UNIVERSITÉ DU QUÉBEC À TROIS-RIVIÈRES

ÉTUDE DES PROPRIÉTÉS RHÉOLOGIQUES, THERMIQUES ET MÉCANIQUES DES NANOCOMPOSITES PRÉPARÉS À PARTIR DE POLYACRYLAMIDE/HYDROXYPROPYLE GAUR/OXYDE DE GRAPHÈNE, ET LEURS APPLICATIONS DANS LA RÉCUPÉRATION AMÉLIORÉE DU PÉTROLE

INVESTIGATION OF RHEOLOGICAL, THERMAL, AND MECHANICAL PROPERTIES OF NANOCOMPOSITES PREPARED FROM POLYACRYLAMIDE/HYDROXYPROPYL GAUR/GRAPHENE OXIDE, AND THEIR APPLICATIONS IN ENHANCED OIL RECOVERY

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“Energy is this invisible link that connects everything;

the materials provide us the evidence”.

-DuongLab

Summary

With the continuous rise in energy demand and decline in conventional reserves, the oil industry is constantly in searching for inventive and novel approaches to optimize hydrocarbon recovery. Oil enhance recovery (EOR) is one of the most important methods to increase the capacity of oil production in the energy sector. One of the EOR methods is polymer injection. Indeed, a gel polymer system can avoid water production by obstructing the high permeability zones and diverting to the low permeability zones in the reservoir. As well, owing to the slow movement of this sort of gel, it can be employed as a viscosity modifier for oil displacement by soaring the viscosity of the fluid, which helps to decrease the mobility ratio. Gel polymer with a suitable viscosity is a key function in EOR applications. This allows the potential to seal problem zones that are producing excess water, even when the fractures conducting water have narrow apertures. By preventing water production, the gel system developed here can effectively delay water loading, thereby avoiding the abandonment or installation of expensive equipment with increased operational costs. This research intended to develop and alter polymer gel chemistry in the reservoir. The new gellant formulation and systems should be able to pass through the narrow fracture apertures and effectively seal the fractures connected to water sources, and also be able to displace the oil to the front. Polyacrylamide (PAM), partially hydrolyzed polyacrylamide (HPAM), and hydroxypropyls gaur (HPG) as polymer solution along with chromium (III) acetate as a crosslinker is often used in EOR applications. However, these polymer gel systems show low viscosity and thermal instability, at high temperatures. Therefore, graphene oxide (GO) can be added to the polymer solution to enhance the properties of gel polymer systems.

The first stage of this study is to enhance the thermal stability and rheological properties of semi-interpenetrating polymer network (IPN) hydrogel. This novel hydrogel is based on partially hydrolyzed polyacrylamide/hydroxypropyl guar (HPAM/HPG) nanocomposite reinforced with graphene oxide (GO) at high temperatures. The morphological observations by scanning electron microscopy were presented in conjunction with the electrical conductivity and rheological properties of HPAM/HPG/GO nanocomposites. FTIR spectra of the IPN nanocomposite hydrogels revealed interactions of GO with HPAM/HPG chains. The IPN nanocomposite hydrogels showed high viscosity stability, and also had higher thermal stability and flow activation energy as compared to IPN hydrogel without GO. The conductivity of nanocomposites was enhanced by increasing the GO concentration up to 0.1 wt.%. But, the effect of GO was not noticeable by further increasing its concentrations. The complex viscosity was increased by increasing the GO contents.

The second stage of this research is to investigate the synthesis of novel graft copolymer nanocomposite based on hydroxypropyl guar (HPG) graft acrylamide (AM) and 2-acryloamido-2-methyl propane sulfonic acid (AMPS) which was reinforced with graphene oxide (GO), and its suitability for the development of the copolymer-based hydrogel systems by chromium triacetate crosslinker to use in oil recovery applications. Therefore, the effect of the incorporation of synthesized GO on the rheological behaviour of the nanocomposite hydrogel system in terms of viscoelastic behavior, long-term aging, viscosity loss, and thermal stability have also been investigated to determine the flow behavior in the reservoir. Finally, the affecting of the graft copolymer nanocomposite and cross-linker concentrations on viscosity, storage modulus, and strength of the hydrogel system were evaluated to determine an optimum gel formation in electrolyte media and EOR application.

The original contributions to knowledge from this research are 1) development of new IPN hydrogel which enhanced oil recovery, 2) formulation of new synthesized graft copolymer nanocomposite hydrogel, which was improved by the dispersivity of the GO into the graft copolymer and to develop the hydrogel system, as well as resistance to salinity and temperature, and 3) a better understanding of the mechanisms contributing to the nanocomposite hydrogel in chemical flooding.

Keywords: Rheological behavior, graphene oxide, enhanced oil recovery, graft copolymer nanocomposite, polymer gel system.

Résumé

Avec l'augmentation continue de la demande en énergie et la diminution des réserves conventionnelles, l'industrie pétrolière est constamment à la recherche d'approches innovantes et nouvelles pour optimiser la récupération des hydrocarbures. La récupération améliorée du pétrole (EOR) est l'un des moyens les plus importants d'augmenter la capacité de production de pétrole dans le secteur de l'énergie. L'une des méthodes EOR est l'injection de polymère. En fait, un système gel-polymère peut empêcher la production d'eau en bloquant les zones à haute perméabilité et en la détournant vers les zones à faible perméabilité du réservoir. De plus, en raison du mouvement lent de ce type de gel, il peut être utilisé comme modificateur de viscosité pour le transfert d'huile, en augmentant la viscosité du fluide, ce qui contribue à réduire le taux de mobilité. Les polymères de gel de viscosité appropriée sont une fonction clé dans les applications EOR. Cela permet de bloquer les zones problématiques qui produisent un excès d'eau, même lorsque les fractures conductrices d'eau ont des pores étroits. En empêchant la production d'eau, le système de gélation développé ici peut effectivement retarder le chargement de l'eau, évitant ainsi l'abandon ou l'installation d'équipements coûteux avec des coûts d'exploitation accrus. Le but de cette étude était de développer et de modifier la chimie du gel polymère dans le réservoir. Les nouvelles formulations et systèmes de gellane doivent être capables de traverser des pores de fractures étroits et de sceller efficacement les fractures reliées aux sources d'eau, ainsi que de transporter le pétrole vers l'avant. Le polyacrylamide (PAM), le polyacrylamide semi-hydrolysé (HPAM) et l'hydroxypropyl guar (HPG) en solution polymère avec de l'acétate de chrome (III) comme réticulant sont souvent utilisés dans les applications EOR. Cependant, à des températures élevées, ces systèmes de gel polymère présentent une faible viscosité et une instabilité thermique. Pour augmenter les propriétés des systèmes de gel polymère, l'oxyde de graphène (GO) peut être ajouté aux mélanges.

La première étape de cette étude consiste à augmenter la stabilité thermique et les propriétés rhéologiques des hydrogels à réseau de polymères semi-réticulés (IPN). Ce nouvel hydrogel est à base de nanocomposite semi-hydrolysé polyacrylamide / hydroxypropyl guar (HPAM / HPG) graphène oxyde (GO). Des observations morphologiques par microscopie électronique à balayage concernant la conductivité électrique et les propriétés rhéologiques des nanocomposites HPAM /HPG/GO ont été présentées. Les spectres FTIR des hydrogels nanocomposites IPN ont montré des interactions GO avec les chaînes HPAM / HPG. Les hydrogels nanocomposites IPN ont montré une stabilité de viscosité plus élevée ainsi qu'une stabilité thermique et une énergie d'activation du flux par rapport aux hydrogels IPN sans GO. La conductivité des nanocomposites a augmenté avec l'augmentation du pourcentage de GO à 0.1wt. %. Cependant, l'effet de GO n'était pas significatif au-delà de 0.1wt.%. La viscosité complexe est augmentée avec l'augmentation du pourcentage de GO.

