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Performance of fly ash based polymer gels for water reduction in enhanced oil recovery: Gelation kinetics and dynamic rheological studies

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Abstract−The complexity of well and reservoir conditions demands frequent redesigning of water plugging polymer gels during enhanced oil recovery (EOR). In the present study, we developed coal fly ash (CFA) based gels from polyacrylamide (PAM) polymer and polyethyleneimine (PEI) crosslinker for water control in mature oil fields. The CFA acts as an inorganic additive to fine-tune gelation performance and rheological properties of PAM/PEI gel system. Hence, effects of various CFA (0.5 to 2 wt%), PAM (2 to 8.47 wt%) and PEI (0.3 to 1.04 wt%) concentrations on gelation kinetics and dynamic rheology of pure PAM/PEI gel and PAM/PEI-CFA composite gels were studied at a representative reservoir temperature of 90 °C. Experimental results reveal that gelation time of pure PAM/PEI gel increases with increasing CFA addition. Further observation demonstrates that increasing PAM and PEI concentrations decreases the gelation times of PAM/PEI-CFA composite gels. Gelation time was found to be within 3-120 hours. Understanding the property of reaction order enables better prediction of gelation time. Dynamic rheological data show that viscoelastic moduli (G′ and G″) of various PAM/PEI-CFA composite gels improved better as compared to the pure PAM/PEI gel across the strain-sweep and frequency-sweep tests. SEM analysis of selected samples at 72 hours and 720 hours of gelation activity consolidated gelation kinetics and dynamic rheological results. These polymer gels are excellent candidates for sealing water thief zones in oil and gas reservoirs.

Keywords: Fly Ash, Polymers, Reaction Order, Water Shutoff, Gelation, Oil Recovery

INTRODUCTION

The petroleum industry is spending huge amounts of money and utilizing the every latest cutting-edge technology to find oil in very risky environments, such as the polar regions of the earth and deep seas, which is an indication that primary and secondary oil production from existing oilfields is reaching a climax. However, existing fields still contain significant but seemingly unrecoverable amounts of hydrocarbons. The recovery of such enormous and untapped quantity of hydrocarbons in the existing mature oilfields is the goal of enhanced oil recovery (EOR). The EOR methods are very important to a perpetual supply of oil [1]. Excessive water production in mature oilfields has been a major concern almost since the beginning [2]. Research studies have shown that about 210 million barrels (33.4 million m^3) of water usually accompanied 75 million barrels (11.9 million m^3) of oil produced on a daily basis [3]. In fact, an estimate of more than 40 billion US dollars is spent annually worldwide to manage unwanted water from oil wells [4]. Water production in oilfields can occur in two ways: first is that which alters in the life of a waterflood and coproduced with oil as part of the fractional flow characteristics in the reservoir rock. The second type of water production is that which competes directly with oil such as water due to coning and high permeability streaks. The reduction of this water is of great concern to the operators in oilfields [5]. To achieve a high success rate when treating water production problems, nature and the cause of the problem must first be identified correctly [5]. Several materials and techniques have been proposed for tackling excessive water production during EOR operations. Generally, these techniques are categorized into two main groups: mechanical and chemical water shutoff methods. The mechanical methods are most suitable for wellbore related problems, but can also be used in combination with the chemical water shutoff methods, depending on the complexity of the reservoir problem. About seven decades ago, the chemical methods [6-21] attracted more industrial acceptability and thus have greater application than the mechanical methods.

Polymer gels are among the chemical methods used for water shutoff treatments in the petroleum industry. Polymer gels are of

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significant interest for their applications in petroleum production, which include water shutoff treatments of oil wells [22]. A typical polymer gel consists of a water-soluble polymer and a crosslinking agent. The low viscosity solution containing the polymer and the crosslinker, often called gelant [23], is converted into a rubber-like gel structure via a crosslinking reaction in which polymer chains are linked together to form a three-dimensional structural network. The majority of gels used presently for water shutoff treatment are either polyacrylamide (PAM) [24-27] or polysaccharides [12,28-31]. However, most of these crosslinked polymer gels still possess inappropriate gelation time, insignificant viscoelastic behavior, and thermal instability, especially at elevated temperatures (>80 °C). Therefore, researchers and operators in oilfields fashioned out the concept of incorporating macro and nanomaterials [1,32-37] in water shutoff polymer gelling solutions to modify and enhance the aforementioned features during EOR processes. The present study reports the gelation kinetics and dynamic rheological properties of coal fly ash (CFA) based polymer gels developed from polyacrylamide (PAM) crosslinked by polyethyleneimine (PEI). The PEI is chosen as the crosslinking agent because of its low level toxicity and better solubility in water. The CFA constitutes many chemical oxides in which silica and alumina are present in high quantity. The high percentage of both chemical oxides could induce the CFA to promote an outstanding viscoelastic and gelation performance when incorporated in the pristine PAM/PEI gel. The effect of various CFA incorporation on the gelation performance and viscoelasticity of pure PAM/PEI gel was investigated. Moreover, the effects of different concentrations of PAM and PEI on the gelation behavior and viscoelastic character of various PAM/PEI-CFA composite gels were studied in detail. This study also establishes the effectiveness of CFA as a potential and promising inorganic additive for modifying and improving the gelation activity and dynamic rheological characteristics of PAM/PEI gel applied for water management in mature oil fields.

EXPERIMENTAL

1. Materials

The PAM (Mw=250,000-500,000; pH=4) and PEI (Mw=70,000; pH=12) used in this study were supplied by the SNF Chemical Co., France. Both PAM and PEI were received as solution. Active contents of PAM and PEI were 20 wt% and 33 wt%, respectively. The CFA used in this study was purchased from a local supplier. All gelling solutions were prepared using brine water containing 2,000 ppm NaCl.

2. Gels Preparation

Pure PAM/PEI (without CFA) gel and various PAM/PEI-CFA composite gels were formulated from CFA, PAM and PEI of different concentrations. The CFA, PAM and PEI were varied from 0.5 to 2 wt%, 2.87 to 8.4 wt% and 0.3 to 1.04 wt%, respectively. Each gelling solution infused with and without CFA was prepared by adding appropriate concentrations of PAM and PEI solutions into 2,000 ppm NaCl brine with complete mixing for 10 minutes using magnetic stirrer. The NaCl brine was chosen to prepare all gelling solutions because NaCl constitutes the major component of salts present in formation water. Following the preparation, all samples were transferred into test bottles and sealed for gelation kinetics performance study by Sydnask technique, while dynamic rheological measurements were conducted at the onset of becoming non-flowing rigid mature gels.

3. Gelation Kinetics Study

Crosslinking properties of pure PAM/PEI gel and various PAM/PEI-CFA composite gels developed were studied. A 15 mL volume of each sample was transferred into a test bottle and sealed before being placed inside the oven. Effects of various CFA, PAM, and PEI concentrations on gelation performance of pure PAM/PEI gel and PAM/PEI-CFA composite gels were systematically observed through the bottle testing method. All bottle experiments were set at a typical reservoir temperature of 90 °C. A Sydnask code was assigned as the bottle testing method. This technique is considered as a convenient and cheap method to study gelation time. The strength of gelants during the gelation activity was expressed as an alphabetic code of A-I and the description of each code is given in Table 1. Note that the gelation time of water shutoff gel is taken as the time when the gelant solution in code A changes to flowing gel code C, which is usually called initial gelation strength (start of gel point) [38].

