Preparation and investigation of the physical and chemical properties of clay-based polyacrylamide/Cr (III) hydrogels as a water shut-off agent in oil reservoirs

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Abstract−The effects of clay (montmorillonite and kaolinite) in the hydrogels were investigated on various properties such as syneresis and strength of thermal and salinity situations in one of the southern Iranian oil reservoirs. The X-ray diffraction (XRD) patterns exhibited a significant increase in interplanar spacing between the montmorillonite clay layers, varying from the initial value of 12.43 °A to 19.45 °A, which evidences the intercalation formation. It was revealed that even increasing of the interlayer spacing due to kaolinite modification had no effect on the clay compositions. Formation water was used to study the strength of the hydrogel in the presence of ions. The results indicated that 15 wt% increase of kaolinite clay (modified and non-modified) leads to 20% decrease of the hydrogels' syneresis. The diffusion of polymer chains between the clay layers increased the elastic modulus (G′) of the prepared hydrogels with modified kaolinite and montmorillonite, where the maximum value of G' was observed in 3 wt% of montmorillonite. Finally, the thermogravimetric analysis (TGA) indicated an increase in the thermal stability of the mentioned hydrogels.

Keywords: Composite, Polyacrylamide, Solvent Method, Clay, Syneresis

INTRODUCTION

A serious problem in oil reservoirs is unwanted water production. In addition, the lifting, handling and disposal of produced water negatively impact the economy of hydrocarbon production [1]. Several mechanical and chemical methods are available for water shut-off treatments in the hydrocarbon wells [2]. Mechanical methods, which include drilling horizontal, multi-lateral wells, and placing a linear to block water production, require a work-over rig. These methods are often expensive [3]. Nowadays, cross-linked polymer systems are the most effective for certain water shut-off (WSO) projects [4]. Gel polymer systems have a penetration tendency in porous media greater than the mechanical methods and cement to provide a deeper barrier against the excess water. Also unlike the physical cement plugging, plugging due to gel polymers can be removed [5]. However, one of disadvantages of these systems is mechanical strength loss during the pump injection and entrance into the formation pores. These mechanical tensions can lead to the breaking of polymer chains and considerable decrease in their molecular weight. So gelant solution containing polymer and cross-linker cannot have much strength in entry to formation, so, when the oil well is built-up, this weak gel system can exit from the porous media easily; consequently, it could not have high performance in reducing the formation permeability [6,7].

Addition of cross-linker to polymer solution improves the mechanical strength of hydrogel [6,8]; however, its extra addition may cause the gel to get syneresis or weaken its strength properties [9-11]. These gels might be damaged in the formation water due to the presence of monovalent and divalent cations, which reduces the strength of the gel and degrades its structure. Therefore, inorganic particles in nanometric scale are added to the polymer structure (composite) to improve its strength and thermal properties [12]. Among the mentioned inorganic materials, clays are mainly used for preparation of polymer nanocomposites (considering their nanometric dimensions and their desired properties for mixing with polymer) [13]. Clay layers are distributed throughout the polymer network by two mechanisms, called intercalation and exfoliation [14,15].

Gao et al. studied the mechanical properties of polyacrylamide-montmorillonite nanocomposite hydrogels and found that some of the hydrogels' properties may be improved in comparison with pure polyacrylamide hydrogels [15]. Churochkina et al. also prepared polymer-clay hydrogels (montmorillonite) by using neutral, cationic and anionic polyacrylamide [16]. They observed that the elastic module of hydrogels containing clay was higher than that of pure hydrogels. Aalaie et al. prepared the polymer-clay nanocomposite of montmorillonite via the solvent method by using chromium (III) acetate as a cross-linker agent, and investigated the effect of clay content and electrolyte environment on swelling and gelatin time [17,18]. Kabiri et al. investigated the porogen efficiency in composite hydrogels based on poly (AA-co-potassium acrylate)-kaolin hydrogels. Interestingly, the porogen lost its effectiveness in the presence of clay, which resulted in slower swelling rate [19]. Nasser et al. studied

the influence of cationic and anionic polyacrylamides (PAM) on the flocculation size, compressive yield stress, and rheological behaviour of kaolinite suspensions. The results showed that the value of compressive yield stress, yield stress, critical stress, and elastic and viscous modulus is strongly dependent upon the flocculation structure, with greater values being observed for the cationic PAM than for the anionic PAM [20]. Sirousazar et al. prepared nanocomposite hydrogels on the basis of polyvinyl alcohol and mineral kaolinite clay via freezing-thawing cyclic method. They did not use any chemical cross-linkers or any intercalants for modification of kaolinite. The results showed that an increase of kaolinite content causes a decrease in the swelling of hydrogels. Also, direct dependence of swelling ratio and dehydration rate to the temperature was observed for all nanocomposite hydrogels [21].