La deuxième phase de cette recherche est l'étude de la synthèse d'un nouveau nanocomposite copolymère greffé à base de liaisons hydroxypropyl guar (HPG) acrylamide (AM) et acide 2-acryloamido-2-méthylpropane sulfonique (AMPS) renforcées par de l'oxyde de graphène (GO), et son aptitude au développement de systèmes hydrogels à base de copolymères par liant triacétate de chrome pour une utilisation dans des applications de recyclage d'huile. Par conséquent, l'effet de l'intégration de GO synthétisé sur le comportement rhéologique du système d'hydrogel nanocomposite en termes de comportement viscoélastique, de vieillissement à long terme, de perte de viscosité et de stabilité thermique a également été étudié pour déterminer le comportement d'écoulement dans le réservoir. Enfin, l'effet du nanocomposite de copolymère lié et de la concentration de liaisons croisées sur la viscosité, le module de stockage et la résistance du système d'hydrogel pour déterminer la formation de gel optimale dans l’environnement électrolytique et l'application de l'EOR ont été évalués.

Les contributions originales aux connaissances issues de cette recherche sont 1) le développement d'un nouvel hydrogel IPN qui améliore la récupération du pétrole, 2) la formulation d'un nouvel hydrogel nanocomposite de copolymère greffé synthétisé qui est amélioré par dispersivité du GO dans le copolymère greffé et de développer le système hydrogel, ainsi que la résistance à la salinité et à la température, et 3) une meilleure compréhension des mécanismes contribuant de l'hydrogel nanocomposite dans les *flooding* chimiques.

Mots clés : Comportement rhéologique, oxyde de graphène, récupération améliorée du pétrole, nanocomposite de copolymère greffé, système de gel

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List of abbreviations

Abbreviations	*Expansion*
AM	Acrylamide
AA	Acrylic acid
AM-AMPS	Acrylamide-co-2-acrylamide-2-methyl propane
AM-VP	Acrylamide-co-vinylpyrrolidone
AMPS	2-acrylamide-2-methyl propane sulfonate
PAM	Polyacrylamide
HPAM	Partially hydrolyzed polyacrylamide
CMC	Carboxymethyl cellulose
EOR	Enhanced oil recovery
CEOR	Chemical enhanced oil recovery
VP	Vinylpyrrolidone
CMG	Carboxymethyl guar
HPG	Hydroxypropyl guar
CMHPG	Carboxymethyl hydroxypropyl guar
IPN	Interpenetrating polymer network
GO	Graphene oxide
PEGDA	Polyethylene glycol diacrylate
MA	Maleic anhydride
SA	Sodium alginate
DMAEMA	2-(Dimethylamino) ethyl methacrylate
BA	Butyl acrylate
DEAM	N, N-ethyl acrylamide
DMAM	N, N-dimethyl acrylamide
HTHP	High-temperature high pressure
TGA	Thermogravimetric analysis
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscopy

TEM	Transmission electron microscopy
EDX	Energy-dispersive X-ray spectroscopy
XRD	X-ray diffraction
KBr	Potassium bromide
FLC	Fluid loss control
NMBA	N, N-methylene-bis-acryl-amide
CPNHG	Copolymer nanocomposite hydrogel
CMT	Cement
YP	Yield point
PV	Plastic viscosity
UCA	Ultrasonic cement analyzer
APS	Ammonium persulfate

Symbols

lb/SK	Pounds per sack
gal/SK	Gallon per sack
bbl/SK	Barrel per sack
Bc	Bearden units of consistency
d	Darcy
md	Millidarcy
G’	Storage Modulus
G’’	Loss Modulus
ppm	Parts per million
F	Fahrenheit
C	Centigrade
FL	Filter press

Achievements as a Ph. D student

During my 3 years of Ph.D. studies, I have published three research articles, as 1st author in ISI journals with relevant impact factors. I also received best poster award at the 10th annual sur concours d'affiches a UQTR in 2020, held at Université du Québec à Trois-Rivières, Québec, Canada. In total since my academic study, I have published 9 articles in ISI journals.

List of articles published

1. **A. Narimani,** F. Kordnejad, M. Hemmati, A. Duong. Synthesis, characterization, thermal and rheological properties of nanocomposites hydrogel based on HPG-g-poly (AM-co-AMPS)/GO for enhanced oil recovery**.** Journal of Dispersion Science and Technology, In reviewing.
2. **A. Narimani,** F. Kordnejad, P. Kaur, J. Trivedi, F. Najmeddine, M. Hemmati, A. Duong. Synthesis and preparation of poly (AM-co-AMPS)/GO nanocomposites hydrogel as a rheology modifier and fluid loss controller for use in oil well cementing. Journal of Dispersion Science and Technology. Published online: 21 Feb 2022.
3. **A. Narimani**, F. Kordnejad, P. Kaur, S Bazgir, M. Hemmati, A. Duong. Rheological and thermal stability of interpenetrating polymer network hydrogel based on polyacrylamide/hydroxypropyl guar reinforced with graphene oxide for application in oil recovery. Journal of Polymer Engineering. 2021, 41, 788-798.
4. **A. Narimani,** H. Hemmati. Electrical and steady shear rheological behavior of polypropylene composites reinforced with single-walled carbon, Polymers, and Polymer Composites, 2014, 22,533-540.
5. **A. Narimani,** M. Hemmati. Effect of single-walled-carbon nanotube (SWNT) on mechanical, rheological, and physical properties of thermoplastic elastomer based on PP/EPDM, Science, and Engineering of Composite Materials, 2014, 21, 15-21.

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Chapter 1

Introduction

1. Introduction

Globally, with the continuous growth of energy demand, it seems that the dominant option among energy sources is renewable energy options. Undoubtedly, the use of these new energy sources such as wind, geothermal and solar are effective measures that can address energy shortages. However, they are not yet a viable alternative to the role of oil in meeting growing energy demand. To date, these demands are now being met by hydrocarbon resources, especially oil, because oil is still the most valuable commodity with a major global economic impact. Therefore, protecting oil reserves as wealth and future heritage is one of the most important and strategic assets in the energy sector. Unconventional oil and gas wells along with the new techniques of oil recovery are becoming a major energy issue. However, at reasonable gas prices and increasing demand for clean fuel, unconventional reservoirs can be developed and produced at economical rate. The oil and gas industry is the most lucrative economic resource but it is facing challenges due to the high cost of drilling and extracting with the price of oil continuously declining in the world [1-2]. On the other hand, excessive water extraction during the life of production wells and oil recovery in mature oil fields leads to a decline in the oil production efficiency, especially for lower pressure reservoirs (Figure 1) [2-3]. The main reason for water production is that the highly permeable layers of the reservoir are connected to an underground aquifer through the existence of fractures in the reservoir rocks, which results in the mixing of water and oil, causing problems in the reservoirs productions [4-6]. Indeed, excessive water production renders the well uneconomical, especially for lower pressure reservoirs, leading to premature abandonment and large volumes of unrecovered reserves. Thus, more efficient, yet cost-effective, environmentally friendly, and novel alternatives are constantly being searched for the process feasibility to meet the current global high-energy demand, as reserve replacement is continuously in decline [1,6].