4. Dynamic Rheological Measurements

Dynamic rheological measurements were performed on the pure PAM/PEI gel and various PAM/PEI-CFA composite gels using the hybrid rheometer. A rheological test was carried out on each sam-

Table 1. Gel strength code proposed by Sydnask

Gel strength code	Gel description
A	No detectable gel formed: The gel appears to have the same viscosity as the original polymer solution
B	Highly flowing gel: The gel appears to be only slightly more viscous than the initial polymer solution
C	Flowing gel: Most of the gel flows to the bottle cap by gravity upon inversion
D	Moderately flowing gel: Only a small portion (5-10%) of the gel does not flow to the bottle by gravity upon inversion (usually characterized as a tonguing gel)
E	Barely flowing gel: The gel can barely flow to the bottle cap and/or a significant portion (>15%) of the gel does not flow by gravity upon inversion
F	Highly deformable non flowing gel: The gel does not flow to the bottle cap by gravity upon inversion
G	Moderately deformable non flowing gel: The gel deforms about half way down the bottle by gravity upon inversion
H	Slightly deformable non flowing gel: Only the gel surface slightly deforms by gravity upon inversion
I	Rigid gel: There is no gel surface deformation by gravity upon inversion

Table 2. Chemical oxides composition of CFA used in this study

Component	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Fe_2O_3	SrO	BaO
CFA (%wt)	21.97	32.94	1.061	0.1581	0.6931	24.318	1.698	3.446	0.1394	0.2404

ple at the onset of becoming non-flowing mature gel. The viscoelastic behavior of each sample was determined using a 40 mm diameter parallel Peltier plate geometry having 1.00 mm gap. The strain-sweep measurements were carried out to measure the dynamic viscoelastic moduli (elastic modulus G′ and viscous modulus G″) in the range of 0.1 to 100% of the strain amplitude under constant frequency of 10 rad s^{-1}. Also, the G′ and G″ were recorded as a function of frequency within the range of 0.1 to 100 rad s^{-1}. All tests were performed at 90 °C. The rheological measurements of each gel reported in this study were carried out after gelation (i.e., when non-flowing rigid gel was noticed during gelation performance study that was conducted using an oven). Whenever a gel sample inside the oven was observed to have attained the point of non-flowing rigid gel, few gel samples were taken quickly and tested on hybrid rheometer machine equipped with parallel plate geometry and tightly covered with solvent trap system to minimize evaporation.

5. Gels Characterization

Particle size distributions of CFA were determined with Turbotrac model S360 particle size analyzer. X-ray florescence (XRF) was used to determine the oxide compositions of CFA. Scanning electron microscopy (SEM) was used to study the pore structures of selected gelants after 3 days and 30 days of aging. The morphological characterizations of selected samples were observed by *JEOL* SEM using 10-15 kV voltage.

RESULTS AND DISCUSSION

1. Gelation Kinetics Study

Bottle screening test is an economical, convenient, and semiquantitative technique for the study of gelation performance due to its visualization in the gel formation process and periodic interval of measurement. In this work, gelation kinetics performance of pure PAM/PEI gel and various PAM/PEI-CFA composite gels was determined using bottle screening test developed by Sydnask.

1-1. Effect of CFA on the Gelation Kinetics

It is important to reiterate that pure PAM/PEI gel and different PAM/PEI-CFA composite gels were developed from 6 wt% PAM and 0.67 wt% PEI, while CFA addition in PAM/PEI-CFA composite gels was varied from 0.5 wt% to 2 wt%. Table 2 depicts the chemical oxides composition of CFA used in this study. The weight percentage summation of Al_2O_3, SiO_2 and Fe_2O_3 (≈58 wt%) indicates that this particular CFA belongs to class C fly ash [39]. Particle size analysis shown in Fig. 1 also indicates that this CFA has a median size and an average particle size of d_{50}=1.745 and 24.58 μm, respectively. The gel strength code technique was used to determine the gelation performance of pure PAM/PEI gel and PAM/

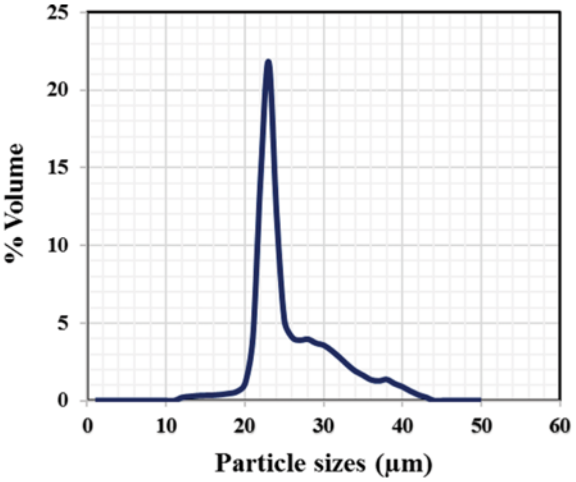

Fig. 1. The particle size distributions of CFA, d_{50}=1.745.

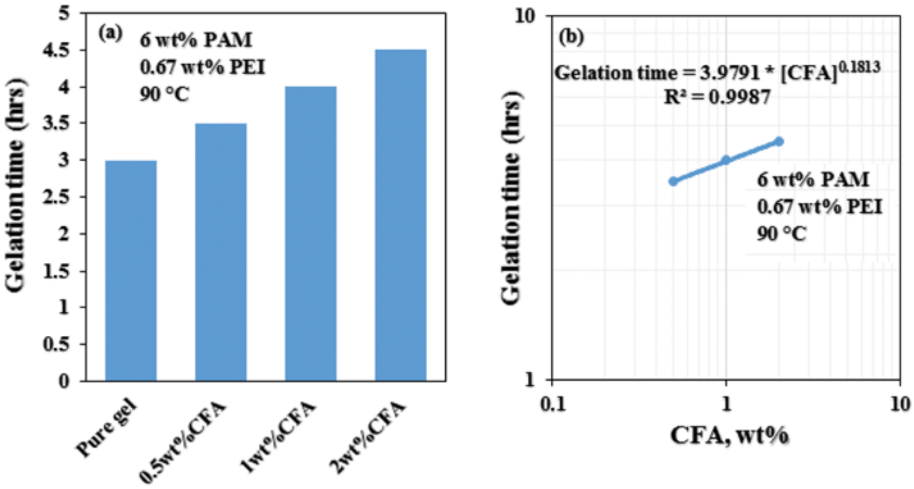

Fig. 2. (a) Gelation time of pure PAM/PEI gel (without CFA) and PAM/PEI-CFA composite gels containing various CFA amounts. Each sample contains 6 wt% PAM and 0.67 wt% PEI; (b) Reaction order of PAM/PEI-CFA composite gels with respect to the CFA.

Table 3. Gelation kinetics of pure PAM/PEI (without CFA) gel and various PAM/PEI-CFA composite gels at 90 °C

Gel composition			Strength code of gel (h)																									
			0.25	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5.5	6	7	8	9	10	11	12	24	48	72	120	240	360	480	720
Pure gel (without CFA)			A	A	A	B	B	B	C	C	D	D	F	F	G	G	I	I	I	I	I	I	I	I	I	I	I	I
0.5 wt% CFA	6 wt% PAM	0.67 wt% PEI	A	A	B	B	B	B	B	C	C	C	F	F	G	G	G	G	I	I	I	I	I	I	I	I	I	I
1 wt% CFA			A	A	B	B	B	B	B	B	C	C	F	F	G	G	G	I	I	I	I	I	I	I	I	I	I	I
2 wt% CFA			A	A	B	B	B	B	B	B	B	C	E	F	F	G	G	I	I	I	I	I	I	I	I	I	I	I
2.87 wt% PAM	2 wt% CFA	0.67 wt% PEI	A	A	A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	C	C	C	C	E
6 wt% PAM			A	A	B	B	B	B	B	B	B	C	E	F	F	G	G	I	I	I	I	I	I	I	I	I	I	I
8.4 wt% PAM			A	B	B	B	B	B	B	B	C	C	E	F	G	H	I	I	I	I	I	I	I	I	I	I	I	S
0.3 wt% PEI	2 wt% CFA	6 wt% PAM	A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	C	E	G	G	H	I	I	I
0.67 wt%PEI			A	A	B	B	B	B	B	B	B	C	E	F	F	G	G	I	I	I	I	I	I	I	I	I	I	I
1.04 wt% PEI			A	B	B	B	B	B	B	B	C	D	F	F	G	G	I	I	I	I	I	I	I	I	I	I	I	I