Since the harsh conditions (high salinity and high shear stress) of oil reservoirs imposed on the gel during the injection lead to its degradation and decrease its efficiency in the water shut-off operation, it seems necessary to improve its chemico-physical properties. On the other hand, kaolinite is an inexpensive filler and has not been utilized in the production of nanocomposite hydrogels, and few studies are available on the kaolinite-based composite hydrogels [19, 21]; therefore, in this research, clay (modified and non-modified kaolinite and montmorillonite) was added to hydrolyzed polyacrylamide gel to improve its properties. At first, kaolinite was modified by using dimethylesulfoxide (DMSO). After preparation of the composite, various properties of the composite were studied. For this purpose, the hydrolyzed polyacrylamide-clay was prepared via the solvent method. Chromium (III) acetate was used as a cross-linker agent. To begin with, the structure of the samples was studied by applying the X-ray diffraction (XRD) tests. Then the gels' syneresis ratio was calculated in the formation water, and the strength property of the samples was determined through MCR300 Rheometer. Finally, thermal stability of the samples was studied by thermogravimetric analysis (TGA). Since the temperature of most Southern Iranian oil reservoirs (Ahwaz-Asmari) is around 90 °C, it was taken as a base temperature in our tests.

MATERIALS AND METHODS

1. Materials

In present work, partially hydrolyzed polyacrylamide (30% hydrolyzed, 65% active content and 13 million Dalton molecular weight) was utilized as a completely water soluble polymer, which was synthesized by Iran Polymer and Petrochemical Institute (IPPI) [2]. Chromium (III) acetate, used as cross-linker, was provided by Aldrich Company. Kaolinite with the d_{001} interplanar spacing of 7.21 °A was supplied by Semirom mine. The clay used in this study was Na-montmorillonite with the d_{001} interplanar spacing of 12.43 °A, which was prepared by Zhejiang Fenghong Clay Chemical Company, China. The formation water sample was received from one of Iranian reservoirs by the National Iranian Oil Company (NIOC) with the composition given in Table 1. Also, 95% dimethylesulfoxide was supplied by an Iranian company.

2. Kaolinite Modification

Kaolinite is distributed hardly in aqueous media and precipitates immediately because of its strong interplanar force. Therefore, in order to increase the d_{001} interplanar spacing of the clay, kaolinite

Table 1. Composition of formation water (The density is 1.45 mg/Lit at 30 °C)

Ion type	Concentration (ppm)
Na^+	54200
Ca^{2+}	8800
Mg^{2+}	1700
SO_4^{2-}	1440
Cl^-	105615
Co_3^{2-}	0
HCo_3^-	390
OH^-	0
TDS (total dissolved solid)	172145
pH	6.8

must be modified. This phenomenon leads to proper location of the polymer chains through the clay layers and their dispersion through the matrix. In this paper, kaolinite was modified by the following method [22]:

1. One gram of the purified clay was poured into a 250 cc volumetric flask, then 100 cc dimethylesulfoxide (DMSO) (the solution of 95% volumetric DMSO in water) was added.

2. The solution was mixed during 192 hrs at 60 °C.

3. Then the solution was centrifuged at 4,000 rpm.

4. The complex kaolinite-DMSO obtained from the centrifugation was dried in 40 °C during 120 hrs until the excess DMSO evaporated completely. The obtained product was used as modified kaolinite.

3. Preparation of Samples

The samples were prepared as below [23]:

1. First, 2% aqueous solution of the clay was prepared and the mixing operation was continued for 24 hrs up to the gel swelling and the system homogenization.

2. The last solution was added to the polymer solution (The optimum concentration of polymer and cross-linker for all samples was 17,000 ppm and 2,000 ppm, respectively. These concentrations were obtained from the bottle test, which was first done by Sydansk) and stirred in high rate mixing for 24 hrs (the clay concentrations of the gelant were set at 3 wt%, 9 wt%, 15 wt% and 30 wt% of the polymer).

3. The cross-linker was prepared; tap water or formation water was used as a solvent.

4. Finally, all solutions prepared in the previous steps were mixed together for 10 min in order to prepare the composite gelant.

After preparation of hydrogels or composites, below tests were done. The XRD test was applied to evaluate the clay structure of the samples. The clay structure of the dried and powdery samples was studied by the XRD apparatus of Philips Xpert model with 40 KV voltage and 40 mA current (λ=1.5406 °A). The samples were then analyzed at an angle range of 0.5°-20° for 2θ.

In the study of syneresis, the initial mixture was weighed and after removing of its segregated water in different times, the remaining hydrogel was weighed again. The syneresis ratio was calculated according to the following formula:

$$\text{Syneresis ratio} = \frac{m_0 - m}{m_0} \tag{1}$$

where, m_0 is the initial weight of the gel and m is the instantaneous weight of the gel.

Finally, these samples were composed of 25 wt% of the formation water and kept at 90 °C to investigate their syneresis property. To prevent the evaporation of samples and reduce error, about 2 grams of melted paraffin was added to each sample.

