boundary between the brine portion at the bottom containing the PPGs and the brine on top were monitored up to a point where the rate of swelling is zero. At that point the hydrogels were removed from the tubes and blotted with a filter paper to eliminate excess water and the final mass (weight) was measured (Ws). All experiments were performed several times until four consecutive mass measurements were the same and within the limits of experimental error of 1 %. The swelling ratio was

Table 1. List of chemicals used to prepare the PPGs

Name	Functionality	Purity (%)	Made By
Acrylamide	Monomer	98.5	Beijing Chemical (China)
N,N-Dimethyl acrylamide	Monomer	98.5	
2-Acrylamido-2-Methylpropane sulphonic sodium salt	Monomer	99.0	
N-Vinylpyrrolidone	Monomer	98.0	
N,N'-Methylenebis (acrylamide)	Cross-linking agent	99.0	
Ammonium chloride	Swelling agent	99.0	
N,N',N,N' tetramethylethylenediamine	Catalyst	99.0	
Sodium persulphate	Initiator	99.0	
Nano clay montmorillonite Na+	Mechanical properties modifier	99.0	Aldrich (USA)
Nitrogen gas	–	99.995	Delvar Afzar Gas Industrial group (Iran)

Table 2. Chemical compositions of synthesized PPG hydrogels and their swelling behaviour in distilled water (DW), injection water (IW), production water (PW), and connate water (CW)

	AM		DA		NVP		AMPSNa		NH_4Cl	MBA	MB	APS	TEMED	SR (DW)	SR (IW)	SR (PW)	SR (CW)
	M R	wt%, g/100 g	M R	wt%, g/100 g	M R	wt%, g/100 g	M R	wt%, g/100 g	wt%, g/100 g	wt%, g/100 g	wt%, g/100 g	wt%, g/100 g	wt%, g/100 g	g/g	g/g	g/g	g/g
PPG1	30	24.87	1	1.16	1	1.30	1	2.68	**0**	0.25	0.25	0.15	0.15	23.0	21.0	20.0	20.0
PPG2	30	24.87	1	1.16	1	1.30	1	2.68	**0.15**	0.25	0.25	0.15	0.15	27.0	23.0	22.0	22.0
PPG3	30	24.87	1	1.16	1	1.30	1	2.68	**0.25**	0.25	0.25	0.15	0.15	29.0	25.0	24.0	23.0
PPG4	30	24.87	1	1.16	1	1.30	1	2.68	**0.5**	0.25	0.25	0.15	0.15	31.0	26.0	25.0	25.0
PPG5	30	24.87	1	1.16	1	1.30	1	2.68	0	**0.25**	0.25	0.15	0.15	23.0	21.0	20.0	19.0
PPG6	30	24.87	1	1.16	1	1.30	1	2.68	0	**0.5**	0.25	0.15	0.15	23.0	21.0	20.0	20.0
PPG7	30	24.87	1	1.16	1	1.30	1	2.68	0	**0.75**	0.25	0.15	0.15	20.0	18.0	17.0	17.0
PPG8	30	24.87	1	1.16	1	1.30	1	2.68	0	0.5	**0.5**	0.15	0.15	22.0	20.0	19.0	18.0
PPG9	30	24.87	1	1.16	1	1.30	1	2.68	0	0.5	**1**	0.15	0.15	21.0	19.0	18.0	18.0
PPG10	30	24.87	1	1.16	1	1.30	1	2.68	0	0.5	**1.5**	0.15	0.15	20.0	19.0	19.0	18.0
PPG11	30	24.87	1	1.16	1	1.30	1	2.68	0	0.5	**2**	0.15	0.15	19.0	18.0	18.0	18.0
PPG12	30	24.87	1	1.16	1	1.30	1	2.68	0	0.5	**2.5**	0.15	0.15	19.0	18.0	18.5	18.0
PPG13	30	24.87	1	1.16	1	1.30	1	2.68	0	0.5	**3**	0.15	0.15	19.0	18.0	17.5	17.5
PPG14	30	24.87	1	1.16	1	1.30	1	2.68	0	0.1	2.5	**0.05**	0.05	65.0	28.0	27.0	25.0
PPG15	30	24.87	1	1.16	1	1.30	1	2.68	0	0.1	2.5	**0.1**	0.05	63.0	27.0	27.0	26.0
PPG16	30	24.87	1	1.16	1	1.30	1	2.68	0	0.1	2.5	**0.2**	**0.05**	64.0	28.0	26.0	25.5
PPG17	30	24.87	1	1.16	1	1.30	1	2.68	0	0.1	2.5	0.2	**0.1**	64.0	27.0	26.0	25.0
PPG18	**24**	23.85	**1**	1.39	**1**	1.55	**1**	3.21	0	0.15	0.15	0.15	0.15	53.0	25.0	23.0	23.0
PPG19	**15**	21.24	**1**	1.97	**1**	2.21	**1**	4.57	0	0.15	0.15	0.15	0.15	102.0	29.0	27.0	26.0
PPG20	**8**	16.92	**1**	2.95	**1**	3.31	**1**	6.83	0	0.15	0.15	0.15	0.15	114.0	29.0	28.0	27.0
PPG21	**5**	13.41	**1**	3.74	**1**	4.19	**1**	8.66	0	0.15	0.15	0.15	0.15	115.0	28.0	27.0	26.0
PPG22	**3**	9.80	**1**	4.55	**1**	5.11	**1**	10.54	0	0.15	0.15	0.15	0.15	116.0	28.0	27.0	25.0
PPG23	2	5.26	1	3.66	1	4.11	2	16.97	0	**0.3**	2.5	0.1	0.05	57.0	20.0	18.5	18.0
PPG24	2	5.26	1	3.66	1	4.11	2	16.97	0	**0.45**	2.5	0.1	0.05	28.0	16.6	17.0	16.0
PPG25	2	5.26	1	3.66	1	4.11	2	16.97	0	**0.65**	2.5	0.1	0.05	27.0	14.5	15.0	14.5
PPG26	2	5.26	1	3.66	1	4.11	2	16.97	0	**0.8**	2.5	0.1	0.05	26.0	15.5	15.0	14.0

calculated as follows:[15]

$$\textit{Swelling ratio} = \frac{W_s - W_d}{W_d} \tag{1}$$

The results of the swelling ratio tests for all 26 PPGs samples are illustrated in Figure 1. Figure 2 shows a typical photography of swelling capacities for PPGs 1 to 4 in distilled and injection waters.