S: syneresis

PEI-CFA composite gels containing various CFA quantities. Fig. 2(a) and Table 3 summarize the outcome of the gelation kinetics performance of pure PAM/PEI gel and PAM/PEI-CFA composite gels as determined through the bottle test method. Note that the gelation time of water shutoff gel is taken as the time when the gelant solution in code A state changes to flowing gel code C. As can be seen in Fig. 2(a), the gelation time of pure PAM/PEI gel (without CFA) began 3 hours after its preparation. At this particular period, there was a noticeable change in the gelant flow as compared to when it was just prepared. The neat PAM/PEI gel could still flow steadily to the bottle cap by gravity inversion. On the other hand, the PAM/PEI-CFA composite gels containing various amounts of CFA displayed different response about the gelation time. It was noticed that the gelation time of pure PAM/PEI gel increased with the increasing CFA addition. Gelation time of composite gels filled with various CFA amounts ranged from 3.5 to 4.5 hours (Fig. 2(a)). This observation indicates that CFA might act as a retarder in polymer gels applied for water control in mature oilfields. A similar study by Patil and Kalgaonkar introduced nanosilica in a conformance sealant which led to variation in the gelation time [34]. Further observation of the gelation behavior of pure PAM/PEI gel and PAM/PEI-CFA composite gels filled with different CFA concentrations for 30 days led to a noticeable transformation in their strengths which were assigned with Sydnask alphabetical codes (Table 3).

Moreover, the gelation time of each PAM/PEI-CFA composite gel at different CFA concentration was used to obtain the reaction order with respect to CFA. A logarithmic plot of the gelation time and CFA concentration axes will give a straight line whose slope is the reaction order with respect to CFA. The reaction order with respect to CFA was found to be 0.1813 from the plot shown in Fig. 2(b). These data suggest that at moderate temperature applications, gelation time can be increased by using high CFA loadings. These data further reveal that CFA can aid in delaying gelation time of water shutoff polymer gels developed from high polymer/crosslinker ratios.

1-2. Effect of PAM on the Gelation Kinetics

Using appropriate and qualitative polymer while designing polymer gel is very crucial to the success rate of water reduction during tertiary operation in oil fields. The previous section has buttressed the impacts of various CFA quantities on the gelation kinetics performance of pure PAM/PEI gel. It is therefore important to further understand the effects of various PAM concentrations on

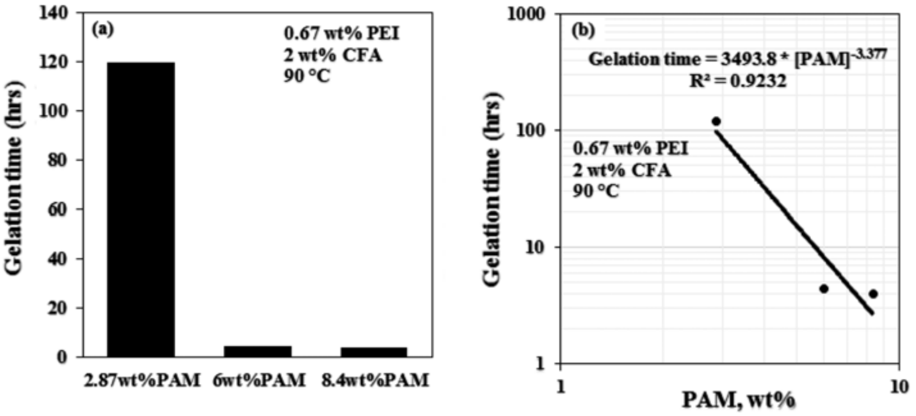

Fig. 3. (a) Gelation time of PAM/PEI-CFA composite gels prepared from different PAM concentrations. Each sample contains 0.67 wt% PEI and 2 wt% CFA; (b) Reaction order of PAM/PEI-CFA composite gels with respect to the PAM.

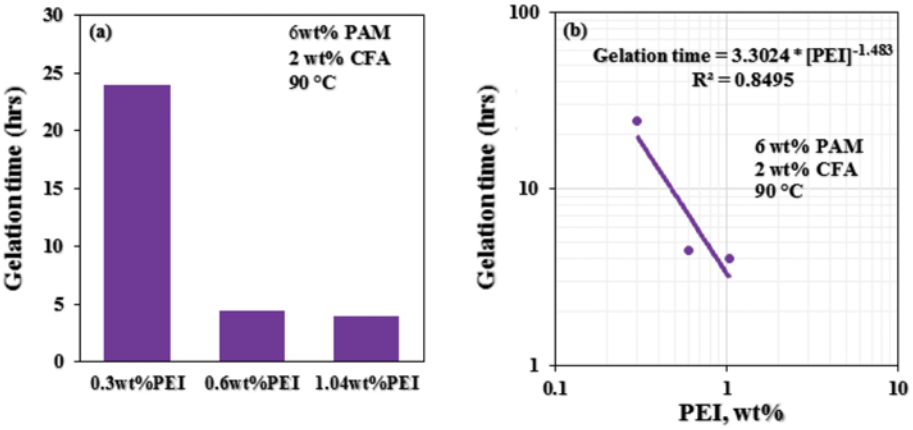

Fig. 4. (a) Gelation time of PAM/PEI-CFA composite gels prepared from different PEI concentrations. Each sample contains 6 wt% PAM and 2 wt% CFA; (b) Reaction order of PAM/PEI-CFA composite gels with respect to the PEI.

gelation kinetics of PAM/PEI-CFA composite gels. PEI and CFA concentrations were kept constant at 0.67 wt% and 2 wt%, respectively, while PAM concentration was varied from 2.87 to 8.4 wt%. The gelation performance statistical data are given in Fig. 3(a) and Table 3. According to Fig. 3(a), gelation time of PAM/PEI-CFA composite gels decreases as PAM concentration increases. In fact, the gelation time of these gelants could have occurred earlier because it is well known that more crosslinking units can be achieved at a higher polymer concentration, which consequently leads to short gelation time [38]. However, CFA acts as a retarder in the PAM/PEI-CFA gelants and ultimately causes gelation time delay. Impregnation of CFA as an inorganic additive in the matrices of crosslinked polymer gels is therefore cost effective, as little polymer with crosslinker can be used with CFA to achieve a prolong gelation time in deep high temperature reservoirs.

In addition, the gelation time of PAM/PEI-CFA composite gels at different PAM concentration was used to obtain the reaction order with respect to PAM. A logarithmic plot of PAM/PEI-CFA composite gels gelation time and various PAM concentration will give a straight line whose slope is the reaction order with respect to PAM. The reaction order with respect to PAM was found to be 3.377 from the plot shown in Fig. 3(b). For PAM/PEI gel systems reported in the literature, the reaction order values with respect to PAM were found to be in the range of 0.79-1.75, obtained by Jia et al. [38] and 1.26, obtained by Al-Muntasheri et al. [40]. In the present study, the reaction order obtained is believed to be high due to the incorporation of CFA in the PAM/PEI gel. Also, previous research study has established that the value of reaction order can be dominated by the polymer hydrolyzing degree [38]. Likewise, the huge numerical coefficient obtained in the equation accounts for the delayed gelation time experienced by the PAM/PEI-CFA composite gel infused with 2.87 wt% PAM. Bai et al. [41] reported a similar observation, explaining the relationship between the natural logarithm of the gelation time and the reciprocal of temperature. Furthermore, these data imply that at low temperature reservoirs, shorter shut-in time can be obtained by using higher polymer concentrations. Likewise, the gelation time can be increased under high temperature applications by using lower polymer loadings. This is the reason for the extended gelation time of PAM/PEI-CFA composite gel containing 2.87 wt% PAM (begins at 120 hrs). However, lowering polymer concentration may lead to weak gels. It is therefore very important to examine the gel strength as a function of composition before field implementation.