To probe the strength property of the composites, dynamic tests were implemented on the samples by using of MCR300 Rheometer manufactured by Anton Paar. Its frequency was adjusted at 1 Hz and its strain range was set to 0.1% to 1000%. Every exam needs one certain concentration of the gel or the composite (5 cc), which is put between low and up rotary surface of the Rheometer. Now the instrument records the output data.

RESULTS AND DISCUSSION

1. XRD Tests

The XRD results give the curves of intensity versus 2θ, in which 2θ has been compared before and after the location of the clay in the polymer matrix. The lower value of 2θ shows an increase in spacing between the clay layers [24].

As Fig. 1 shows, the d_{001} interplanar spacing of Na-montmorillonite is 12.43 °A, and its angle is $2\theta=7.115°$ in the Bragg equation. After mixing of the clay with the polymer, this peak inclines to lower angles, which is an indicator for polymer diffusion through the clay layers ($2\theta=4.54°$).

Fig. 1 shows an increase in the mixing time, indicating that it had no effect on the interplanar spacing of clay in the polymer matrix, and that the two peaks occurred approximately at the same angle.

In Fig. 2, the effects of mixing rate on polymer/clay are illustrated. Increasing of the mixing rate leads to exfoliation structure. There would be no peak at low angles any more by increasing of the mixing rate. The absence of diffraction peaks for polymer/clay suggests that montmorillonite has been exfoliated and dispersed in the polymer matrix to form a nanocomposite structure [25].

Fig. 3 indicates the effect of mixing time, mixing rate and temperature on the polyacrylamide-kaolinite samples. The polymer and clay concentrations were 17,000 ppm and 15 wt%, respectively. As shown, a wide peak is observed in the angle range of 2θ to 8°
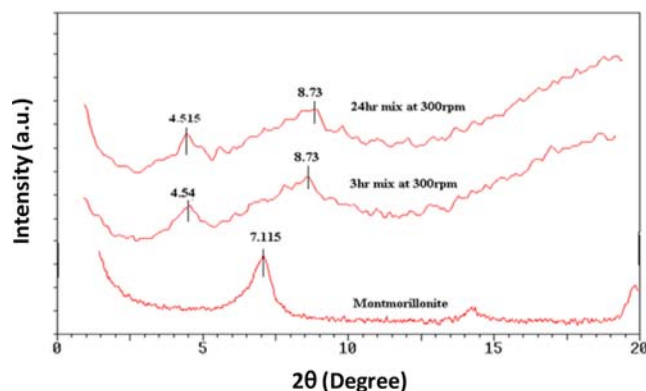

Fig. 1. Comparison between the XRD patterns of polymer/montmorillonite prepared at different mixing times, concentration of 17,000 ppm polymer and 6% clay at ambient temperature.
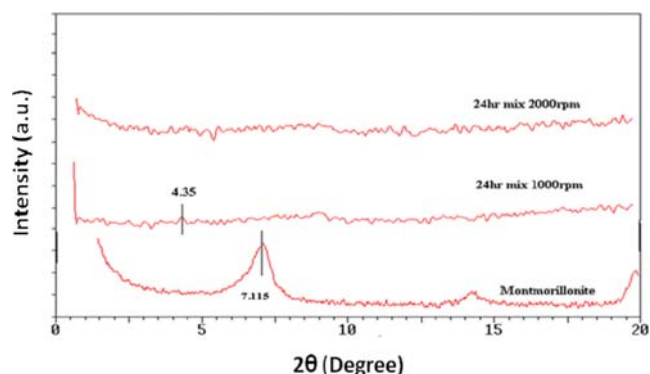
Fig. 2. Comparison between the XRD patterns of polymer/montmorillonite prepared at different mixing rate, concentration of 17,000 ppm polymer, 1,950 ppm cross-linker and 15% clay at ambient temperature.
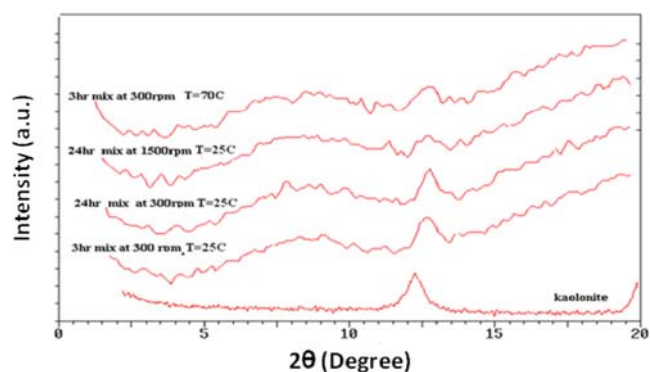

Fig. 3. X-ray diffraction curve for sample prepared by polymer and non-modified kaolinite for concentration of 17,000 ppm polymer and 15% clay.

in all occasions, which represents divergence of kaolinite layers' and polymer chains' diffusion through the clay layers. The wide peak also represents an extensive range of interplanar spacing, averagely 8°, which increases suddenly around 5° and terminates decreasingly around 11°, resulting in scarce exfoliated layers of kaolinite in the polymer matrix to form a composite structure [25]. There is another peak of about 12.645° sharper than the previous one at 2θ, which belongs to kaolinite layers that have not been deformed in the polymer matrix so that the polymer shows no diffusion between these layers obviously. As shown in Fig. 3, the sharpest peak occurs for pure kaolinite, representing a strong interplanar force inside. Due to the strong interplanar force in kaolinite and the probable precipitation in water, it was modified in order to achieve a stable suspension in water and also divergence of the clay layers.