For each sample at room temperature, three specific weighed amounts of each dry powder samples (Wd) were sprinkled gently into three separate 50 mL test tubes filled with two types of water (injection or production). When the swelling rate reached zero at room temperature, hydrogels were removed from the test tubes and blotted with a filter paper to eliminate excess water and the final mass was measured (Ws). Bottled swollen PPGs were poured into special 25 mL glass tubes and then completely filled up with connate brine. The glass tubes were sealed; the level was marked, and then aged in an oven at 145 °C (see Figure 4). The swelling ratio was monitored every day by monitoring the interface boundary between the brine portion at the bottom containing the PPGs and the brine on top. The ones which lost 25 % of the original volume were removed from the oven and considered to be a syneresis gel (results are shown in Figures 3 and 4). The particle samples that passed the syneresis test for 100 days (PPGs 23, 24, 25, and 26) were selected for further investigation to determine salinity, pH, and temperature effects on swelling ratio (results of salinity, pH, and temperature effects on swelling ratios are shown in Figures 5, 6, and 7). Syneresis tests were performed in triplicate for each one of 26 different PPG samples and results showed some scatter. However, for the samples that passed the syneresis test, experiments were performed several times untill four consecutive results were the same and within the limits of experimental error of 1 %.

The film samples that passed the syneresis test (PPGs 23–26) were selected for elastic modulus assessment. The samples had been swollen in injection water at room temperature and aged for 24 h in connate water at 145 °C. Several aged gel films each with a diameter of 25 mm were cut to fit the rheometer plate geometry and the viscoelastic properties of each sample were measured at 25 °C. An Anton Paar MCR-501 rheometer (Graz, Austria) was used to measure storage (G') and loss (G") moduli at constant angular frequency while varying the strain from 0.01 to 100 %. All experiments were performed several times until four consecutive

Table 3. Chemical composition of injection water (IW), production water (PW), and connate water (CW)

Property	IW	PW	CW
Formation	–	–	Yamama
Specific gravity @ 60 °F	1.03	1.087	1.1575
Concentration	mg/L	mg/L	mg/L
K	230	25	51
Na	12 695	20 450	66 289
Ca^{2+}	800	15 145	17 046
Mg^{2+}	1373	1844	2200
Fe^{2+}	1.4	1.2	1
Cl^-	21 910	47 240	138 394
SO_4^{2-}	2950	480	440
HCO_3^-	180	320	355
Total (mg/L)	40 139.4	85 505.2	224 776

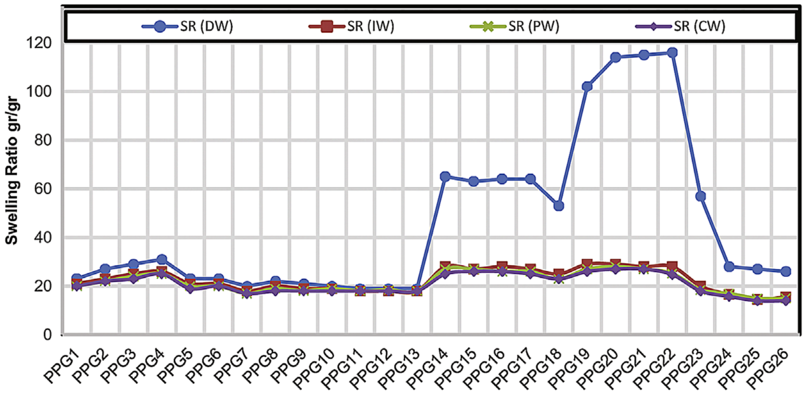


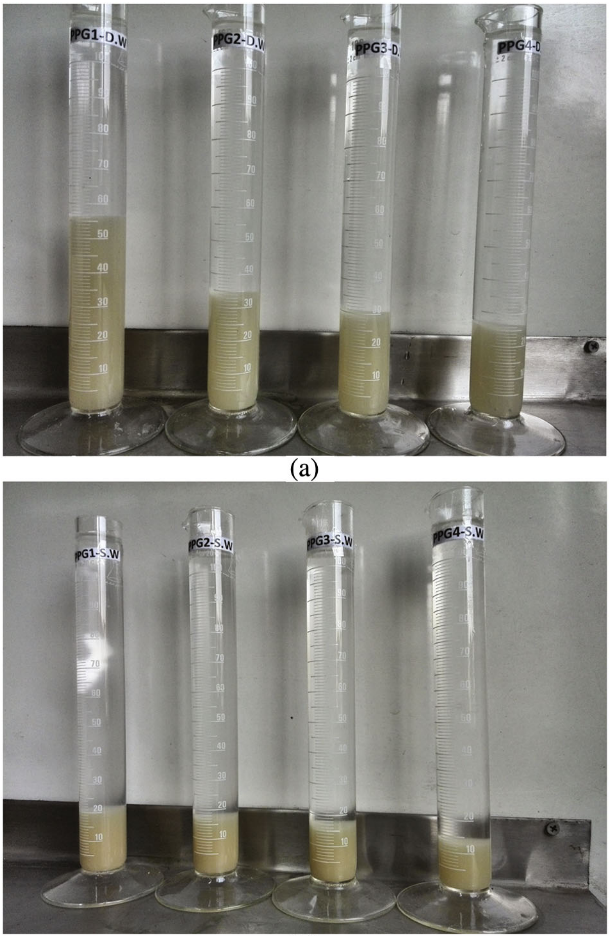
Figure 1. Swelling behaviour of PPG samples in distilled (DW), injection (IW), production (PW), and connate (CW) waters.

rheology results were the same and within the limits of experimental error of 1 %.

RESULTS AND DISCUSSION

Swelling Ratio

Table 2 presents the swelling ratio of synthesized samples in distilled, injection, production, and connate water. Results show that PPG swelling ratio depends on its composition and its surrounding environmental conditions.



(a)

(b)

Figure 2. Swelling capacity of PPGs 1–4 in: (a) distilled water and (b) injection water.