1-3. Effect of PEI on the Gelation Kinetics

Utilization of appropriate crosslinker concentration has direct impact on the physical properties of water shutoff polymer gel. Polymer acts as the skeleton in the gel structure, while the crosslinker is a bridging agent that brings polymer molecules together. Therefore, the crosslinker plays a significant role in the gelation activity. Effect of different PEI concentrations on the gelation behavior of PAM/PEI-CFA composite gels is discussed in this section. The PEI concentration was varied from 0.3 wt% to 1.04 wt%, while PAM and CFA concentrations were fixed at 6 wt% and 2 wt%, respectively. Gelation performance of PAM/PEI-CFA composite gels containing various PEI concentration is shown in Fig. 4(a) and Table 3. As can be observed in this figure, gelation time is around 4-24 h for all the formulations. It is evident that the gelation time of PAM/PEI-CFA composite gels decreases as the PEI concentration increases. Moreover, the gelation time achieved by these gelants could have been shorter without the inclusion of CFA. However, the addition of CFA plays a significant role by further delaying the gelation periods of these composite gels. Thus, high PEI concentration can increase the possibility of PEI attacking the carbonyl carbon attached to the amide group. Hence, increasing the PEI concentration is not recommended for water shutoff polymer gels. On the contrary, the higher concentration of crosslinker can greatly affect the gel stability due to excessive crosslinking properties [38].

The gelation time of PAM/PEI-CFA composite gels at different PEI concentration was used to obtain the reaction order with respect to PEI. A logarithmic plot on both gelation time and PEI concentration axes gives a straight line whose slope is the reaction order with respect to PEI. The reaction order with respect to PEI was 1.483 from the plot shown in Fig. 4(b). According to previous studies on water shutoff PAM/PEI gel systems, the reaction order values for PAM/PEI gels with respect to PEI crosslinker were within 0.99-1.63, obtained by Jia et al. [38] and 0.91, obtained by

Al-Muntasheri et al. [40]. The reaction order obtained in the current study with respect to PEI is fairly in agreement with the values obtained by these researchers. Based on this result, the gelation time can be fine-tuned by varying the concentration of PEI. However, high concentration of the crosslinker can lead to gel syneresis. Table 4 summarizes the gelation time of pure PAM/PEI gel and various PAM/PEI-CFA composite gels developed in this study.

2. Dynamic Rheological Properties

2-1. Effect of CFA on the Viscoelastic Behavior of Pure PAM/PEI gel

The strain-sweep measurements for pure PAM/PEI gel and PAM/PEI-CFA composite gels were carried out to understand the effect of various CFA amount on the viscoelastic behavior of these cross-linked polymer gels. The PAM and PEI concentrations were fixed at 6 wt% and 0.67 wt%, respectively. Dynamic rheological tests of these samples (and subsequent sections) were determined at the onset of becoming a mature gel in a typical reservoir temperature of 90 °C. Fig. 5(a) and (c) shows the dynamic rheological data (G′ and G″) for pure PAM and PAM/PEI-CFA composite gels incorporated with different CFA quantities. The G′ was practically higher than G″ for pure PAM/PEI gel and PAM/PEI-CFA composite gels at about 0.15% of the strain, indicating that the pure PAM/PEI gel

Table 4. Gelation time of pure PAM/PEI gel and various PAM/PEI-CFA composite gels at 90 °C

Gel composition			Temperature (°C)	Gelation time (hrs)
Pure gel (without CFA)	6 wt% PAM	0.67 wt% PEI	90	3.0
0.5 wt% CFA			90	3.5
1 wt% CFA			90	4.0
2 wt% CFA			90	4.5
2.87 wt% PAM	2 wt% CFA	0.67 wt% PEI	90	120
6 wt% PAM			90	4.5
8.4 wt% PAM			90	4.0
0.3 wt% PEI	2 wt% CFA	6 wt% PAM	90	24
0.67 wt%PEI			90	4.5
1.04 wt% PEI			90	4.0

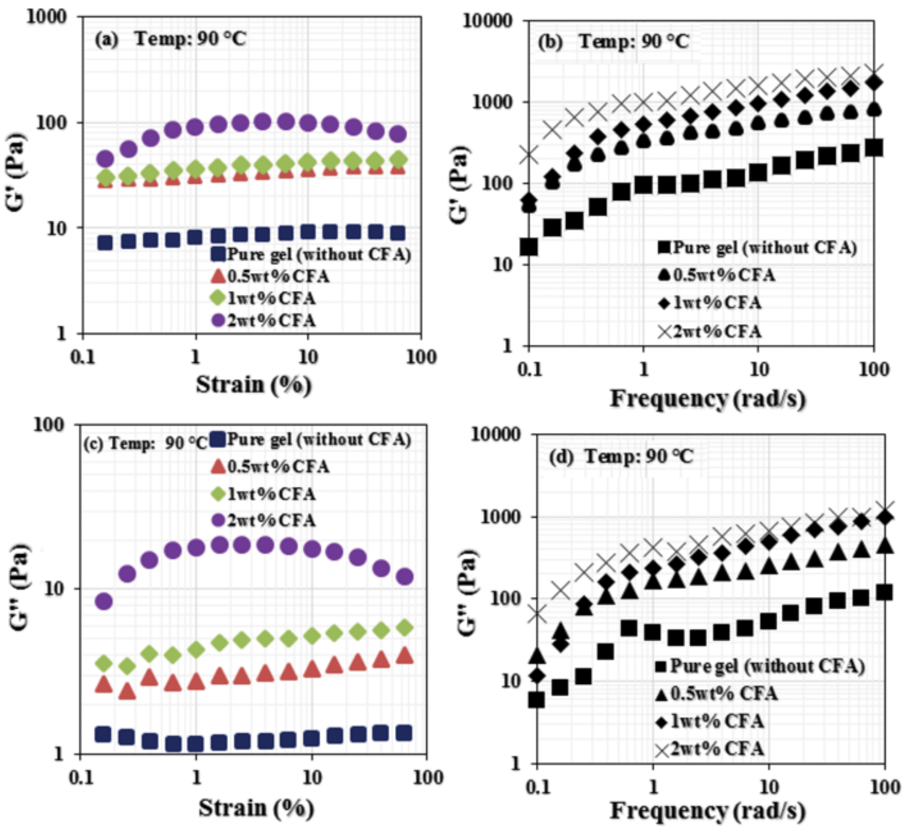

Fig. 5. Strain-sweep measurements for pure PAM/PEI gel and PAM/PEI-CFA composite gels containing various CFA amounts. Each sample contains 6 wt% PAM and 0.67 wt% PEI: (a) Elastic modulus, G′ (Pa) versus strain amplitude (%); (b) Elastic modulus, G′ (Pa) versus frequency (rad/s); (c) Viscous modulus, G″ (Pa) versus strain amplitude (%); (d) Viscous modulus, G″ (Pa) versus frequency (rad/s).

and PAM/PEI-CFA composite gels are solid-like. The strain dependence of G′ of pure PAM/PEI gel and PAM/PEI-CFA composite gels at 90 °C signifies a region of viscoelasticity with a plateau in G′ nearly constant throughout the strain amplitude. It is also evident that the PAM/PEI-CFA composite gels containing various CFA amounts demonstrated more solid-like behavior (G′>G″, Table 5) than the pure PAM/PEI gel [27,35,42].