Fig. 4 illustrates the results of the XRD tests for the modified and non-modified kaolinite. Modification of kaolinite causes increases interplanar spacing due to the reaction between silica surface and DMSO groups. In this case, Bragg equation and 2θ values represent an increase in the interplanar spacing from initial case of 7.21 °A to 10.82 °A. Also observable are two peaks for the modified kaolinite. The first peak from the left relates to the diffusion and reaction between DMSO group and silica surface. The second peak relates to increase of kaolinite without modified treatment. Fig. 4 also shows the results of kaolinite sample preparation with modified kaolinite.
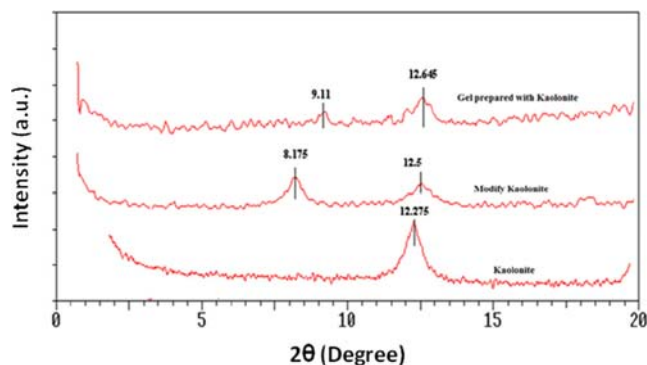
Fig. 4. X-ray diffraction curve for sample prepared by polymer and modified kaolinite for concentration of 17,000 ppm polymer and 1,950 ppm cross-linker and 15% clay at 25 °C.

Fig. 6. The effect of modified kaolinite on syneresis for composite with concentration of 17,000 ppm polymer and 2,437 ppm cross-linker at 90 °C.

According to the Bragg equation, the interplanar spacing reduced from 10.82 °A for the modified clay to 9.71 °A, which indicates the improper reaction between clay and polymer. It seems that DMSO restricts the diffusion of polymer chains, and prevents their diffusion through the clay layers [26]. Moreover, it causes some modified clays to transform into their initial from. As shown, reduction of the first peak (from the left) and also increasing of the second peak of the composite gel in contrast with the modified kaolinite confirm this fact.

Finally, it can be mentioned that polymer is able to diffuse into montmorillonite (leading to form nanocomposite structure) and non-modified kaolinite layers (leading to form composite structure), though modification of kaolinite prevents the diffusion of polymer chains through the clay layers.

2. Syneresis Tests

The effect of montmorillonite on the syneresis ratio of hydrogels has been depicted in Fig. 5. The syneresis was reduced by about 10% in comparison with the pure gel for only 15 wt% concentration of clay after nine days. For low concentrations of the clay (less than 9 wt%), variation of syneresis is approximately the same as the pure hydrogel (the difference of syneresis with the pure hydrogel is higher than 10%). As concentration of the clay increases by 30 wt%, a sharp increase in the syneresis causes a major difference between synersis of composite and pure gel. These behaviors could be explained as follows.
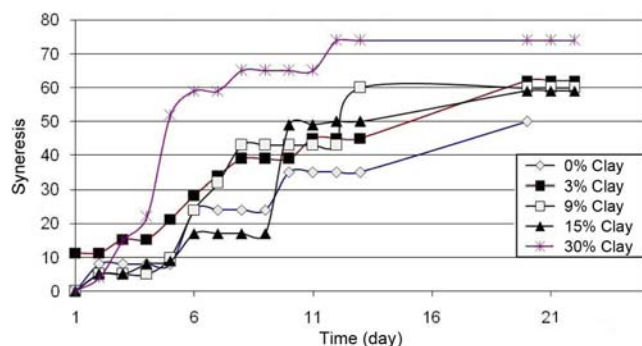