Therefore, the dependency determination of PPG swelling ratio on its ingredients and the selection of the most influential ones was investigated in this study. This goal was pursued by constructing a linear mathematical model in terms of mass percentage of PPG constituents for each type of water (see Table 2). Sensitivity analysis is one of the important practices in the engineering calculation as a tool to figure out the main important parameters controlling the process.[24] The coefficients used to fit the model represented the statistical significance of constitutes (input parameters). In this regard, we transformed them to be uncorrelated and have equal variances. A t-test was also done and the parameters were sorted by their absolute value of t-ratio in Table 4, showing the most significant effect at the top. Coloured items had probabilities less than 0.05 and are considered significant.[25] As is clear, AM, DA, and AMPSNa are the most impactful constitutes on PPG swelling ratio for all types of water. The effects of each constitute are explained as follows.

As is shown in Table 2, increasing NH_4Cl mass percentage up to 0.02 g/g (2 %) increased the swelling ratio (see the composition of PPG 1 to PPG 4). Increasing the mass percentage of NH_4Cl more than 0.02 g/g (2 %) did not affect swelling ratio significantly (see the composition of PPG 3 to PPG 4). It has also been shown that the NH_4Cl concentration could be used as a controller of the swelling capacity via its effect on hydrolysis of the $-CONH_2$ group.[17]

The cross-linker concentration has a critical effect on the structure and properties of the gel. The chemical composition of PPG 5 to PPG 7 illustrates the relationship between swelling capacity and cross-linker concentration. The swelling capacity was reduced when the cross-linker concentration increased.

The swelling capacity in water is related to the hydrophilic group in the polymer molecule. Thus, the number of hydrophilic groups and the cage size of the 3D cross-linked gel have a significant effect on swelling capacity. With an increase in cross-linker concentration, more hydrophilic groups will take part in the gelation reaction, resulting in lower hydrophilicity. At the same time, because of steric hindrance, the swelling capacity will be reduced somewhat when the cross-linker concentration is too high.[17]

Table 2 indicated that the swelling ratio of the nano-composite gels decreased slowly as the mass percentage of the clay increased (see PPG 8 to PPG 13). The reinforcement of polymer gel with clay by forming an intercalated composite has been studied for almost 30 years.[26] Shi et al.[27] studied the interfacial effects on the influence of nano-composite strength based on the assumption

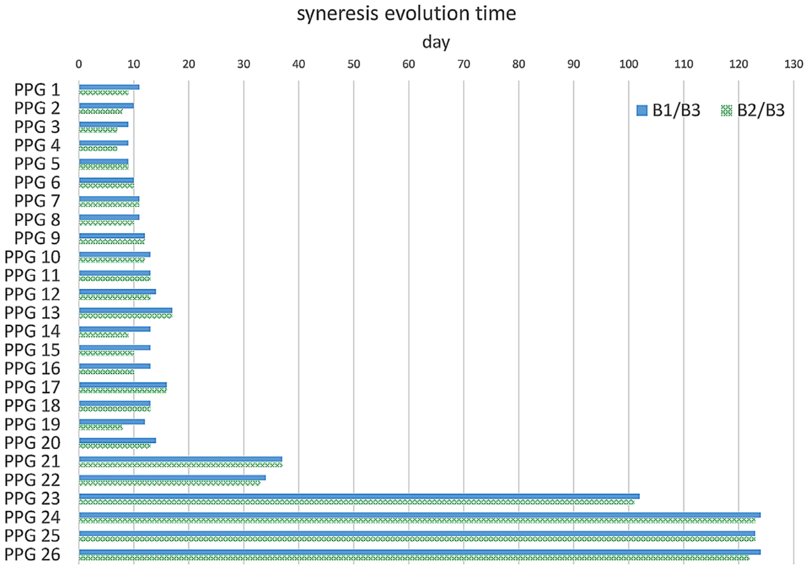


Figure 3. Monitoring syneresis evolution time (in days) of the synthesized PPGs. I/C: PPG samples swelled in injection water at room temperature and aged in connate water at 145 °C. P/C: PPG samples swelled in production water at room temperature and aged in connate water at 145 °C.

that the polymers are binding directly on the surface of clay particles. The thin flat clay particles had two different surfaces. The planar surface is negatively charged and the thin edge is positively charged.[28] The surface property, the trace impurity, and the geometry of clay particles play an important role in the synthesis of composite material. Other reports have shown that adding clay to homopolymer PPGs drastically improves their mechanical properties.[29] It was found that the swelling capacity

Figure 4. Swelled PPGs: (a) before aging and at room temperature; (b) after aging for 120 days, at 145 °C. Blue line shows the volume of swelled PPGs at room temperature. It can be seen that aging process at high temperature causes the PPGs to undergo syneresis. PPGs 23–26 showed partial syneresis, lost less than 25 % of original volume, and were considered to pass the test.

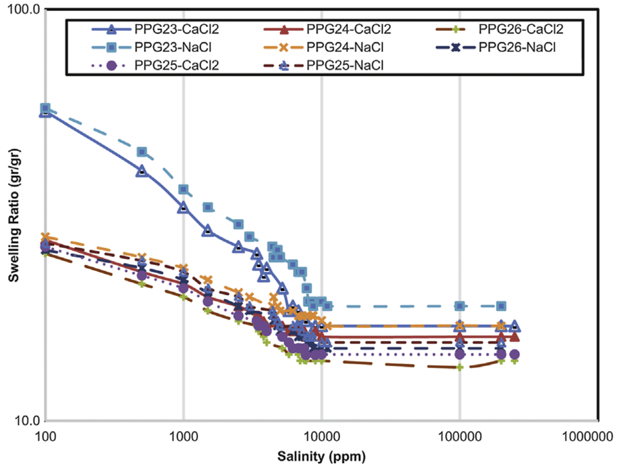


Figure 5. Effects of $CaCl_2$ and NaCl concentration on PPGs swelling ratio.