Additionally, Fig. 5(b) and (d) reveals the variation in the viscoelastic response of pure PAM/PEI gel and PAM/PEI-CFA composite gels filled with various CFA. As can be seen in both figures, G′ was higher than the G″ in all the gelants across the whole frequency range. The difference between G′ and G″ is more noticeable at low/high (0.1/100 rad/s) frequency range. More importantly, these rheological data indicate that frequency also has a direct

Table 5. Dynamic moduli (G′ (Pa) and G″ (Pa)) of pure PAM/PEI gel and PAM/PEI-CFA composite gels at 90 °C

						Dynamic moduli (Pa) (onset of becoming mature gel)	
Gel composition			Strain-sweep test	Strain amplitude (%)	Temperature (°C)	G′	G″
Pure gel (without CFA)	6 wt% PAM	0.67 wt% PEI	10 rad s^{-1}	0.15	90	7.37	1.32
0.5 wt% CFA			10 rad s^{-1}	0.15	90	28.14	2.67
1 wt% CFA			10 rad s^{-1}	0.15	90	30.38	3.53
2 wt% CFA			10 rad s^{-1}	0.15	90	45.06	8.49
2.87 wt% PAM	2 wt% CFA	0.67 wt% PEI	10 rad s^{-1}	0.15	90	8.67	0.83
6 wt% PAM			10 rad s^{-1}	0.15	90	45.06	8.49
8.4 wt% PAM			10 rad s^{-1}	0.15	90	43.27	4.62
0.3 wt% PEI	2 wt% CFA	6 wt% PAM	10 rad s^{-1}	0.15	90	30.23	3.94
0.67 wt%PEI			10 rad s^{-1}	0.15	90	45.06	8.50
1.04 wt% PEI			10 rad s^{-1}	0.15	90	74.47	9.56

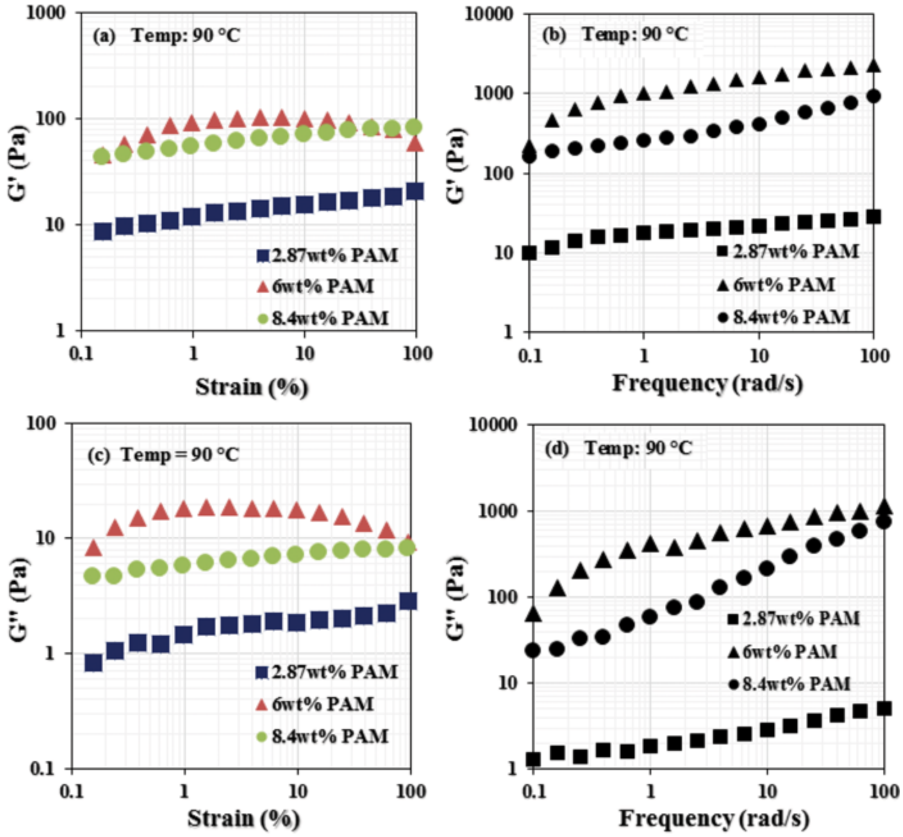

Fig. 6. Strain-sweep measurements for PAM/PEI-CFA composite gels developed from various PAM concentrations 0.67 wt% PEI, 2 wt% CFA concentrations: (a) Elastic modulus, G′ (Pa) versus strain amplitude (%); (b) Elastic modulus, G′ (Pa) versus frequency (rad/s); (c) Viscous modulus, G″ (Pa) versus strain amplitude (%); (d) Viscous modulus, G″ (Pa) versus frequency (rad/s).

influence on the strength of these gels. Obviously, an increase in the gel strength is noticed as CFA is introduced in pure PAM/PEI gel matrix. The enhancement in the viscoelastic properties of pure PAM/PEI gel is indicative of good interaction and strong bond network between the CFA and PAM/PEI molecular chains.

2-2. Effect of PAM on the Viscoelastic Behavior of PAM/PEI-CFA Gels

Fig. 6(a) and (c) represents the strain-sweep measurements of PAM/PEI-CFA composite gels containing PAM concentrations ranging from 2.87 wt% to 8.4 wt%. The PEI and CFA concentrations were fixed at 0.67 wt% and 2 wt%, respectively. In these plots, these composite gels began to exhibit solid-like (G′>G″) behavior starting from 0.15% of the strain amplitude (Table 5). The G′ was higher than the G″ across the whole range of strain amplitude. Besides, the viscoelastic behavior (G′ and G″) of PAM/PEI-CFA composite gels increases with the increasing PAM concentration [26]. Moreover, the improved viscoelastic properties of PAM/PEI-CFA composite gels with increasing PAM concentration might have recorded fewer numerical values without the inclusion of CFA. Undoubtedly, apart from the fact that increasing PAM concentration resulted in increased viscoelastic properties of PAM/PEI-CFA composite gels, the CFA impregnation in the composite gels further enhanced their viscoelastic properties.

Fig. 6(b) and (d) shows the results of the frequency-sweep measurements of PAM/PEI-CFA composite gels containing different PAM concentrations. The viscoelastic moduli of the PAM/PEI-CFA composite gels increase considerably from 2.87 wt% to 6 wt% PAM, and a decrease in the viscoelastic moduli was noticed at 8.4 wt% PAM. Rheological test of this particular PAM/PEI-CFA composite gel containing 8.4 wt% PAM was repeated twice and same results were obtained. The decrease in the viscoelastic response of this specific composite gel may be ascribed to the adsorption of PAM molecular chains onto the CFA surface or ionic interactions between the negative charges emanating from CFA and PAM molecules [32]. Besides, the decrease in the strength (viscoelastic moduli) of this composite gel may be due to syneresis. According to El-Karsani et al. [43], a water shutoff polymer gel system can lose some of its strength due to syneresis effect. Polymer gel possessing sufficient strength is one of the key factors influencing the success rate of water mitigation during EOR applications.

2-3. Effect of PEI on the Viscoelastic Behavior of PAM/PEI-CFA Gels

The strain-sweep measurements of PAM/PEI-CFA composite gels containing various concentrations of PEI are shown in Fig. 7(a) and (c). The PAM and CFA concentrations were kept constant at 6 wt% and 2 wt%, respectively, while PEI concentration was varied from 0.3 wt% to 1.04 wt%. It is evident that G′ is higher than G″ across the entire strain amplitude. Table 5 shows the data of viscoelastic moduli of PAM/PEI-CFA composite gels embedded with various PEI concentrations at 0.15% of the strain amplitude