Fig. 5. The effect of montmorillonite on syneresis for nanocomposites with concentration of 17,000 ppm polymer and 2,437 ppm cross-linker at 90 °C.
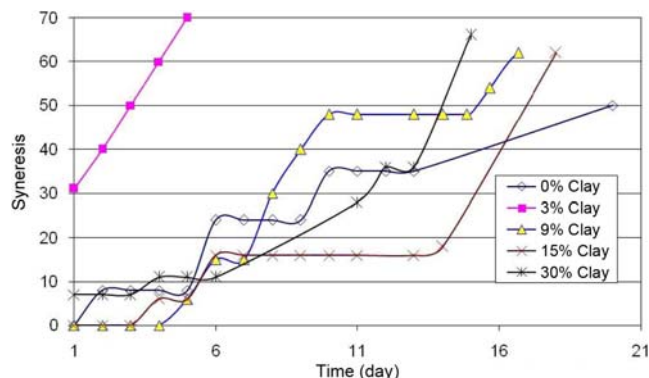
Non-uniform distribution of electrical potential in heterogeneous polyelectrolyte gels can make trapping of the counter ions. As a result, these ions become inactive by osmosis phenomenon and thus they would not have any share in the osmosis pressure, which is the major factor in gel swelling. In the case of clays, uniform charges and potential distribution occur from the anionic layers of nano clays into gel composite. Some counterions of nanoclays at different local volumes of the clay remain and do not play any role in gel osmosis. Therefore, the clay's counterions cannot cause gel swelling. So, hydrophilic groups will decrease with increasing of the clay amount in the nanocomposite network, which will lead to the diminishing of the osmosis pressure difference between the polymer matrix and the external solute [9]. On the other hand, bond formation (columbic force) between the hydrolyzed poly acryl groups and the surface negative charges on the clay can cause decreasing in the density of hydrophilic groups and consequently, in water adsorption with the addition of clay [27].

Fig. 6 indicates the effect of different modified kaolinite contents on hydrogel syneresis ratio. For low concentrations of clay (less than 3 wt%), addition of clay increases the syneresis ratio, but more addition of nano particles up to 9 wt% makes no syneresis during 5 days, while the syneresis for pure hydrogels, which is initially about 10%, increases by passing of the time. By increasing of the clay concentration up to 15 wt% after 14 days, the composite syneresis ratio increases to less than 20%, while the syneresis ratio of pure gel goes up to 40%. The low content of the interplanar cations of kaolinite is in analogy with montmorillonite [28]. As mentioned above, in the case of montmorillonite clay, shrinkage of polymer chains and consequent pushing of water molecules can happen due to interaction between the clay surface with negative charge and the carboxylate groups situated on the polymer chains. So, kaolinite clay acts as a barrier against the multivalent cations and prevents the overlapping of polymer carboxylic groups by these ions.

The amount of syneresis for the samples prepared has been evaluated by non-modified kaolinite in Fig. 7. According to the results, only concentrations higher than 15 wt% of clay cause reduction of the syneresis phenomenon. In this case, the syneresis ratio is near to the previous case, so that for 15 wt% of the clay concentration, the syneresis ratio is less than 20% after 15 days, whereas it is about 40% for the pure gel. However, the lag in the syneresis ratio of this
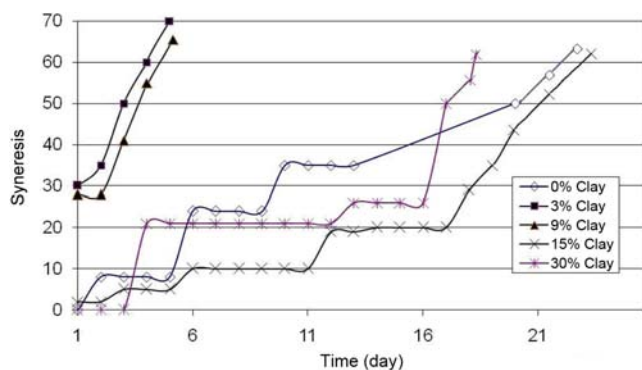
Fig. 7. The effect of non-modified clay on syneresis composite with concentration of 17,000 ppm polymer and 2,437 ppm cross-linker at 90 °C.

case is higher than the previous one. For 30 wt% of the clay concentration, the syneresis ratio is about 25% after of 15 days, while for the pure gel, it is around 40%. Furthermore, for this concentration (30 wt%), the syneresis ratio increases faster than that of the pure gel.

It seems that in modified kaolinite, the existence of DMSO chains through the clay layers restricts the diffusion of polymer chains and prevents the decrease in the density of the hydrophilic groups of gel network. However, in non-modified kaolinite, the polymer chains could diffuse between the clay layers, causing a reduction in the density of the hydrophilic groups. This is clearly seen in the comparison of 9 wt% and 15 wt% concentrations of the clay composites, prepared by modified and non-modified kaolinite. As shown in Figs. 6 and 7, syneresis ratio for modified kaolinite is less than that of non-modified clay.

Finally, it is concluded that the presence of anionic surface may cause shrinkage increasing, and so the interaction between these surfaces and the carboxylic groups of polymer chains can result in the shrinkage of polymer chains. But in kaolinite clay, barrier property can reduce shrinkage in some certain concentrations.