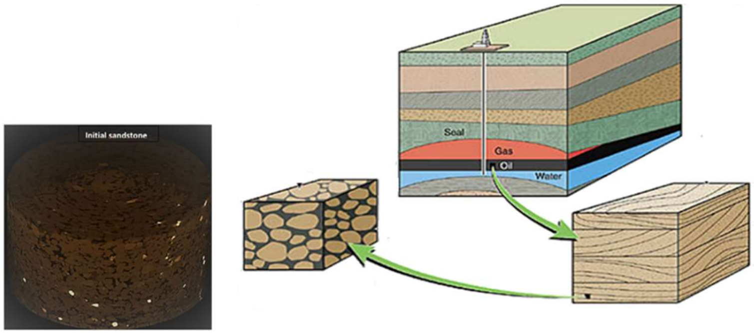

Figure 1. The oil reservoir [3].

Mobilizing and recovering hydrocarbons from geological formations is crucial to meet the unceasing global energy needs. Hydrocarbon can be recovered in three production stages primary, secondary and tertiary processes. However, the conventional recovery methods (primary and secondary) are insufficient. During the production period of the oil reservoir, because of the gradual pressure drop in a reservoir, only about 30-40% of the reservoir oil is available to be extracted by conventional methods, while most of the oil in the reservoirs cannot be extracted by the usual methods, especially when the oil is heavy (high viscosity) as shown in chart 1. With oil fields development and water breakthrough in oil wells, water wells have become predominant and water injection into such formations is less effective as a substantial amount of oil is left behind after recovery, thus creating the need for EOR. On average, oil recovery from the primary and secondary production stage is approximately one third of the original oil in place, while the remaining two third can be partially recovered through EOR which are key drivers for incremental oil recovery. However, in most conventional reservoirs, the produced water is re-injected into the reservoir to keep the pressure up or for increased recovery. The goal of this work is to formulate a potential gel polymer systems and reinforcement of polymer solutions for use in EOR applications [1-2,6-7].

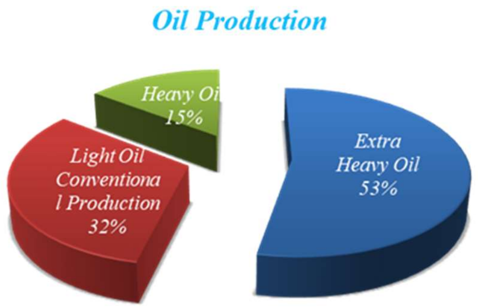

Chart 1. Oil production.

1.2. Enhanced oil recovery (EOR)

Enhanced oil recovery (EOR) technologies (Table 1) are known for increasing oil recovery, however, the selection of the most suitable method to adopt for specific field applications is challenging. It is not only the current decline in conventional reserves but also the continuous rise in energy demand, several processes and technologies have been used in this regard to enhance or maintain recovery from reservoirs and fields. EOR processes facilitate effective displacement of oil towards the producing well, thus production from matured fields is enhanced as the injected chemicals or gases interact with the formation rock and oil systems thereby creating a favorable condition for better recovery [1,6,8-9]. However, it is also essential to evaluate qualitatively mechanisms that influence recovery potentials [1]. EOR processes involve the injection of steams (thermal EOR), chemical based fluids (chemical EOR), and gases into a reservoir (gas EOR) have also been applied in oil fields [1, 9].

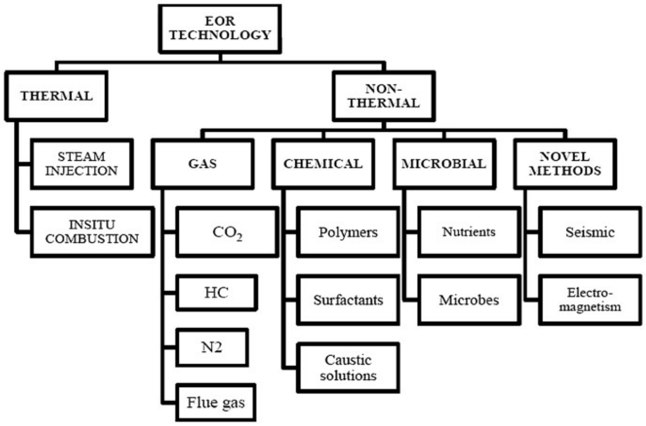

Table 1. Classification of EOR technologies [9].

1- Thermal recovery

Thermal recovery introduces heat to the reservoir to reduce the viscosity of the oil, as highlighted in Figure 2. Many times, steam is applied into the reservoir, thinning the oil and enhancing its ability to flow. First applied in Venezuela in the 1960s, thermal recovery now accounts for more than 50% of applied EOR in Canada and USA.

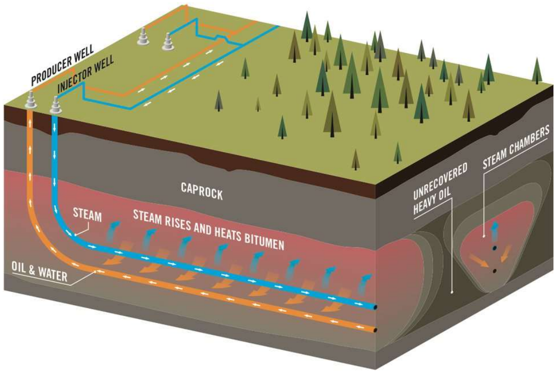

Figure 2. Thermal recovery process [9].

2- Chemical injection

Chemical injection EOR helps to free trapped oil within the reservoir. This method introduces long-chained molecules called polymers into the reservoir to increase the efficiency of waterflooding or to boost the effectiveness of surfactants, which are cleansers that help lower surface tension that inhibits the flow of oil through the reservoir. The most common chemicals EOR are polymer injection, surfactant, alkaline, surfactant-polymer, and alkaline-surfactant-polymer flooding.

3- Gas injection

Figure 3 depicts the gas injection in EOR application. It is used by injecting natural gas, nitrogen, or carbon dioxide (CO_2) into the reservoir. The gases can either expand and push gases through the reservoir or mix with or dissolve within the oil, decreasing viscosity and increasing flow [10].

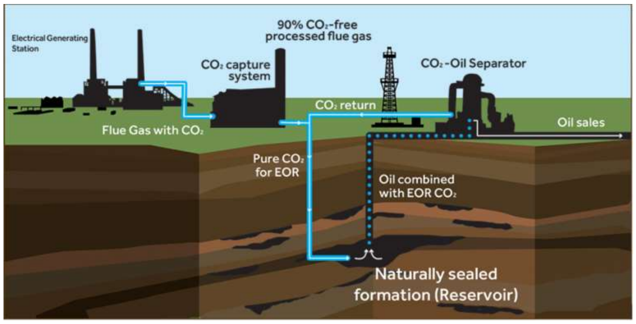

Figure 3. CO_2 recovery process [10].

1.3. Gel polymer injection

Polymers are often applied in oil recovery applications not only as gel polymers for water production control in-depth reservoir formation but also for oil displacement in polymer flooding as shown in Figure 4 [11]. The hydrophilic polymers boost remarkably the viscosity of the injection water and decrease the mobility ratio of water to oil, to enhance the sweep efficiency in the reservoir [12]. On the other hand, EOR methods assisted with other techniques including mechanical separation, cement injection, and water shut-off treatment to reduce unwanted water from the reservoirs, and help to increase oil efficiency [13]. Among the available techniques, an injection cross-linked polymer system comprising of a polymer or copolymer solution and a water-soluble crosslinker is extensively employed in EOR applications and treatments [3]. Under specific conditions (temperature and time), polymer chains are linked together by a crosslinker as a bridging agent to generate a three-dimensional hydrophilic network structure. Gel treatments are the most effective means of reducing water channeling through fractures or high permeability layers. In fractured reservoirs, formed gels can be extruded into fractures. Nevertheless, typical water shut-off gel formulations are too concentrated to extrude through the narrower fractures prevalent in tight gas and shale formations.