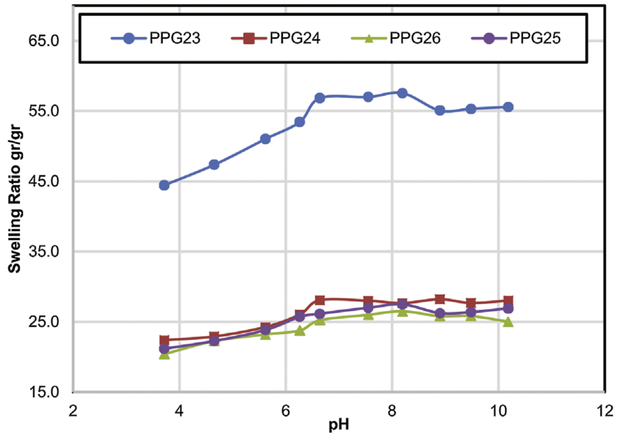


Figure 6. Effect of pH on PPGs swelling ratio.

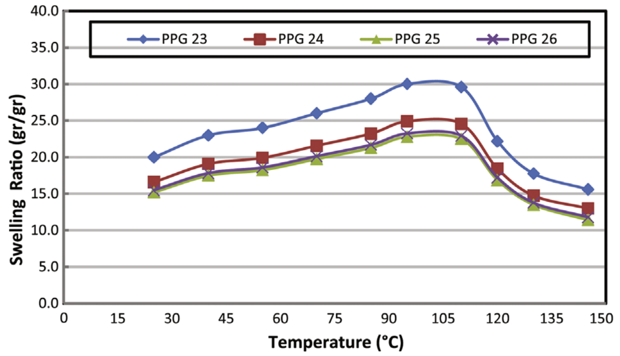


Figure 7. Effect of temperature on PPGs swelling ratio.

reduces when the concentration of nano-clay montmorillonite Na^+ increased but the changes were insignificant for these special compositions. Figure 1 also agrees with the same trend. Peroxide compounds can be used as initiators to initiate the polymerization to accelerate the reaction; a catalyst was used to increase the dissociation rate at room temperature. Peroxide compounds will produce free radicals during their dissociation at proper conditions but the initiator concentration is not critical for the structure and properties of the gel. The chemical composition of PPG 14 to PPG 16 illustrates the relationship between swelling capacities and initiator concentration. The swelling capacity did not decrease when the initiator concentration increased. Figure 1 shows the effect of peroxide compounds on swelling ratio. By comparing the swelling capacity of PPG 16 and PPG 17 it can be seen that catalyst concentration did not affect the swelling capacity significantly. This could be attributed to the fact that the catalyst increases the rate of a chemical reaction without itself undergoing any permanent chemical change.

For synthesizing PPGs, four different kinds of monomer are used by decreasing the AM/(DA + NVP + AMPSNa) molar ratio the swelling ratio and syneresis resistance increased (see chemical compositions of PPG 18 to PPG 22 in Table 2). Moreover, to make a conclusion based on Figure 1, it can be concluded at this point that high salinity water results in a smaller swelling ratio, the hydrogels exhibited very high swelling ratio values in distilled water; this behaviour can be explained in terms of the repulsive interactions between the negatively charged groups in polyelectrolyte polymeric chains and their high affinity with water in the absence of metallic ions. By increasing the salt concentration, the interaction between the negatively charged polymeric chains with cationic divalent metals resulted in ionic cross-linking and reduced the hydrogel volume.[30] A sharp decrease in the swelling ratio was observed when comparing the results for distilled water brine with higher salinity brines which are injection, production, and connate water (see Figure 1), presumably because the anionic moieties in the polymeric network in both cases were the limiting reagents for the ionic cross-linking, thereby reducing the swelling ratio.

Aging (Syneresis Monitoring)

The measured syneresis times of 26 synthesized PPGs are shown in Figure 3 and the analysis of constitute impacts on the syneresis time is presented in Table 5. I/C means PPG samples swelled in

Table 4. Impacts of constitutes on the swelling ratio of PPGs in different environmental conditions

SR (DW) (R^2=0.92)			SR (IW) (R^2=0.95)		
	|t-ratio|	Prob>|t|		|t-ratio|	Prob>|t|
AM	10.53	<.0001	AM	11.11	<.0001
DA	5.81	<.0001	DA	10.46	<.0001
AMPSNa	3.78	0.0016	AMPSNa	4.46	0.0004
MBA	2.74	0.0146	MBA	4.11	0.0008
NH_4Cl	2.04	0.0581	NH_4Cl	3.66	0.0021
NVP	1.11	0.2816	NVP	3.00	0.0085
MB	1.03	0.3185	MB	1.26	0.2258
TEMED	0.55	0.5876	TEMED	0.56	0.5853
APS	0.25	0.809	APS	0.39	0.7026

SR (PW) (R^2=0.95)			SR (CW) (R^2=0.94)		
	|t-ratio|	Prob>|t|		|t-ratio|	Prob>|t|
AM	11.04	<.0001	AM	10.44	<.0001
DA	10.22	<.0001	DA	9.72	<.0001
AMPSNa	4.11	0.0008	AMPSNa	5.01	0.0001
MBA	3.77	0.0017	MBA	4.07	0.0009
NH_4Cl	3.61	0.0023	NH_4Cl	3.51	0.0029
NVP	2.18	0.0441	NVP	2.11	0.0513
MB	1.38	0.1875	MB	1.40	0.1799
TEMED	1.17	0.2599	TEMED	1.11	0.2816
APS	0.73	0.4789	APS	0.39	0.702

injection water at room temperature and aged in connate water at 145 °C, and P/C means PPG samples swelled in production water at room temperature and aged in connate water at 145 °C.

PPG 5 to PPG 7 illustrate that increasing cross-linker concentration will improve syneresis resistance. As the mass percentage of the clay increases (see PPG 8 to PPG 13), the syneresis resistance of nano-composite improves, decreasing the ratio of AM/ (DA + NVP + AMPSNa) molar ratio has a positive effect on syneresis resistance (see syneresis samples of PPGs 18–22 in Figure 3).

In PPGs 23 to 26, the concentration of nano-clay montmorillonite Na^+ was considered a high value (0.025 g/g (2.5 wt%)) to enhance the syneresis resistance and improve the mechanical properties of the synthesized hydrogel samples while cross-linker concentration varied from 0.003 to 0.008 g/g (0.3 to 0.8 wt%). The results indicate that increasing cross-linker concentration decreased the degree of swelling ratio (Figure 1), while the syneresis resistance improved (Figure 3).