3. Study of Rheological Properties

One of the important variable parameters of the gelant solution during the injection was the rheological property, by which gel performance could be evaluated.

In general, gelant can experience a high stress during its entrance into the porous media and flowing through it. This may lead to degradation of polymer chains and reduction of their molecular weight. So one of the most significant characteristics of gels is their stability and resistance against the applied stresses during the injection. The mechanical strength of a gel can be represented by its viscoelastic properties such as elastic module (G') and viscous module (G''):

$$\gamma(t) = \gamma_o \cos(\omega t) \tag{2}$$

Here, the shear stress was measured from the resultant torque as below:

$$\sigma = G^* \gamma_o \cos(\omega t + \delta) \tag{3}$$

The following equations were then used to calculate characteristic storage (G') and loss modulus (G'') from complex modulus, G^*, and phase angle δ:
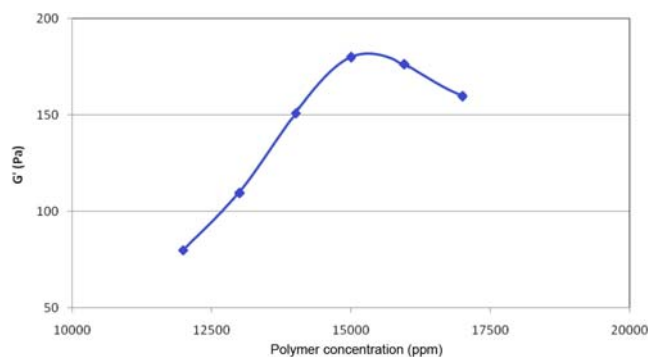
Fig. 8. Variations of G' for different concentrations of polymer (concentration of 2,437 ppm cross-linker at T=90 °C).

$$G' = G^* \cos\delta \tag{4}$$

$$G'' = G^* \sin\delta \tag{5}$$

$$G^* = G' + iG'' \tag{6}$$

A frequency of $\omega=1$ Hz and a deformation amplitude of $\gamma_o=0.01$ were selected to ensure that oscillatory deformation was within the linear regime [18].

3-1. Effect of Polymer Concentration on G'

Variations of elastic property in terms of polymer concentration for the strain variations equal to 1% are illustrated in Fig. 8. The increase in polymer concentration brings about an increase in elastic property, which would be maximized in the polymer concentration of 15,000 ppm. However, higher increase in polymer concentration up to 17,000 ppm would cause higher reduction of G'. For low concentrations of polymer (less than 15,000 ppm), the polymer acts as a limiting agent and G' grows by increasing of the polymer concentration. But, for high concentrations of polymer (greater than 15,000 ppm), the cross-linker acts as a limiting agent. In this state, the cross-linker can be able to bond with the majority of negative charge sites on the polymer chains, though some of them remain without bonds. Increasing of polymer concentration raises negative polymer sites in the gelant solution, and results in the reduction of elastic property. Therefore, the more bonds between polymer and cross-linker, the more elastic property of the gel [27].

3-2. Effect of Clay Concentration on G' and G''

Fig. 9 shows that addition of clay to polymer causes an increase
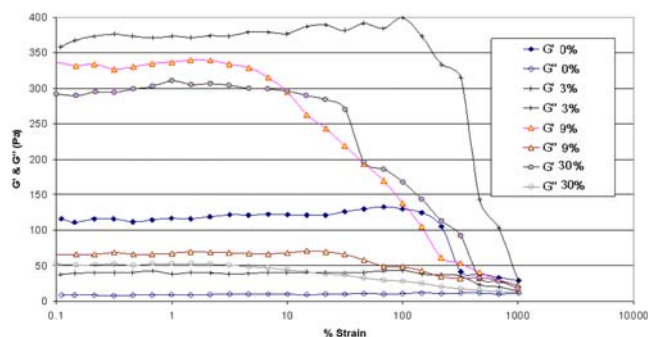

Fig. 9. The effect of montmorillonite content on G' and G'' of nanocomposite with concentration of 17,000 ppm polymer and 2,437 ppm cross-linker at 90 °C.

in the formed composite's G′. It has been suggested that the reinforcement properties of polymer/clay are attributed mainly to the hybrid effects of interfacial properties and restricted mobility of the polymer chains [27]. Shi et al. studied the interfacial effects on the strength of nanocomposites based on this assumption that polymers are binding directly on the surface of clay particles [29]. The restricted mobility of the reinforcement mechanism was described and studied by Kojima et al., who suggested that the constrained mobility of polymer chains had an energy-dissipation effect under shearing [30]. It sounds as if the addition of clay to hydrogel, just like the addition of cross-linker, increases the elastic property. Fig. 9 also depicts that the higher increase in montmorillonite concentration, the greater reduction of G′. This may be explained by the fact that high concentrations of clay can cause the clay to agglomerate and cluster within the polymer matrix (because of no proper dispersion in the polymer matrix). This could be considered as an important factor in reducing the elastic property.