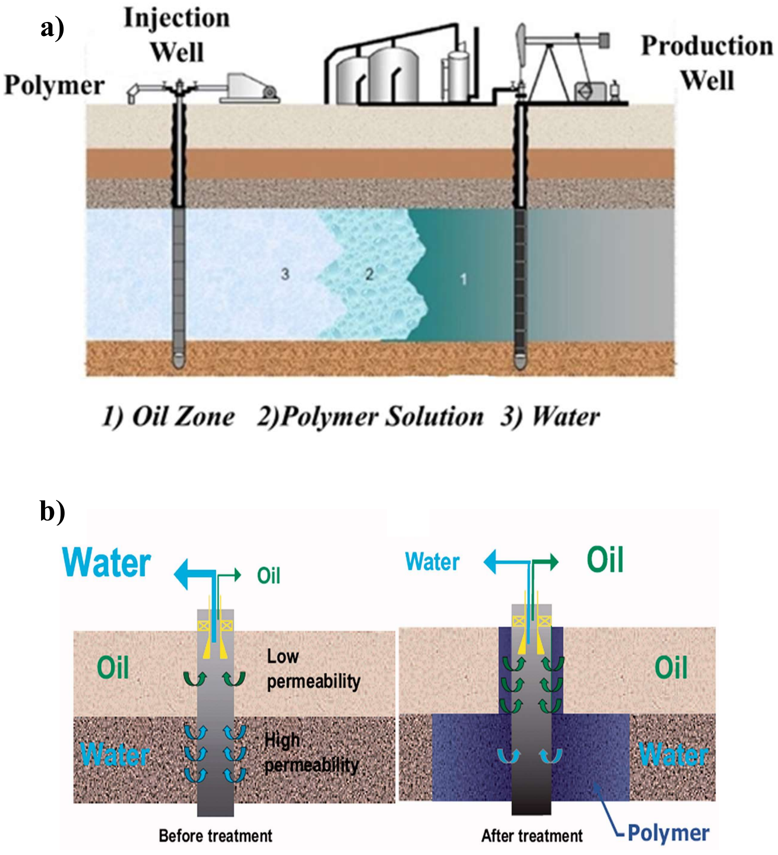

Figure 4. a) Polymer flooding, and b) Polymer injection process [7-8].

1.4. Hydrogel systems in EOR application

Hydrogels are a sort of hydrophilic polymers, which can be constituted by physical and chemical as a crosslinker with water-soluble monomers, and they can absorb and keep a large volume of water or other aqueous fluids for several hours while being under pressure as illustrated in Figure 5. The low viscosity solution containing the polymer and the crosslinker often called the gellant, is converted into a rigid structure due to the cross-linking reaction. The crosslinker is a compound that links polymer molecules together to form a network structure [14]. Cross-linking is a stabilizing process in polymer chemistry that creates a network structure, and as a result, they harden and form an immobile gel. Gel systems with metallic crosslinkers have been used in EOR applications. The commonly used metallic crosslinkers are multivalent cations such as Cr^{3+}, $Al^{3+,}$ or Zr^{4+} [11]. A metallic crosslinking agent links to the polymer through ionic bonds. The gel polymer properties depend directly on the degree of cross-linking. However, the gelling time and gel strength would alter according to changing two parameters of polymer and crosslinker concentration. Then, the percentage change between these two parameters leads to a variety of hydrogel systems and gel treatment. In fact, this hydrogel acts as a flow blocking or diverting agent in the reservoir [14-15]. Indeed, a gel polymer system can avoid water production by obstructing the high permeability zones and diverting to the low permeability zones in the reservoir. As well, owing to the slow movement of this sort of gel, it can be employed as a viscosity modifier for oil displacement, by soaring the viscosity of the fluid which helps to decrease the mobility ratio [15-16]. However, some of the limitations of polymer solution and gel systems are the sensitivity of polymers to thermal (i.e., high-temperature reservoir), chemical (i.e., high salinity), and mechanical degradation that may cause problems of injectivity and formation plugging [1, 9].

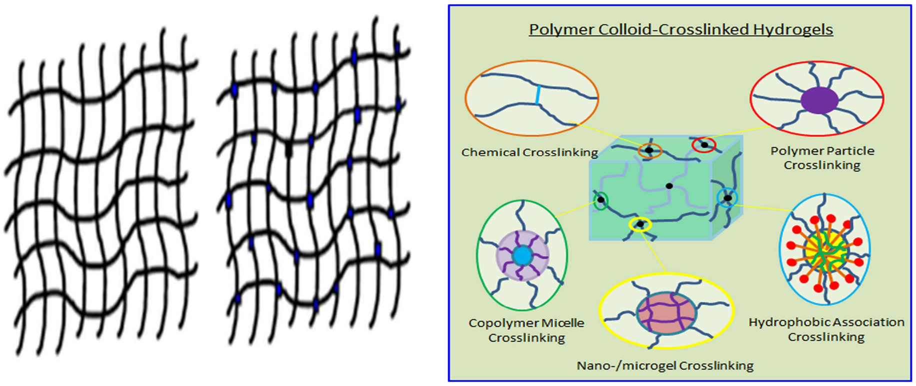

Figure 5. Hydrogel polymers [16].

1.5. Effective parameters in hydrogel injections

In this section, the definitions and factors affecting the polymer gel systems in EOR are discussed which are as follows:

1.5.1. Polymer behavior in porous media

The oil reservoir is a porous media consisting of interconnecting pores. The viscosity obtained from the polymer flow in the porous media indicates that the viscosity is higher than the results obtained from the laboratory measurements. In other words, the mobility of the polymer will be less than expected. This unexpected decrease in mobility is due to a significant reduction in the relative permeability of the pores. Therefore, the use of polymer systems with correct viscosity for oil extraction and water production control has been extensively important [17-18].

1.5.2. The reservoir permeability

The reservoirs have different permeabilities which are defined as the capacity of a rock layer to transmit water or other fluids, including oil as shown in Figure 6. The standard unit for permeability is the Darcy (d) or, more commonly, the millidarcy (md). It is categorized between low to high and by porosity (amount of interconnection of pore space). Permeability plays a major role in oil recovery processes as adequate permeability can improve reservoir fluid displacement. Permeability-porosity relationships depend on the complexity of the geometry of the porous media which makes it difficult to anticipate the fluid behavior. The reservoir is divided into two main rock formations, including limestone and sandstone. In EOR, reservoir permeability is an important factor. The presence of gaps and changes in permeability can have a great impact on the fluid flow in a reservoir and thus affect oil recovery. Because areas of high-permeability reservoirs, as well as high gaps, have less resistance to flow, most injectable fluids follow this path while on the contrary, most of the remaining oil is in areas with low permeability [19-20].

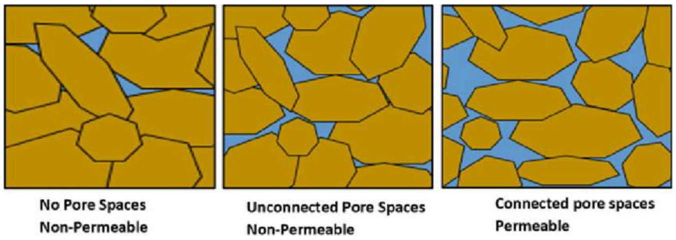

Figure 6. Reservoir permeability [17].