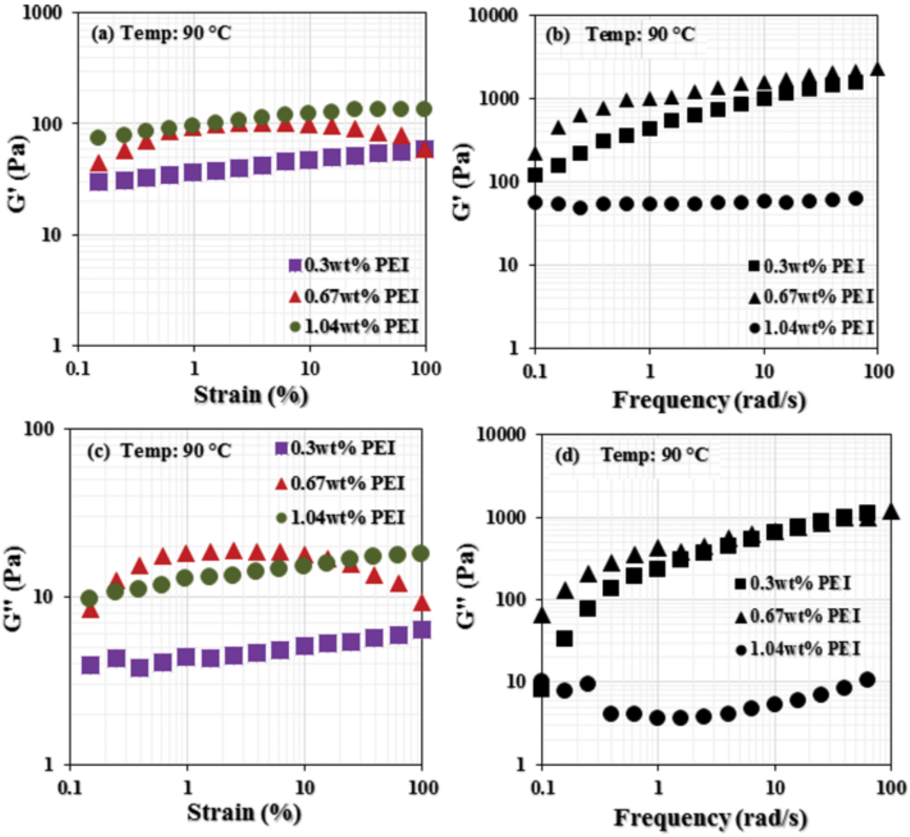

Fig. 7. Strain-sweep measurements for PAM/PEI-CFA composite gels developed from different PEI concentrations with fixed 6 wt% PAM, 2 wt% CFA concentrations (a) Elastic modulus, G′ (Pa) versus strain amplitude (%); (b) Elastic modulus, G′ (Pa) versus frequency (rad/s); (c) Viscous modulus, G″ (Pa) versus strain amplitude (%); (d) Viscous modulus, G″ (Pa) versus frequency (rad/s).

when noticeable changes in the values of G′ and G″ began. Fig. 7(b) and (d) shows the results of frequency-sweep measurements of PAM/PEI-CFA composite gels embedded with different PEI concentrations. The viscoelastic moduli of the PAM/PEI-CFA composite gels nearly display similar trend at 0.3 wt% and 0.67 wt% PEI concentrations, while a decrease in the viscoelastic moduli was observed at 1.04 wt% PEI concentration. Also, repeated rheological tests of this particular PAM/PEI-CFA composite gel containing 1.04 wt% PEI produced similar results. The decrease in the viscoelastic moduli of this particular PAM/PEI-CFA composite gel is attributed to excessive crosslinking, which may eventually lead to syneresis [41] and disruption of gel stability. It is necessary to point out that the final gel strength is actually not predominated by the crosslinker concentration, which is dependent on polymer concentration [38]. Therefore, high PEI crosslinker concentration (>1 wt%) is not recommended due to its great impact on the gel stability.

3. Morphology of Selected Gels

Examining the microstructure of gel provides useful information about pore-interconnectivity. Fig. 8(a) and (b) provides a snapshot of pure PAM/PEI gel and PAM/PEI-CFA composite gels incorporated with various CFA quantities (0.5 wt% to 2 wt%) before and after gelants formation. Surface morphologies of these samples were examined by scanning electron microscopy (SEM) after 72 hours and 720 hours of gelation. Fig. 9(a)-(d) shows the SEM micrographs of pure PAM/PEI gel and PAM/PEI-CFA composite gels filled with different CFA amounts after 72 hours of gelation process. The SEM results consolidate the viscoelastic data obtained for these gels. As can be seen in Fig. 9(a) and (b), the virgin PAM/PEI gel and the PAM/PEI-CFA composite gel containing 0.5 wt% CFA exhibited porous structures in several regions, though these pores were noticed to be larger in the micrograph of neat PAM/PEI gel than that of PAM/PEI gel embedded with 0.5 wt% CFA. These pores contribute to the water holding capacity during gelation process in oil reservoirs. This observation also explains why the neat PAM/PEI gel achieved low viscoelastic properties [1]. Conversely, SEM micrographs of PAM/PEI-CFA composite gel filled with 1 wt% CFA (Fig. 9(c)) and PAM/PEI-CFA composite gel filled with 2 wt% CFA (Fig. 9(d)) were observed to be dense with "net-like" structural pattern and without any conspicuous pores. The absence of porous structures in the micrographs of both samples could be attributed to the high CFA contents.

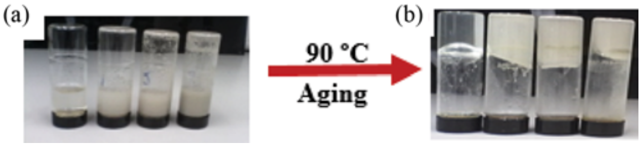

Fig. 8. (a) Pure PAM/PEI gel and PAM/PEI-CFA composite gels filled with various CFA amounts before gelants formation; (b) Pure PAM/PEI gel and PAM/PEI-CFA composite gels filled with various CFA amounts after gelants formation [From left (Fig. 8(a) & (b)): pure PAM/PEI gel and PAM/PEI-CFA composite gels containing 0.5 wt%, 1 wt% and 2 wt% CFA].

The pure PAM/PEI gel and PAM/PEI-CFA composite gels filled with various CFA amounts were again examined after 720 hours of gelation activity. Fig. 10(a)-(d) reveals the surface morphology

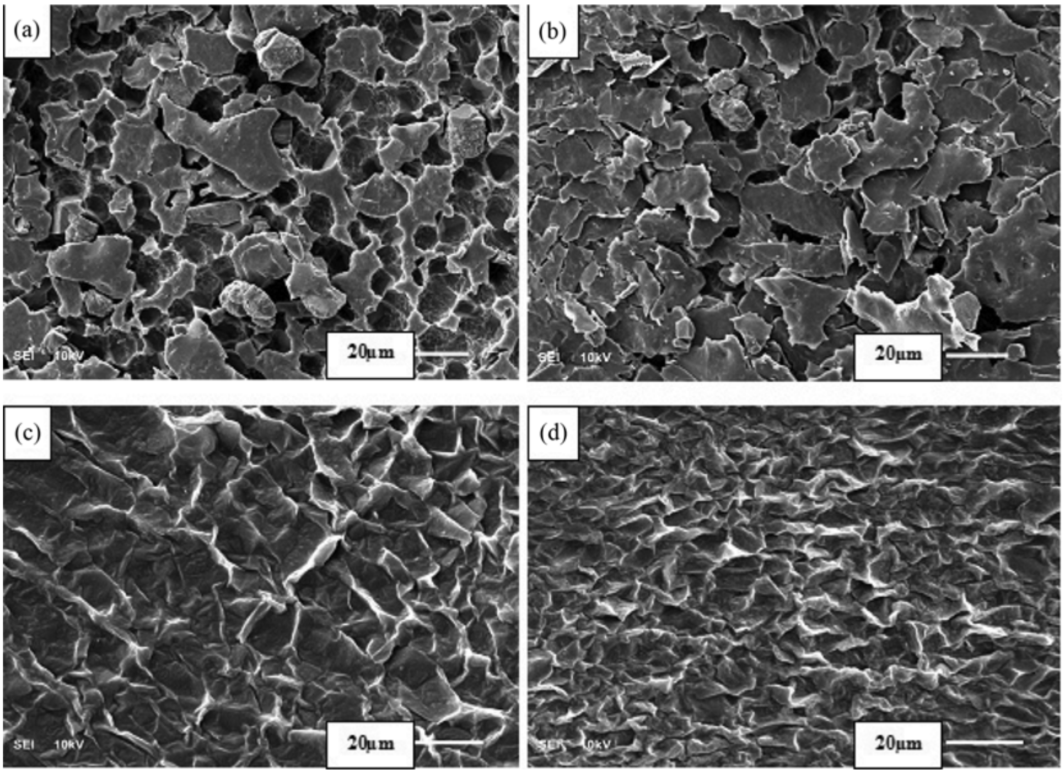

Fig. 9. SEM micrographs after 3 days: (a) pure PAM/PEI gel (without CFA); and PAM/PEI-CFA composite gels containing (b) 0.5 wt% (c) 1 wt% (d) 2 wt% CFA. Each gel contains 6 wt% PAM and 0.67 wt% PEI concentrations.