The 0.3 g/g (30 wt%) of a 2:1:1:2 molar mass ratio of AM, DA, NVP, and AMPSNa monomers with 0.0045 g/g (0.45 wt%) N,N-methylenebis (acrylamide) and 0.025 g/g (2.5 wt%) nano-clay montmorillonite Na^+ exhibited the highest stability of the investigated PPGs under oil reservoir with high salinity and temperature. Swollen PPGs tend to be more thermally stable in injection and production water than in distilled water while a smaller swelling ratio is observed in high salinity water. More thermal stability could be related to increase of cross-linking density at a smaller swelling ratio.

Determining the effect of parameters such as salinity, pH, and temperature on the swelling ratio of PPGs is highly significant because of the reservoir condition. Consequently, in this research, the effect of $CaCl_2$ and NaCl concentration on swelling ratio was investigated. Dried hydrogels (W_d) were allowed to hydrate in $CaCl_2$ and NaCl solutions with different concentrations. After being fully hydrated, the samples were taken out and weighed (W_s) after the excess water on their surface was gently removed by filter paper. The swelling ratio was then calculated by Equation (1) and the result was illustrated in Figure 5.

By increasing $CaCl_2$ and NaCl concentrations, a rapid shrinkage of the swelling ratio was observed in the low concentration region; also increasing the salt concentration beyond a certain amount had no effect on the swelling ratio of the PPGs product. For example, the swelling capacity of PPG 23 decreases from 57.5 g/g to approximately 19.5 g/g while the NaCl concentration increases from 100 mg/L to 7500 mg/L. Increasing NaCl concentration more than 7500 mg/L had no effect on the swelling ratio of the same PPGs product. The swelling ratio of PPG 23 to PPG 26 for different $CaCl_2$ concentrations is illustrated in Figure 5. The swelling capacity of PPG 23 decreases from 56.5 g/g to approximately 18.5 g/g when the $CaCl_2$ concentration increases from 100 to 5800 mg/L; however, higher $CaCl_2$ concentrations (more than 5800 mg/L) did not affect the swelling ratio.

Table 5. Impacts of constitutes on the syneresis time of PPGs in different environmental conditions

I/C (R^2=0.99)			P/C (R^2=0.99)		
	|t-ratio|	Prob>|t|		|t-ratio|	Prob>|t|
AM	40.77	<.0001	AM	39.91	<.0001
DA	16.28	<.0001	DA	15.82	<.0001
AMPSNa	2.83	0.0121	AMPSNa	2.61	0.0188
MB	1.82	0.0871	MB	2.42	0.028
MBA	1.49	0.1555	MBA	1.59	0.1307
NVP	1.25	0.2298	NVP	1.26	0.2254
NH_4Cl	0.90	0.384	NH_4Cl	1.15	0.2661
TEMED	0.73	0.4773	TEMED	0.99	0.3348
APS	0.15	0.88	APS	0.65	0.525

It has been shown that at a constant salt concentration, the swelling ratio of PPG 23 is higher in NaCl solution than $CaCl_2$, also the minimum swelling ratio (Plato) was observed in a lower salt concentration of $CaCl_2$ rather than a concentration of NaCl. The same trend could be observed for PPGs 24, 25, and 26. These phenomena can be attributed to the state electric repulsive force and charge balance. At a low salt concentration the electric repulsive forces will separate the molecules in gel and create more space for water coming in. However, when the gel is swollen in high-salinity water, the negatively charged group will be balanced by the cations and will restrict further water absorption.

For pH investigation, weighed dried (W_d) hydrogels of PPGs 23, 24, 25, and 26 were allowed to hydrate in buffer solutions with different pH values from 3.7 to 10 at 25 °C. After being fully hydrated, the samples were taken out and the excess water on their surface was gently removed by filter paper and then the swelled hydrogels were weighed (W_s). Swelling ratio was calculated by Equation (1) and the result is illustrated in Figure 6. In acidic conditions, the swelling capacity increases with an increase of pH and approaches a stabilized value at $pH = 6.5$. The pH influence can be attributed to the release of proton ions in an acidic condition, which shields the electric repulsive force of the charged groups.[18] On the other hand, the PPGs hydrophilicity and swelling capacity increased when the cross-linker concentration decreased and it results in the higher value of swelling ratio for PPG 23.

To investigate the effect of test temperature on PPGs properties, known dry mass (W_d) hydrogels of PPGs 23, 24, 25, and 26 were allowed to hydrate in injection water at different temperatures. After being fully hydrated, the samples were taken out and hydrated masses (W_s) of PPGs were measured after the removal of excess water using filter papers. The swelling ratios were then calculated by Equation (1) and the results are illustrated in Figure 7. Up to 110 °C, the swelling ratio increased as the temperature increased. However, for temperatures above 110 °C, the trend was reversed and swelling ratio decreased with increasing temperature. The effects of temperature on swelling ratio have been investigated by many researchers. At higher temperatures, amide groups ($-CONH_2$) will convert to acidic carboxylic groups ($-COOH$) by hydrolysis.[13] Our laboratory results indicate that swelling capacity of PPGs 23, 24, 25, and 26 increases with an increase in temperature up to 110 °C. However at higher temperatures, water expulsion will reduce the volume of the particle gel due to gel syneresis and hydrolysis of the amide groups will enhance posterior ionic cross-linking with metal cations present in the water.[13] Molecular structure degradation due to thermal effect is also common.[23] Replacing acrylamide by heavier molecular monomers in the recipe (Table 2) improved the thermal stability of new synthesized PPGs. Results of the syneresis monitoring section confirm this (see Figure 3). In other words, increasing molecular mass of PPGs will enhance their thermal stability.