In Fig. 10, for modified kaolinite, no increase in G′ is observed with the addition of clay. Clay modification can reduce the interaction between polymer chains and clay, and as shown in figure, no improvement in this property is noticed.

The effect of non-modified kaolinite on the strength property of composite is described in Fig. 11. In the section of syneresis study, low concentrations of clay have been were neglected; because they possess no proper performance for preparation of composite. So,

only high concentrations of clay (15 wt% & 30 wt%) have been studied. As Fig. 11 shows, increasing concentration of clay (non-modified kaolinite) causes an increase in the G′ of composite. Figs. 10 and 11 (for clay concentrations greater than 15 wt%) indicate that modification of kaolinite has a negative effect on the elastic property of gel for using non-modified clay that allows the polymer chains to diffuse through clay layers. While for the case of using modified clay, the space within the layers would be occupied by DMSO molecules and thus prevent the diffusion of polymer chains through the clay layers. A drastic increase in the elastic properties of the hydrogels prepared by montmorillonite is observed due to formation of nano-structure and diffusion of polymer chains through the clay layers. Consequently, diffusion of polymer chains through the clay layers is an important factor in increasing of the elastic property. As the hydrogels prepared with non-modified kaolinite are compared with hydrogels prepared with montmorillonite, one could understand that in the case of using montmorillonite, the specific area increases extensively because of its nanostructure and dispersion of the clay layers. So the amount of G′ would be maximized for low concentrations of clay. However, in the case of using non-modified kaolinite, the specific area of clay decreases, because of the partial dispersion of the clay layers. Consequently, high concentrations of clay are required to increase the specific area, and the elastic property would be maximized for high concentrations of clay.

3-3. Effect of Aging on Elastic Property

To investigate the effect of aging on elastic property, a sample composed of 17,000 ppm composite polymer and 2,437 ppm cross-linker was kept at 90 °C during two time intervals (one and seven days) (Fig. 12). During the aging time, the amount of G′ and G″ for the seven-day composite was increased with respect to the one-day composite. The results related to this section are similar in case that cross-linker is added to the gel. This in turn increases the bonds between polymer and cross-linker agents, which can result in the rising of G′ and G″. In addition, time increasing can lead to rise in the number of bonds between cross-linker and polymer and consequently going up of elastic property.

4. Thermal Analysis

To evaluate the thermal behavior of composite, the differential thermal analysis (DTA) apparatus made by the PL Thermal Sciences Company (model PL-500 STA) was used. The samples were heated from the ambient temperature to 700 °C with the rate of 10 °C/
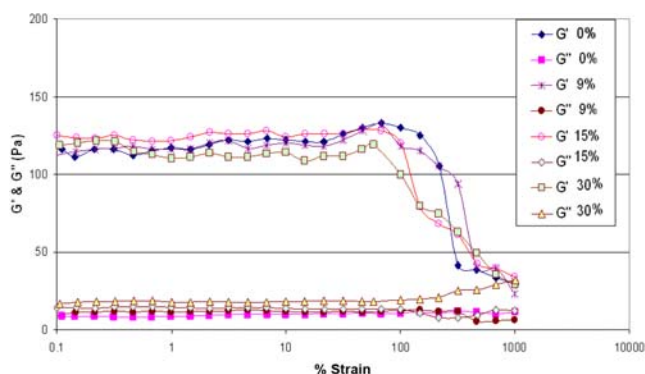
Fig. 10. The effect of modified kaolinite content on G′ and G″ of composite with concentration of 17,000 ppm polymer and 2,437 ppm cross-linker at 90 °C.
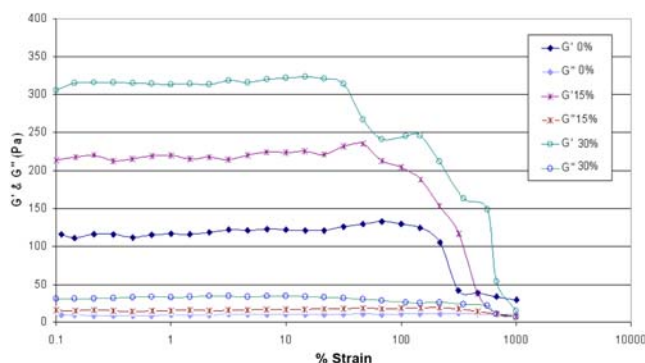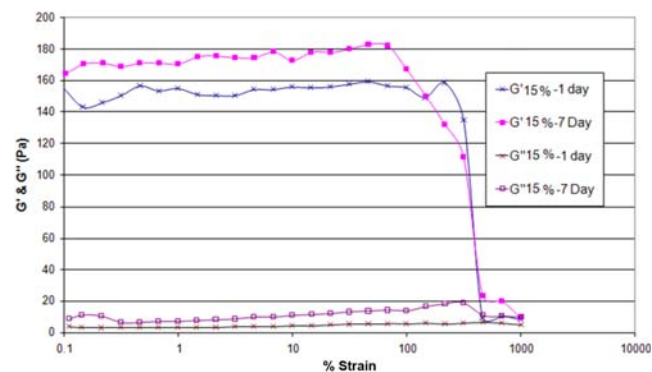
Fig. 11. The effect of non-modified kaolinite content on G′ and G″ of composite with concentration of 17,000 ppm polymer and 2,437 ppm cross-linker at 90 °C.