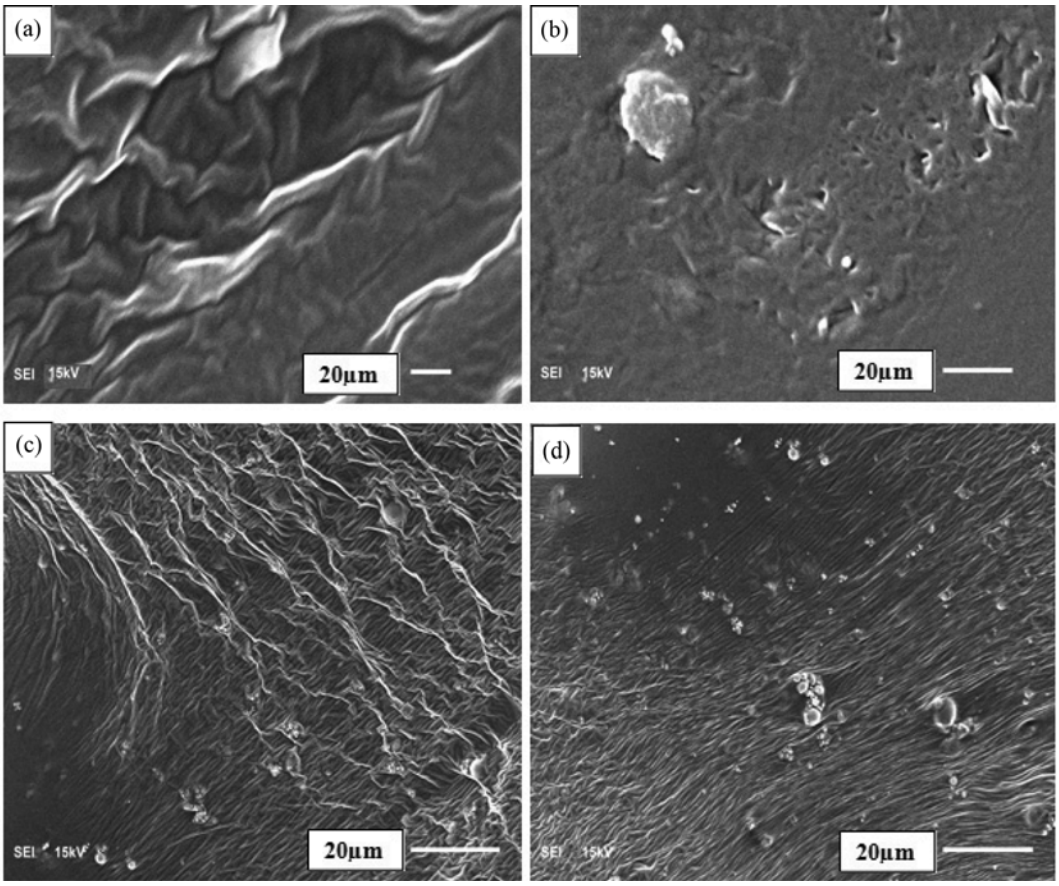

Fig. 10. SEM micrographs after 30 days: (a) pure PAM/PEI gel (without CFA); and PAM/PEI-CFA composite gels containing (b) 0.5 wt% (c) 1 wt% (d) 2 wt% CFA. Each gel contains 6 wt% PAM and 0.67 wt% PEI concentrations.

of these gels. The pure PAM/PEI gel (Fig. 10(a)) and PAM/PEI-CFA composite gels (Fig. 10(b)-(d)) containing various CFA quantities exhibit dense surfaces. These SEM observations attest to the possibility of shrinkage and reduction in the weight of these gelants caused by syneresis after several days of aging. Zhang et al. [44] reported a similar case in their study. It is desired that crosslinked polymer gel for water shutoff treatments has several pore networks capable of holding water in thief zones without adverse effect on the viscoelastic properties of the gel.

4. Reaction Mechanism

The reaction mechanism governing gel formation between PAM and PEI in NaCl brine solution dispersed with CFA is believed to have occurred through a substitution reaction where the nucleophilic amine nitrogen on PEI substitutes the acrylamide pendant groups on the PAM, resulting in a covalent bond between the nitrogen on PEI and the amide group on PAM. Previous research studies have shown that variety of polymers containing acrylamide pendant groups react with nitrogen on PEI via a transamidation reaction pathway to produce gels [38,40,41]. Fig. 11 illustrates the synthesis pathway of a typical PAM/PEI gel incorporated with the CFA. To understand the synergistic effect and impact of CFA inclusion within the PAM/PEI gel matrices, structural characterizations were conducted on the CFA, pure PAM/PEI gel (without CFA) and PAM/PEI-CFA composite gels containing various CFA, PAM and PEI concentrations by using XRD instrument. Fig. 12 depicts the XRD structural pattern revealing the major minerals present in CFA to be mullite, quartz, lime and hematite are present in small quantities. From the XRD pattern of CFA-free PAM/PEI gel shown in Fig. 13, the pure PAM/PEI gel does not reveal any noticeable peak as a result of the amorphous nature of the polymer, PAM and the crosslinker, PEI [45,46]. On the other hand, the XRD patterns of PAM/PEI-CFA composite gels containing various CFA contents (Fig. 13) are quite distinct from that of the pure PAM/PEI gel. Note that PAM and PEI concentrations were fixed at 6 wt% and 0.67 wt%, respectively. The PAM/PEI-CFA composite gels filled with 0.5 and 1 wt% CFA exhibited broad peaks at $2\theta=20.3^{\circ}$-27.9°. These peaks partly indicate the dispersion of CFA in the gelants' matrices and also suggest the presence of crystalline phases, such as mullite and quartz [47]. In the case of PAM/PEI-CFA gel incorporated with 2 wt% CFA, its XRD spectrum exhibits an intense protruding sharp peak at $2\theta=29.1^{\circ}$ (Fig. 13), which is caused by the increase of CFA addition in the gel matrix and also indicates high crystalline domain [47]. Additionally, Figs. 14-15 reveal the XRD diffractograms of PAM/PEI-CFA composite gels prepared from various concentrations of PAM polymer and PEI crosslinker. As can be seen in Fig. 14, PEI and CFA concentrations were kept constant at 0.67 wt% and 2 wt%, respectively, while in Fig. 15, PAM and CFA concentrations were fixed at 6 wt% and