Rheology

The film's samples of PPGs 23, 24, 25, and 26 were selected for rheology tests. It is well known that the cross-linker concentration directly affects the mechanical deformation of hydrogels. As the mass percentage of the cross-linking agent varied from 0.003–0.008 g/g (0.3–0.8 wt%), the degree of swelling was greatly reduced (Figure 1). The syneresis resistance improved (Figure 3) and storage modulus up to the onset of elastic to viscous phase (G'_l) increased (see Figure 8). Although higher storage modulus were observed at higher cross-linker mass percentages, the onset of elastic to viscous phase (G'_λ) decreased dramatically. Increasing strain percentage to a value more than G'_λ was caused by a sharper drop of storage modulus in PPG products with higher concentration of cross-linker. Faster structural damage of PPG products which contain a higher concentration of cross-linker explains these phenomena. This fact points out that at higher values of strain (which is the case in the PPG injection procedure) increasing cross-linker concentration will produce unwanted PPG products. At higher cross-linker concentration, higher loss modulus was observed (see Figure 9). Results presented in Figure 8 indicate that the onset of the elastic to viscous phase for PPG products with a higher concentration of cross-linker has happened at a much lower value of strain. Loss modulus was increased to higher values by increasing strain percentage. In other words, at a higher value of strain, increasing cross-linker concentration will produce unwanted PPG products.

Mathematical Models for Explaining the Rheological Behaviour of Selected PPGs

The viscoelastic materials like PPGs exhibit both viscous and elastic behaviour. Maxwell Spring-dashpot models are used to simulate the rheological behaviour of such viscoelastic materials (see Figure 10). The spring (elastic component of the response) and the dashpot (viscous component of the response) obey the relations for tensile and shear. Equation (2) is the Maxwell equation which relates the stress to the strain. This equation can be solved for the stress $\sigma(t)$ once the strain $\varepsilon(t)$ is specified, or for the strain if the stress is specified.[31]

$$k\dot{\varepsilon} = \dot{\sigma} + (\sigma/\tau) \tag{2}$$

In the case of the dynamic response, the time dependency of both the stress and the strain are in the form of $exp(i\omega t)$. All time derivatives will therefore contain the expression $(i\omega)exp(i\omega t)$, so Equation (3) gives the following:[31]

$$k(i\omega)\varepsilon_0 \times \exp(i\omega t) = (i\omega + 1/\tau j)\sigma_0 \times \exp(i\omega t) \tag{3}$$

Since the complex modulus is $G^* = \frac{\sigma_0^*}{\varepsilon_0^*}$ then the following is true:[31]

$$G^* = \frac{\sigma_0^*}{\varepsilon_0^*} = \frac{k(i\omega)}{i\omega + 1/\tau j} = \frac{k(i\omega\tau j)}{1 + i\omega\tau j} \tag{4}$$

Multiply by $\frac{1-i\omega\tau j}{1-i\omega\tau}$ to yield:

$$G^* = \frac{k\omega^2\tau^2}{1+\omega^2\tau^2} + i\frac{k\omega\tau}{1+\omega^2\tau^2} \tag{5}$$

$$G'' = \frac{k\omega\tau}{1+\omega^2\tau^2} \tag{6}$$

$$G' = \frac{k\omega^2\tau^2}{1+\omega^2\tau^2} \tag{7}$$

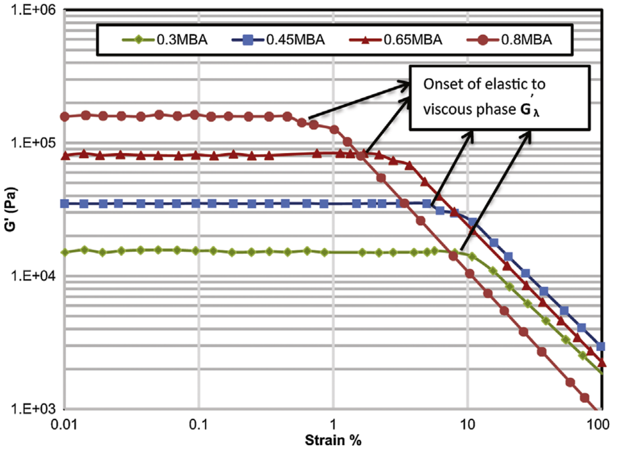


Figure 8. Effect of cross-linker concentration on PPGs storage modulus with strain amplitude sweep from 0.01 to 100 % at a constant frequency.

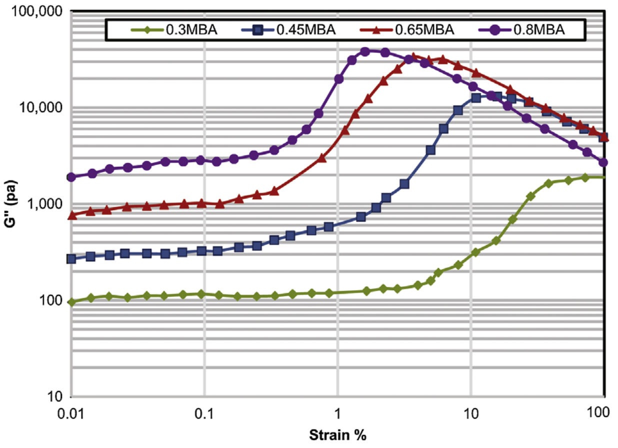


Figure 9. Effect of cross-linker concentration on loss modulus with strain amplitude sweep from 0.01 to 100 % at a constant frequency.

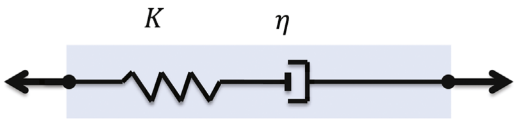


Figure 10. The Maxwell model.

The real and imaginary components of the complex modulus are given explicitly in Equation (5), also loss factor ($tg\delta$) which is the ratio of the loss (G'') modulus to the storage (G') modulus can be calculated by Equation (8) as follows:[31]

$$tg(\delta) = G''/G' = \left(\frac{k\omega\tau}{1+\omega^2\tau^2}\right) / \left(\frac{k\omega^2\tau^2}{1+\omega^2\tau^2}\right) = \frac{1}{\omega\tau} \tag{8}$$

The storage modulus and the loss modulus were obtained by an Anton Paar MCR-501 rheometer at constant angular frequency while varying the strain from 0.01 to 100 %. Therefore the loss factor ($tg\delta$) which is the ratio of the loss (G'') modulus to the storage (G') modulus was calculated. The result is shown in Figure 11.