1.5.3. Rheological behavior and shear stability

The fluid deforms or flows by exposing a Newtonian fluid to shear force (stress). The ratio of shear stress to shear rate for a Newtonian fluid is a constant value called viscosity. Polymeric solutions for all concentrations used are non-Newtonian fluids and are classified in the group of pseudoplastic fluids. The pseudoplastic fluid is a fluid that creates less resistance to flow by increasing the shear rate. Long flexible polymer chains are susceptible to shear rate resulting in the breaking of the polymer chains and a reduction in viscosity. Laboratory studies show that most polymer solutions in reservoirs must be at a temperature of less than 250 °F because severely broken polymer chains lose their effectiveness [18]. If we consider the ratio of shear stress to shear velocity as the apparent viscosity of a pseudoplastic fluid, apparent viscosity decreases with increasing shear rate. In other words, pseudoplastic fluid has a higher viscosity at a low shear rate and a lower viscosity at a high shear rate [18-19].

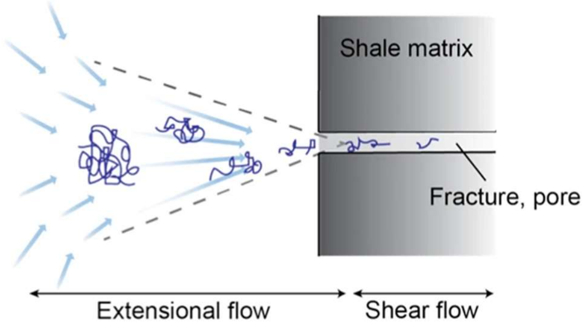

Figure 7. Polymer rheology behavior [19].

As observed in Figure 7, polymer chains, especially polyacrylamide, are susceptible to untwine by shear rate. It means that the polymer chains tend to break into several smaller molecular chains. Due to the disentanglement of the polymer chains and their arrangement in the direction of flow, the shear rate of this failure increases. But the severity of the shear rate has a big impact on the break of polymer chains. Such a breaking causes changes in the molecular weight, and the viscosity of the polymer solution. In addition, this effect when applied to equipment such as injection pumps can be more [2,18,20]. Assuming that the fractures in unconventional reservoirs are very narrow, a water shut-off agent for the fractured unconventional reservoir will need to be of lower initial viscosity than those of the higher concentration, partially crosslinked gels used in conventional fractured reservoir [20].

1.5.4. Polymer molecular weight

Polymer molecular weight is an important factor that leads to a change in fluid viscosity. Under similar conditions, a high molecular weight polymer results in a better property such as mechanical, rheological than a low molecular weight polymer.

1.5.5. Salinity

The distilled water is a good solvent for most polymers because the polymer molecule expands completely in water and increases its contact with the solvent, resulting in increasing the viscosity. But, by adding salt to the water, the electrolytes of salt neutralize the charge of the polymer molecule, making the polymer incapable to expand as a result, the polymer solution has lesser viscosity (Figure 8). Salinity and hardness such as cations Mg^{2+} and Ca^{2+} also greatly reduce the viscosity of polyacrylamide-based polymer hydrogel systems. Salinity prevents the opening of chains of the polymer when the polymer is dissolved in water. It is because the salt limits the accessibility of polymer to enough water for the formation of the structure [19-20]. Studies show that at high temperatures, the acrylamide groups in polyacrylamide decompose, particularly in saltwater [21-22].

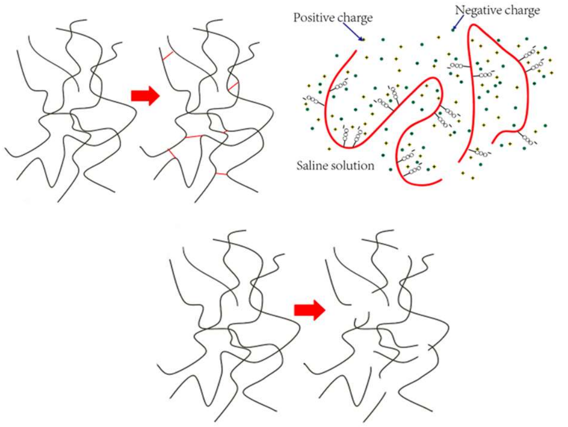

Figure 8. Polymer behavior in saline solution [22].

As a result, the reservoirs have a heterogeneous structure with different natural fractures that differ in terms of porosity, permeability, and porous media [7]. Furthermore, the flow rate corresponds to the shear rate of the polymer solution, which would alter from the well surface to the reservoir [7]. As well, harsh conditions of reservoirs such as salinity and high temperature, affect the stability and viscosity of solutions during the recovery process [8]. Therefore, all these factors can reduce the efficiency of oil recovery and production.

Gel polymer represents a convenient performance when their viscosity stability, salinity resistance, gel strength, gelation time, and thermal stability are at the desired level. Hence, rheological behaviors and thermal properties of the gel polymer solution play an important key in EOR applications [23-24]. The knowledge of these properties assists in the selecting, designing, and processing of the fluid into porous media like the oil reservoir [24-25]. As a consequence, the proper selection of gel polymer system is a key point and it depends on the reservoir conditions including lithology of formation, salinity, water hardness, and temperature [2, 4, 26].

1.6. Polymer materials in hydrogel system

Synthetic polymers such as polyacrylamide (PAM), partially hydrolyzed polyacrylamide (HPAM) [26] and natural polymers including xanthan, [27] guar [28] as common water-dissolvable polymers that have been used in oil fields including drilling fluid and oil well cementing as well in EOR applications such as control of water production (water shutoff) and polymer flooding [26,28].

However, there are some requirements for the use of water-soluble polymers in the oil sector, such as solubility, stability viscosity, compatibility with water for injections and formations, long-term resistance to hydrolysis, thermal stability, etc. Only a small number of polymers, copolymers, or polymer systems have these features. As a result, it is important to choose the right polymer and to use it in the propagation method. Since polyacrylamides and their families meet the above-mentioned specifications, they are the main choice for use in EOR applications, drilling fluid, and also oil well cementing [26-28].

1.6.1. Partially hydrolyzed polyacrylamide (HPAM)

HPAM belongs to the family of polyacrylamide (PAM) as a synthetic polymer, which is the final product of the copolymerization of acrylamide and sodium acrylate (Figure 9). Sodium acrylate can be obtained by neutralizing acrylic acid [21]. Both hydrolyzed and non-hydrolyzed polyacrylamides are highly polar due to the presence of carboxyl and amide groups. Ebrahim et al. [21] reported the preparation of partially hydrolyzed polyacrylamide by copolymerization of acrylamide and sodium acrylate. A redox system including sodium metabisulphite and potassium persulphate was used to initiate free-radical copolymerization.

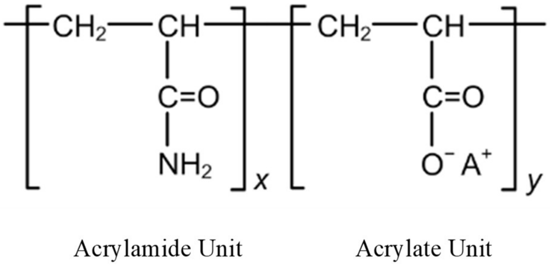

Figure 9. Chemical structure of HPAM.