Fig. 12. The effect of aging on G′ and G″ of hydrogel with concentration of 17,000 ppm polymer and 2,437 ppm cross-linker at 90 °C.
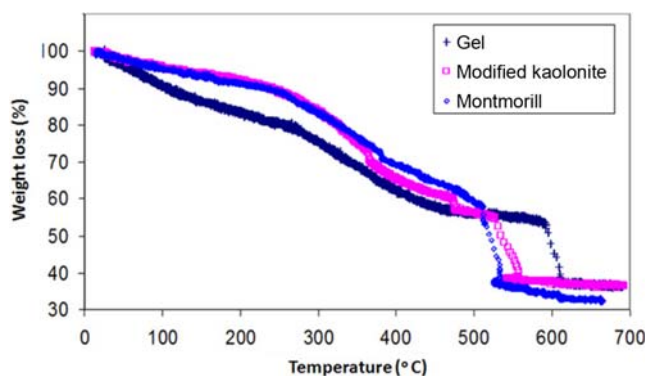
Fig. 13. TGA curves for polymer, polymer/modified kaolinite composite and polymer/montmorillonite nanocomposite (concentration of 17,000 ppm polymer, 2,437 ppm cross-linker and 15 wt% clay).

min. The variations in the percentage of weight reduction were recorded in terms of temperature.

Thermal stability represents the ability of materials in maintaining their physical properties when exposed to high temperatures. One of the important characteristic of composites is their thermal stability upon high temperatures.

The thermal analysis test was performed for three samples with the same concentrations of polymer and cross-linker. The utilized clays were montmorillonite and modified kaolinite with 15 wt%. As shown in Fig. 13, the presence of clay delays the thermal degradation of composites. The comparison between the samples containing clay and the samples without clay shows a reduction of weight percent in the water evaporation region of both samples, so that at about 260 °C, the weight of gel reduces by about 80%, while the weight of the composites made by montmorillonite and modified kaolinite decreases by about 88%. This indicates that the thermal strength of gel increases with the addition of clay. Bonds between clay surfaces and water molecules led to the removal of water from the composite network at high temperatures. On the other hand, there was no considerable difference for thermal analysis curves between the composites made by different clays.

CONCLUSIONS

Composite and nanocomposite hydrogels were prepared by polyacrylamide and triacetate chromium as a cross-linker, using the solvent method. The influence of clay (montmorillonite) on hydrogel was investigated in water shut-off system to control water production in one of the Southern Iranian oil reservoirs conditions. A summary of the results follows:

1. Addition of montmorillonite clay to polymer caused an increase in the interplanar spacing, from the initial value of 12.43 °A to 19.57 °A, which shows polymer diffusion through the clay layers in nanocomposite.

2. The mixing rate has strong effect on the dispersion of silica layers in nanocomposite gel (as in the rate of 2,000 rpm, no peak is observed in low angle) and leads to the formation of exfoliation structure.

3. Modification of kaolinite causes an increase in the interplanar spacing from 7.21 °A to 10.82 °A. The use of modified kaolinite

for sample preparation did not cause an increase in the interplanar spacing.

4. The use of modified kaolinite (the clay concentration of 15 wt%) in the syneresis tests after 14 days decreased the syneresis value to less than 20%, while for pure gel, it was about 40%. However, in high concentrations of clay (30 wt%), there were no reductions in the ratio of syneresis.

5. The reduction of syneresis for the samples prepared by nonmodified clay happened at high concentrations of clay (greater than 15 wt%). Besides, the addition of montmorillonite clay to gel caused no reduction in the syneresis ratio.

6. Addition of montmorillonite to composite gel can lead to the improvement of its elastic property, where this property is reduced by increasing of the clay addition. The elastic property increases by addition of non-modified kaolinite, whereas modified kaolinite has no effect on the increasing of elastic property.

7. Aging increases the elastic module of the nanocomposite prepared by montmorillonite.

8. Addition of nanoparticles (montmorillonite and modified clay) leads to delay in the thermal degradation of composites.

Overall, nonmodified kaolinite-based hydrogels have several advantages over modified kaolinite ones, including simplicity, rapidity, cheapness, and lower toxicity of the reactants. Hence, in addition to their higher strength and lower ratio of syneresis, nonmodified kaolinite composites may be recommended as an excellent candidate for water shut-off operations.

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