Based on Equation (6), at constant angular frequency ($\omega = constant$), τ, which is a useful measure of the response time of the material's viscoelastic response, was calculated. Also, for each PPG sample, k is calculated at constant angular frequency while varying the strain from 0.01 to 100 % by Equation (9). Figure 12 depicts the effect of cross-linker concentration on k which is an indication of PPGs' stiffness with units of N/m^2.

$$k = \frac{G''(1+\omega^2\tau^2)}{\omega\tau} \tag{9}$$

For each PPG sample with known τ and k, η, which presents the viscosity of PPGs with units of $N \cdot s/m^2$, was calculated at constant angular frequency (see Figure 13) while varying the strain from 0.01 to 100 % by the following equation:[31]

$$\eta = \tau \times k \tag{10}$$

Results in Table 6 indicate that a decrease of mass percentage of the cross-linker (W) will lead to lower onset of elastic to viscous phase in terms of storage modulus while syneresis resistance was improved and storage modulus, up to onset of elastic to viscous phase (G'_λ), was increased.

By plotting (G'_λ) versus $W(\lambda_L - \frac{1}{\lambda_L^2})$, it can be seen that this ratio, up to onset of elastic to viscous phases, is almost constant. The experimental data revealed that our new synthesized performed particle gel product is exhibiting a linear relationship between the mass percentage of the cross-linker (W), extension ratio (λ_L), and the onset of elastic to viscous phase in terms of storage modulus. Therefore, the least squares method was used to present a polynomial correlation in term of $W(\lambda_L - \frac{1}{\lambda_L^2})$. The model's statistical summaries of fit are illustrated in Figures 14 and 15, and Table 6.

$$G'_\lambda = -1913717 \times W \times \left(\lambda_L - \frac{1}{\lambda_L^2}\right) + 172\,350 \tag{11}$$

Consider a case where based on the reservoir conditions, a thermally stable preformed particle gel (PPGs) with an onset of elastic to viscous phase and an extension ratio of 20 000 Pa and 1.04, respectively, was required. By referring to Figure 14 or Equation (11), one can determine that the required cross-linker concentration for synthesizing the enhanced preformed particle gels should be 0.0069 g/g. The results of rheological measurements of synthesized PPGs with 0.0069 g/g cross-linker concentration will confirm the reliability of the proposed model. This procedure was performed for several other points, and for each point the measurements were repeated several times until results were the same and within the limits of experimental error of 1 %.

It is worth mentioning that the swelling ratio and resistance to syneresis of the new upgraded PPGs depend strongly on its composition and environmental conditions. Aging under simulated reservoir conditions was performed to select the best thermally stable PPGs. The rheological characteristics and mechanical properties of those thermally stable were then evaluated and the elastic phase storage modulus of PPGs were correlated to their intrinsic properties. This new class of thermally stable PPGs could offer the industry an avenue to achieve increased incremental oil recovery for reservoirs with harsh salinity and temperature conditions.

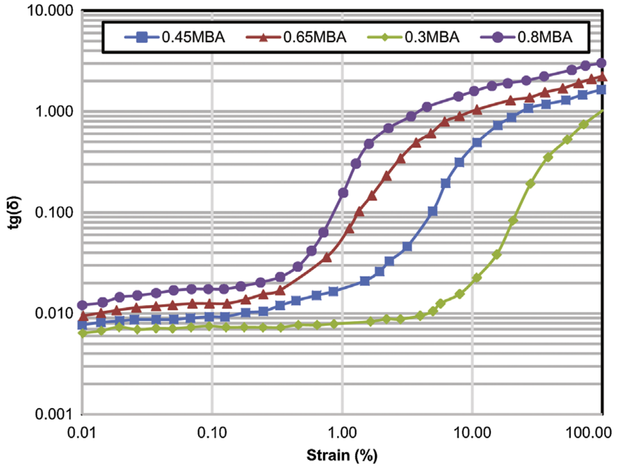


Figure 11. Effect of cross-linker concentration on loss factor (tgδ) with strain amplitude sweep from 0.01 to 100 % at a constant frequency.

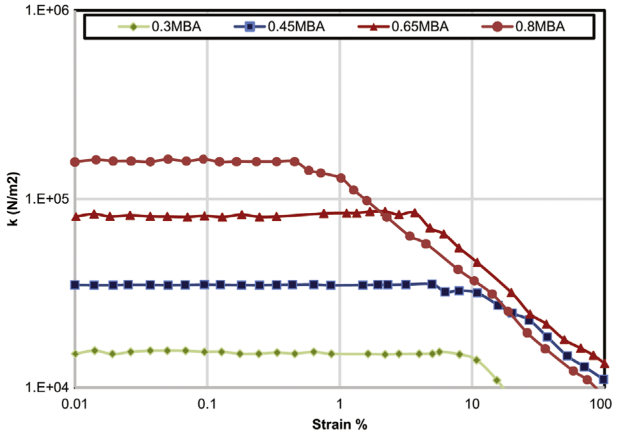


Figure 12. Effect of cross-linker concentration on (k) with strain amplitude sweep from 0.01 to 100 % at a constant frequency.

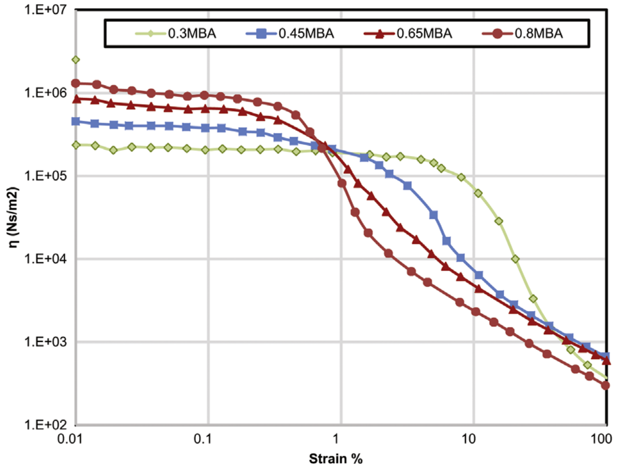


Figure 13. Effect of cross-linker concentration on (η) with strain amplitude sweep from 0.01 to 100 % at a constant frequency.