With an increasing temperature, the degree of hydrolysis also increases, so to achieve the best condition of the product, it is necessary to control the temperature during polymerization and acrylamide hydrolysis. The amount of amide groups that are converted to carboxylate is called the degree of hydrolysis. Rabiee et al. [29] showed that the ratio of carboxyl and amide groups as well as the molecular weight influence the HPAM properties. Borthakur et al. [30] explained the copolymerization of polyacrylamide with sodium acrylate and hydro groups creates an anionic polymer that makes it soluble in water. The ratio of the two functional groups in the final copolymer is determined by the ratio of sodium polyacrylate to acrylamide at the beginning of the process. Nasiri et al. [22] showed that there is a sample of HPAM that has a high molecular weight and contains 65% to 70% acrylamide and the rest of acrylate. HPAM with a cross-linker is mixed to create a gellant that is injected from the surface into the reservoir for shut-off purposes to block thief zones producing excessive water. Under the effect of temperature and time, HPAM and crosslinker react to make a three-dimensional network structure [14]. However, HPAM is sensitive to the salinity and has poor shear resistance, as well as its molecular chain breaks while passing through the porous media at high speed, both of which affect the shear stability of HPAM, decreasing the viscosity and mechanical properties of polymer solution [31]. HPAM is also not stable upon increasing the temperature, because of NH_2 group hydrolyzation, which results in a significant decrease in the viscosity and strength of hydrogel [16]. Sorbie et al. [32] presented an excellent review on the thermal and the chemical degradation of polymer solutions and Sheng et al. [33] summarized the current limits for using polymers under harsh reservoir conditions. Therefore, to improve shear stability, and mechanical properties of HPAM, mixing with natural polymers, like hydroxypropyl guar (HPG), can be highly effective. Furthermore, some of the acrylamide (AM)-based copolymers are used to prevail over the limitations of HPAM under harsh reservoir conditions. AM monomers copolymerized with one or two monomers as a modifier [34]. 2-acrylamide-2-methyl propane sulfonate (AMPS) or vinylpyrrolidone (VP) as monomer modifiers have the potential to improve the chain stability of AM in harsh conditions of the reservoir. [4,34] The introduction of the sulfonic acid group into AM enhances the salt tolerance attributes of AM monomer. Indeed, AMPS is a sort of vinyl monomer including sulfate groups with high durability, and also excellent salt tolerance which will result in the provision of high molecular weight copolymers that is desirable for EOR applications [35-36].

Moradi et al. [37] produced AM-AMPS copolymer by copolymerization of AM and AMPS. Rashidi et al. [38] reported that the incorporation of AMPS monomer improves the thermal stability of AM and their solubility in the presence of divalent cations. Doe et al. [39] presented that AM-VP copolymer by copolymerization of AM with VP. Incorporating VP into AM decreases the thermal hydrolysis of AM in the presence of divalent cations while improving the shear stability of AM due to the large size of the VP group. The performance of other AM-based copolymers in polymer flooding is summarized by Kamal et al. [40]. Therefore, in recent years, most research has been focused on acrylamide-based homopolymer, copolymer, and terpolymer for developing the hydrogel system that can be used in oil reservoirs with highly resistant to thermal hydrolysis and viscosity stability in the harsh conditions of the reservoir.

1.6.2. Polysaccharides

Polysaccharides and biopolymers including xanthan gum and guar are natural polymers that are highly used in EOR processes. These biopolymers have stable chain structures that provide high mechanical resistance to mechanical shear. Spiral construction increases the resistance of this polymer in saltwater and reduces its sensitivity to multivalent ions [1]. Xanthan gum and guar gum are hydrophilic polysaccharides from the seed of the guar plant called galactomannan. Galactomannans are polysaccharides consisting of a mannose backbone with galactose side groups the chemical structure of guar gum [41-42]. Guar gum as shown in Figure 10, is highly dispersible into the water and brines and salinity. Guar gum showed non-Newtonian viscosity behavior and also can be cross-linked by cross linkers such as borate and zirconium to create the high strength gels (network structure) [42]. One advantageous property of guar gum is that it can thicken in presence of water. In addition, it is used widely in the oil industry as a thickener for hydraulic fracturing of rock formations and enhancing oil recovery (EOR). Disadvantages of using guar gum include its low thermal stability as well the main limitation of this biopolymer is its poor resistance to microbial degradation. The most widely known derivatives of guar gum include carboxy methyl guar (CMG), hydroxy propyl guar (HPG), and carboxy methyl hydroxy propyl guar (CMHPG) [43]. HPG is commonly applied in gel polymer injection and, particularly in hydraulic fracturing. The use of the HPG as a natural polymer that is not only less sensitive to shearing but is also applied as a great viscosity modifier [16, 44-45]. HPG chains can be grafted by AM monomer which causes a further increase of shear resistance in the copolymer structure [44]. HPG has an outstanding ability to carry the solid particles within the created mechanical fracture in the reservoir during the fracture operation. These particles help to keep the fractures open so that the oil can easily egress from the deeper reservoir to the well surface [46]. Artificially inducing fractures is the key technique that has transformed previously unproductive low permeability reservoirs into economically viable projects. Hydraulic fracturing technique involves pumping high quantities of pressurized fluids into the wellbore which creates fractures and cracks in the reservoir, thereby increasing the effective permeability. The induced fractures become flow paths connecting the reservoir to the wellbore, thereby increasing gas flow rates [44-46]. Accordingly, the HPG based hydrogel system with borate as s crosslinker is highly used in this treatment technique.

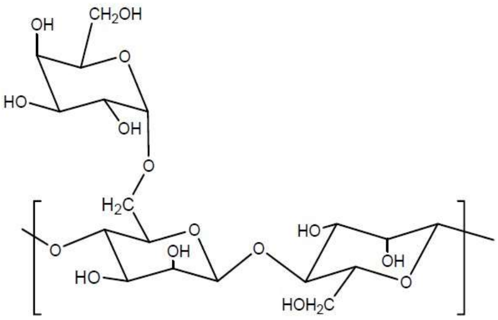

Figure 10. Chemical structure of guar gum.

1.7. Preparation of hydrogel system by interpenetrating polymer network and graft copolymerization methods

IPN technique is the admixture of two polymers, which have been cross-linked and/or synthesized to improve the new admixture polymer properties. Through this method, various polymer compounds can be prepared based on the desired properties of both polymers by changing their compositions [47, 50]. Furthermore, when one polymer is cross-linked and the other polymer is not networked, a semi-IPN is created. In contrast, when both are cross-linked, a full IPN is created as observed in Figure 11[51]. The present study is limited to the use of semi IPN hydrogel in the presence of the crosslinker as a cross-linked polymer hydrogel. This polymer gel system can flow while having a cross-linked structure in porous media. In fact, weak crosslinked gel systems can remove the difficulty of high permeability zones in a non-homogenous reservoir and enhance control of water production. It can also be applied due to the slow-motion of gels in zones with high permeability as an oil displacement by decreasing the mobility ratio as well as reducing the viscous fingering simultaneously [10,23, 51-52].

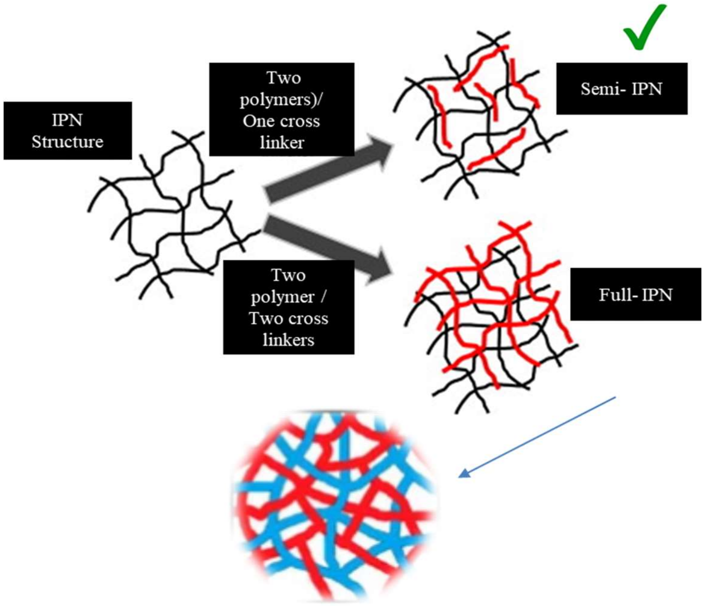

Figure 11. Semi and full interpenetrating polymer network [52].