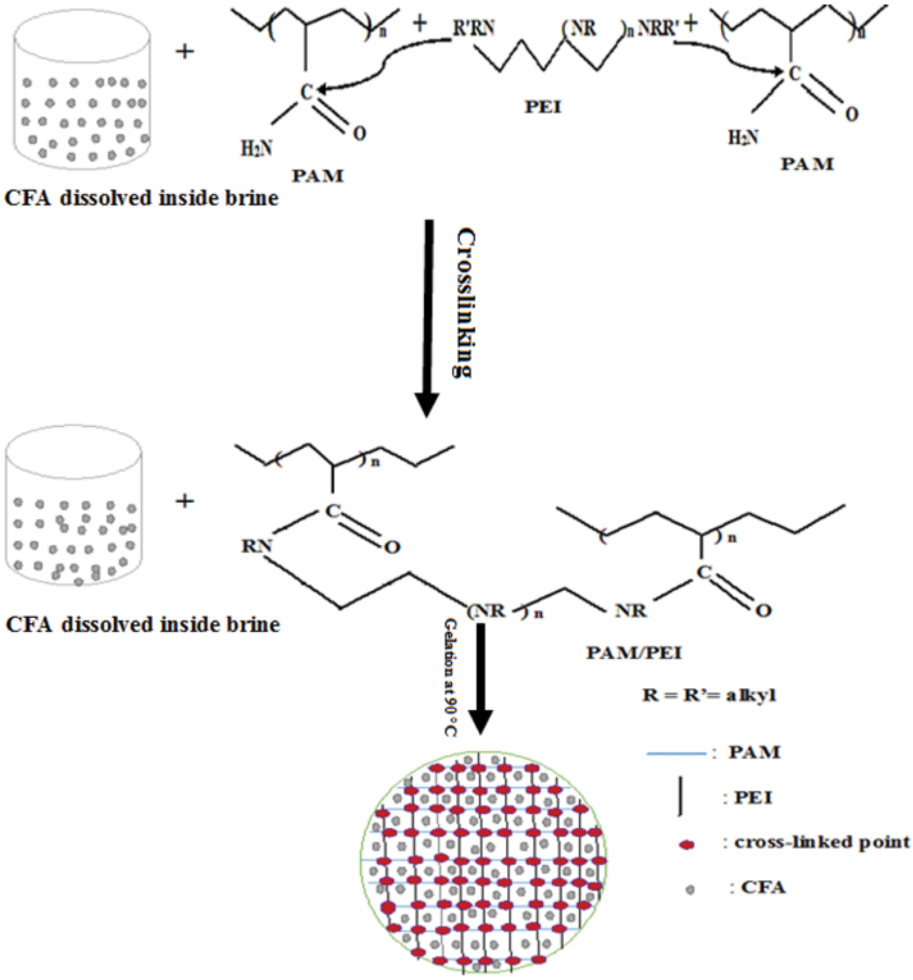

Fig. 11. Synthesis pathway of a typical PAM/PEI gel incorporated with CFA.

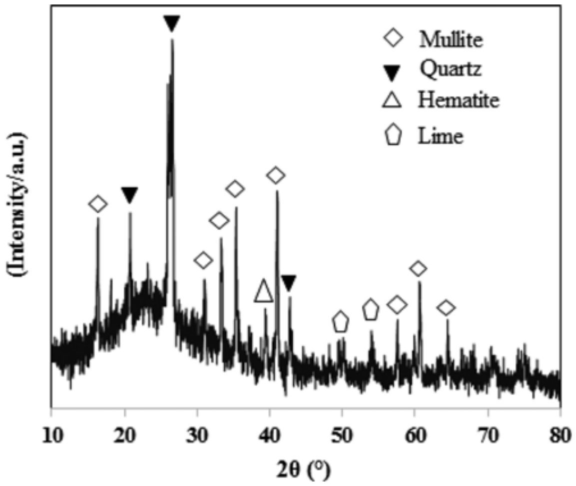

Fig. 12. XRD diffractogram of CFA used in this study.

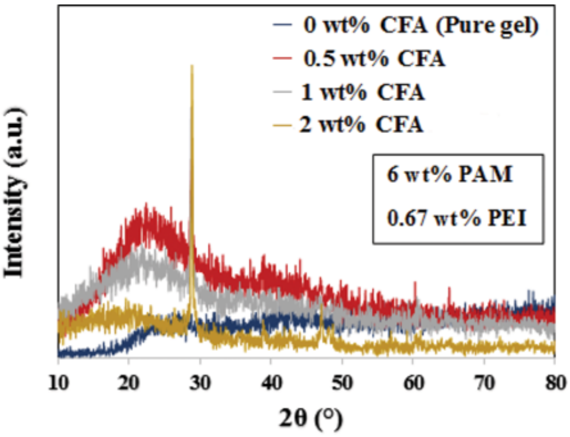

Fig. 13. XRD diffractogram patterns of pure PAM/PEI gel (without CFA) and PAM/PEI-CFA composite gels containing various CFA amounts. PAM and PEI concentrations fixed at 6 wt% and 0.67 wt%, respectively.

2 wt%, respectively. According to the XRD spectra of various PAM/PEI-CFA composite gels in Figs. 14-15, the interaction of CFA particles in the matrices of these composite gels became more conspicuous at $2\theta=29.5^{\circ}$-30.5°, 40°, 45°, and 45°-50°. The peaks intensities are very prominent especially at $2\theta=29.5^{\circ}$-30.5°. These observations undoubtedly confirm the considerable impact, dominance and interaction of mullite (alumina (Al_2O_3) and silica SiO_2), quartz

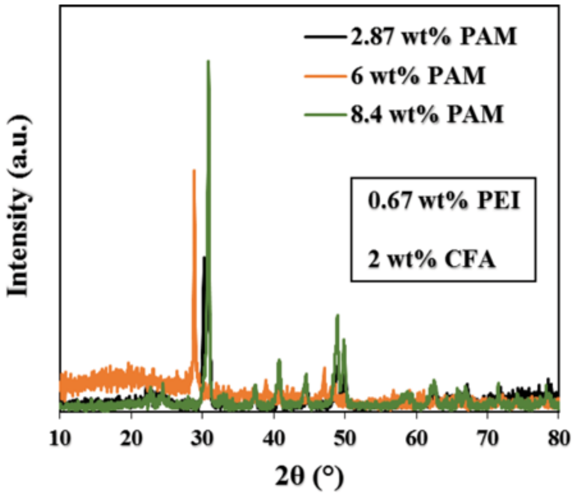

Fig. 14. XRD diffractogram patterns of PAM/PEI-CFA composite gels containing various PAM concentrations. PEI and CFA concentrations fixed at 0.67 wt% and 2 wt%, respectively.

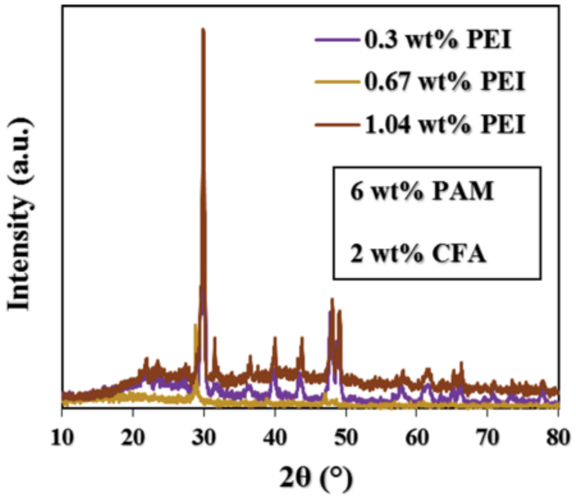

Fig. 15. XRD diffractogram patterns of PAM/PEI-CFA composite gels containing various PEI concentrations. PAM and CFA concentrations fixed at 6 wt% and 2 wt%, respectively.

(SiO_2), lime (CaO) and hematite (Fe_2O_3) in the structural networks of various PAM/PEI-CFA composite gels that were developed. Besides, the sharp peaks at various 2θ angles indicate the presence of crystalline domains in the various PAM/PEI-CFA composite gels.

CONCLUSION

Coal fly ash (CFA) based polymer gels were formulated from polyacrylamide (PAM) and polyethyleneimine (PEI) for water management during tertiary applications in oilfields. Polyethyleneimine (PEI) is chosen as the crosslinking agent. Effects of various CFA (0.5 to 2 wt%), PAM (2 to 8.47 wt%) and PEI (0.3 to 1.04 wt%) concentrations on gelation kinetics and dynamic rheological properties of pure PAM/PEI gel and PAM/PEI-CFA composite gels were investigated at a typical reservoir temperature of 90 °C. Experimental results reveal that gelation time of pure PAM/PEI gel increases with increasing CFA addition. Additionally, increasing PAM and PEI concentrations decrease the gelation times of PAM/PEI-CFA composite gels. Gelation time was found to be in the range of 3-120 hours. Likewise, good understanding of the reaction order allows effective prediction of gelation time. Dynamic rheological results show that the elastic modulus G' and the viscous modulus G'' improved considerably in various PAM/PEI-CFA composite gels than pure PAM/PEI gel across the strain-sweep and frequency-sweep tests. The enhancement in the viscoelastic properties of these composite gels indicates good interaction and strong bond network between the CFA and PAM/PEI molecular chains. SEM micrographs of pure PAM/PEI gel and PAM/PEI-CFA composite gels filled with CFA proved the consistency of gelation kinetics and rheological data. It is strongly recommended that the quantity of CFA should be kept within 1 wt% in water shutoff polymer gels. Future study will focus on core flooding experiment to investigate the effectiveness of PAM/PEI-CFA composite gel in porous media.

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