Table 6. Relationship between storage modulus up to the onset of elastic to viscous phase (G'_{λ}, *Pa*) and $W(\lambda_L - \frac{1}{\lambda_L^2})$

Weight percentage of cross-linker (W)	Onset of elastic to viscous phase (Strain %)	Extension ratio $\lambda_L = L/L0$	$W(\lambda_L - \frac{1}{\lambda_L^2})$	Storage modulus (Actual)	Storage modulus (Predicted)	Error (%)	Mean confidence interval (lower 95 %)	Mean confidence interval (upper 95 %)
0.8	0.005	1.005	0.0119	150 000	149 500	0.33	144 440	154 560
0.65	0.025	1.025	0.0476	80 000	81 313	1.64	78 482	84 145
0.45	0.057	1.057	0.0729	34 000	32 888	3.27	29 500	36 276
0.3	0.100	1.100	0.0821	15 000	15 299	1.99	11 297	19 301

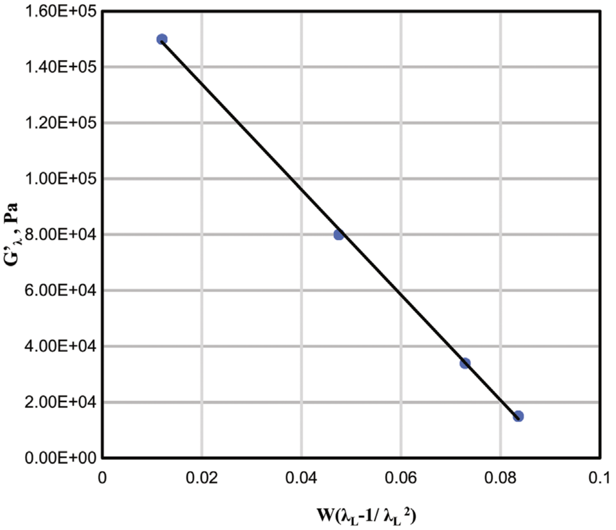


Figure 14. Plot of G'_{λ}(the onset of elastic to viscous phase) versus W **(λ_L-1/ λ_L^2)** demonstrating a linear relationship (*W* is weight percentage of cross-linker and λ_L is PPGs extension ratio).

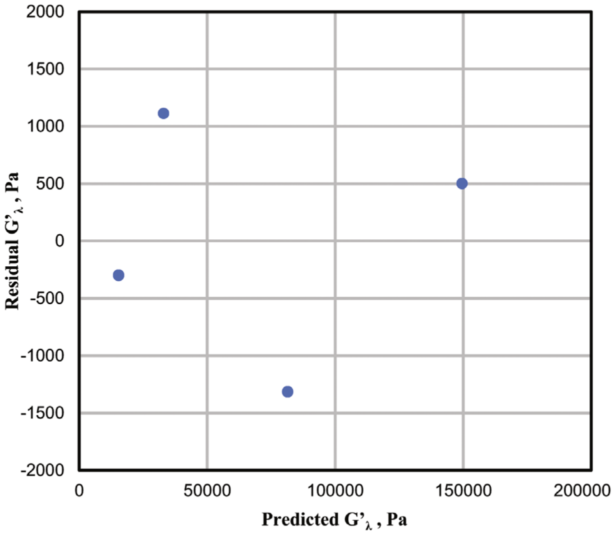


Figure 15. Plot of Residual G'_{λ} versus Predicted G'_{λ}. (G'_{λ} is the onset of elastic to viscous phase).

CONCLUSIONS

1. PPGs injection is one of the most popular technologies for conformance control in heterogeneous oil reservoirs. Moreover, the conditions of oil reservoirs which need conformance control include wide ranges of temperature and water salinity. Therefore, the structural improvement of PPGs which can withstand harsh reservoir conditions is of vital importance. In this study, new enhanced PPGs were developed for use in oil reservoirs with a temperature of 145 °C and a water with total dissolved solids of 225 000 mg/L.
2. A series of well-characterized laboratory scale PPG products were successfully synthesized. It has been shown that swelling ratio and syneresis resistance of new upgraded PPGs depend strongly on its composition and its surrounding environmental conditions, such as brine composition, pH, and temperature.
3. The 0.3 g/g (30 wt%) of a 2:1:1:2 molar mass ratio of AM, DA, NVP, and AMPSNa monomers with 0.0045 g/g (0.45 wt %) N,N-methylenebis (acrylamide), and 0.025 g/g (2.5 wt %) nano-clay montmorillonite Na^+ exhibited the highest stability of the investigated PPGs under oil reservoir with high salinity and temperature.
4. As the mass percentage of the cross-linker increased, the degree of swelling was greatly reduced, the syneresis resistance improved, and storage modulus up to onset of elastic to viscous phase increased but the onset of elastic to viscous phase (G'_{λ}) decreased dramatically.
5. Increasing the strain percentage to a value more than G'_{λ} caused a sharper drop of storage modulus in PPG products with higher concentrations of cross-linker.
6. Results indicated that the onset of elastic to viscous phase for PPG products with a higher concentration of cross-linker is happening in much lower value of strain; also it was found that there is a linear relationship between mass percentage of cross-linker (*W*), extension ratio (λ_L), and onset of elastic to viscous phase in terms of storage modulus.

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NOMENCLATURE

AM	acrylamide
AMPSNa	2-acrylamido-2-methylpropane sulphonic sodium salt

APS	sodium persulphate
CW	connate water
DA	N,N-dimethyl acrylamide
DW	distilled water
G'	storage modulus
G''	loss modulus
G^*	complex modulus
G_λ'	point of elastic to viscous phase onset
IW	injection water
MB	nano clay montmorillonite Na^+
MBA	N,N-methylenebis (acrylamide)
NVP	N-vinylpyrrolidone
PPGs	preformed particle gels
PW	production water
SR	swelling ratio
TEMED	N,N,N',N' tetramethylethylenediamine
W	mass percentage of cross-linker
W_d	mass of dry PPG powder
W_s	mass of swelled PPG powder
σ	stress
ε	strain
ω	angular frequency
tgδ	loss factor
λ_L	extension ratio

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