Alvand et al. [11] reported an improvement in the behavior of sulfonated polyacrylamide with the addition of laponite and chromium (III) as a weak hydrogel system. Alvand et al. [23] showed an enhancement in the rheological behavior of sulfonated polyacrylamide by mixing with a natural polymer like scleroglucan in the presence of chromium (III) as a weak hydrogel system by IPN technique. Rahmatpour et al. [47] described the novel semi-IPN nanocomposite hydrogels based on guar gum, HPAM, and montmorillonite which is mixed by chromium (III) acetate. This displayed good shear and thermal resistance and salt tolerance ability in EOR applications. Kheirabadi et al. [51] synthesized a novel full IPN hydrogel focus on anionic monomers of AMPS/acrylic acid-sodium acrylate via solution polymerization technique in an aqueous media with the incorporation of GO. Karadag et al. [53] reported that highly hydrogel nanocomposite systems by using the semi IPN technique of AM/AMPS monomers and carboxymethyl cellulose with clay such as montmorillonite through free radical polymerization by using ammonium persulfate in the presence of poly ethylene glycol diacrylate (PEGDA) as a cross-linker.

There is another method to enhance the AM monomer properties by the graft copolymerization of AM as a main monomer and AMPS as modifier monomer grafted onto the natural polymer chains. The graft copolymerization structure was shown in Figure 12. The graft copolymer as a polymer solution reacted with various crosslinkers to make the hydrogel with great thermal, salt, and shear stability, owing to the linking of AM with an ionic comonomer in its matrix and grafted with natural polymer in the backbone. [6, 13].

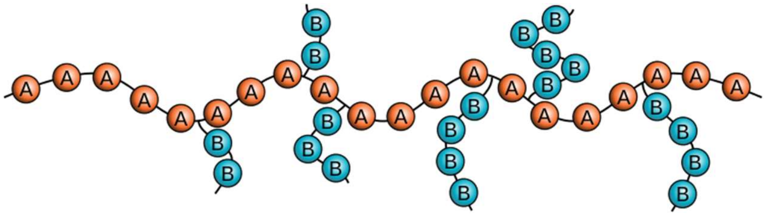

Figure 12. Graft copolymerization structure (A polymer or monomer 1, and B polymer or monomer 2) [Wikimedia].

Mohammadi et al. [3] described the inverse emulsion copolymerization of AMPS and AM to make a high-weight nanostructure polymer that is mixed with chromium (III) acetate using EOR application. Singh et al. [13] synthesized a graft polymer nanocomposite hydrogel system, based on poly (AM -g-starch)/clay, by using a method of radical polymerization. Li et al. [31] synthesized a new hydro soluble sulfonated copolymer AMPS/DMAEMA/MA that demonstrated good shear and thermal resistance and salt tolerance ability in EOR applications. Khakpour et al. [34] present the terpolymer AM/BA/AMPS by micellar copolymerization method, which leads to improving its thermal stability and mechanical properties. Liu et al. [54] described three types of copolymers, by free-radical copolymerization: AMPS with AM, DMAM, and DEAM. AMPS/DMAM showed suitable water-retaining capacity at a high temperature. Zhu et al. [55] synthesized a superabsorbent composite, poly (AMPS-co-AM)/ kaolin, by using a method of radical polymerization. This hydrogel showed good water and salt solution absorbency at a high temperature. Atassi et al. [56] showed the improvement of mechanical strength properties of nanocomposite hydrogel by grafting P(AMPS-co-AA-co-AM) chains onto the backbone of a renewable and biodegradable substrate of chitosan in the presence of basalt.

However, the application of this sort of conventional hydrogels are somewhat limited, because of the low network strength and reduced thermal stability of polymer or copolymer solutions when passing into porous media and also after long-term aging which leads to the reduction of hydrogel viscosity, especially in reservoirs with high-temperature [8, 26]. Polymers when dissolved in water are applied in oil recovery as they increase the viscosity of the displacing water and improve sweep efficiency, although, gel polymer systems tend to lose efficiency in prolonged processes. This is primarily owing to shear degradation of the polymer solution and gel polymer which causes viscosity reduction during high shear rates generation by the rotating bit in the well bore, resulting in system instability. Therefore, introducing nanoparticles into the polymer structure of hydrogel due to their outstanding properties, corresponding mechanical strength, thermal stability, and salt tolerance [8] to enhance the strength and thermal properties of conventional hydrogels can be considered a beneficial method [8, 26, 57].

1.8. Hydrogel nanocomposite and nanotechnology

Nanotechnology is a new technology that has gained great attention in the oil industry. Adding nanoparticles to fluids enhances the effectiveness of oil recovery processes by causing a decline in the interfacial tension and changing the rock wettability [58-59]. In the last half-century, industrial processes have generally experienced a change in material applications due to the shift from conventional bulk materials to nanoscale and nano materials. This has led to innovative applications in a wide range of science and technology fields worldwide, thus interest and investment are increasing in the fields of nanoscience and nanotechnology. This technology involves the use of small-sized materials which can be considered the nanometer (nm) length scale. Despite the relevance of nanoparticles in oil and gas engineering processes, reservoir engineering, specifically, EOR has attracted the most attention in recent times [9]. Nanoparticles behave quite differently from bulk materials owing to their size-dependent properties. As a result, the performance of hydrogel as a polymer or graft copolymer solution in reservoir conditions can be improved by the incorporation of nanoparticles [8]. Hence, more recently, graphene oxide (GO) has highly gained attention in this regard and is used as a thermal, electrical, and mechanical strength enhancer for hydrogel polymer systems in harsh conditions [60-61]. Nanoparticle like GO as a multifunctional group shows high thermal properties that exhibit great stability over a wide range of temperatures and suitable rheological and flow behavior with water-soluble polymer [9]. Although the addition of GO, increases the cost of materials a little bit, but all the advantages associated with GO, make it worth it. For example, Haruna et al. [26] reported that the addition of GO increased the viscosities and high-temperature stability of the base polymer fluid, and also the elastic properties of the dispersion. Aliabadian et al. [59] showed that adding the GO to the HPAM solution enhanced oil recovery by the core flow test. Nwidee [9] reported that the thermal properties of nanoparticle-based fluids exhibit higher thermal conductivity and surface area than conventional base fluids. Nguyen et al. [62] demonstrated that the addition of the GO soared the thermal and viscosity stability of polymer solution in EOR at HTHP offshore reservoirs. Pan et al [63] prepared PAM/GO hydrogels with high mechanical strength, excellent environmental stability due to the effect of multifunctional crosslinker of GO as shown in Figure 13.

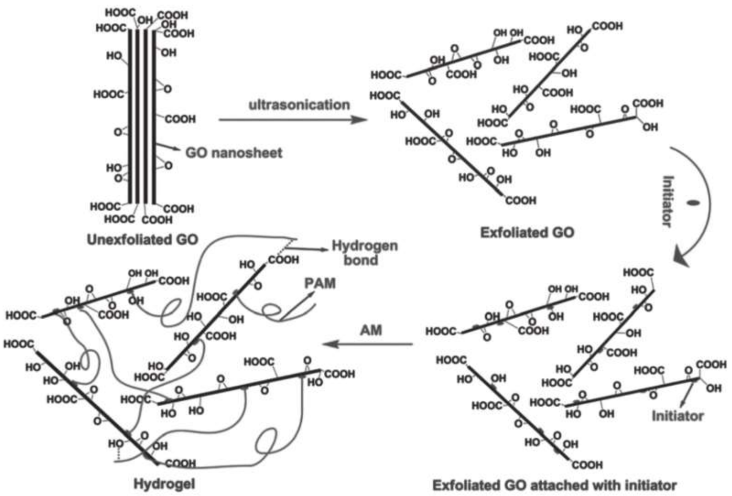

Figure13. Schematic representation of the synthesis of PAM-GO hydrogels.

Fan et al. [64] ascribed the nanocomposite hydrogel with the excellent mechanical performance which has been synthesized by free radical polymerization of AM and SA in the presence of GO in an aqueous system followed with ionically crosslinking of calcium ions. Boroujeni et al. [65] studied the improvement of mechanical strength of GO-g-poly (AMPS-co- AM), GO was grafted with AM and AMPS monomers by free-radical copolymerization. Dai et al. [66] reported that the hydrogels were synthesized by grafting copolymerization AA and AM onto carboxymethyl cellulose with the incorporation of GO. Adding the GO enhanced the thermal stability of the hydrogels in the porous media. Jafarigol et al. [49] showed that graft copolymer nanocomposite hydrogel with excellent mechanical strength copolymerized by AM with AA that grafted with CMC and reinforced by GO sheet. Tarash et al. [67] reported the great toughness and suitable mechanical strength of the full IPN nanocomposite hydrogel based on a new kind of κ-carrageenan (κ-Car)/polyacrylamide/GO. Therefore, regarding EOR, nanoparticles applications can be a novel EOR pathway for resolving reservoir challenges with harsh conditions.

1.9. Graphene oxide

In the last decades, graphene oxide (GO) become a new topic in research related to materials science and nanotechnology [68-69]. GO is an important derivative of graphene which is produced by chemical modifying graphene (Hummer's method) [70]. GO has highly been considered and employed as a thermal and mechanical strength enhancer along with great electrical conductivity for hydrogel polymer systems in harsh conditions. GO has a great surface area, with plenty of oxygen functional groups such as epoxide, hydroxyl, on its surface, and carboxyl, carbonyl on its edges, as shown in Figure 14 [63, 71-72]. These provide a wide range of active sites on the surface, causing a better crosslinking with the polymer chains [65, 73]. Furthermore, the hydrophilic groups of GO result in better dispersity in an aqueous solution and are employed with hydrophilic polymers as a reinforcer [73-74]. Hence, GO can help in improving the mechanical strength and thermal stability of polymer hydrogels [63, 73]. Graphite oxide has a layered structure with a long distance between the layers.

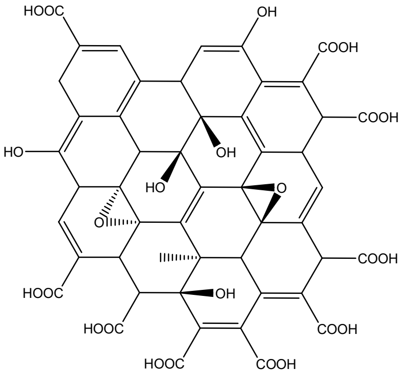

Figure 14. Chemical structure of GO.

Interestingly, carbon nanotube (CNT) unlike GO has a strong tendency to agglomerate during processing and have a limited production because of the expensive raw materials. However, GO has the simplicity of its construction, suitable thermal stability, and is easy to produce because of the accessibility of raw materials like graphite in nature. This has been able to provide a suitable alternative to nanotubes in nanoscience today [68-69]. In addition, GO exhibits better stability in solution as opposed to the carbon nanotubes, silica nanoparticles that are thermodynamically unstable with high aggregation tendencies. The reinforcement/toughening contribution of GO in polymer matrices depends on dispersion uniformity and efficient interfacial adhesion between the GO and polymer matrix to transfer the mechanical load from the matrix to the GO. This load relied on the effective interfacial stress transfer at the polymer-graphite interface, which was often dependent on the polymer [69, 72, 74].

The most common method of producing graphene oxide is the Hummers method. In this method, briefly, 1 g of graphite powder, 33 mL of H_2SO_4, and 1.25 g of $NaNO_3$ are stirred for 1 hr. in an ice bath. Secondly, 6 g of $KMnO_4$ is added slowly into the above mixture solution for 2 hr. The mixture is stirred at 35°C in the water bath for 4 hr and then slowly diluted with water. Then, the mixture is stirred for 30 min at 95°C. Finally, 120 mL of H_2O_2 (10%) is added to the mixture. The sample is washed with 10% HCl solution, centrifuged, and washed with deionized water repeatedly followed by drying in a vacuum oven at 50°C for 12 hr to obtain graphene oxide [70]. Figure 15 displays the dispersion of GO nanosheets by using the ultrasonic water bath.

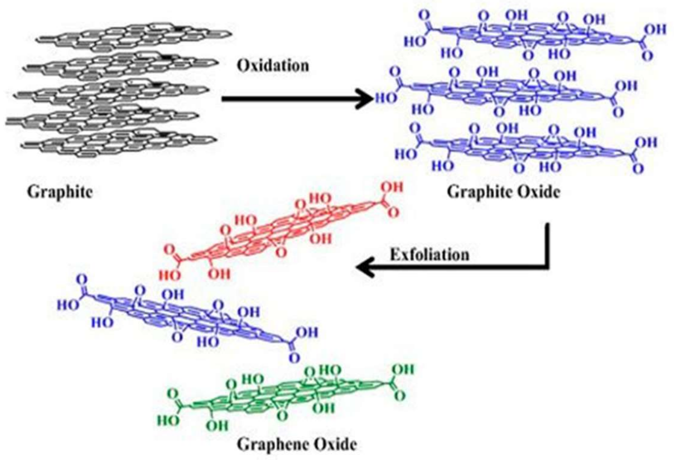

Figure 15. Schematic of GO dispersion [71].

GO nanosheets tend to form agglomerates with increasing concentration which reduces their reinforcing effect [74]. In addition, GO particles trend to the sedimentation in solution, which may cause plugging of the pores in the reservoir, owing to nonuniformed dispersions and sedimentation of particles [6, 16]. Therefore, the GO concentration is the key factor for the performance of the hydrogel network. The selection of ideal particle type, concentration, dispersals, or stabilizers of the nanoparticles in gel polymer and polymer flooding is crucial. Therefore, an important challenge is to achieve the uniform dispersion of GO in the IPN and copolymer matrix and to study its effect on the network structure of hydrogel. This is because the rheological behavior, thermal stability, and viscosity of the hydrogel depend on the GO concentration as well as the interactions between the GO and polymer matrix. As a result, the major issue of the polymer solution and also the development of a novel gel system is to achieve the polymer hydrogel with suitable viscosity, strength, and thermal stability by using accurate GO concentrations in electrolyte media in a high-temperature reservoir [10,75].

1.10. Project overview

One of the problems encountered in using polymer systems in porous media such as EOR and controlling water production in oil reservoirs is the decline in the properties of these systems as a result of the harsh conditions of oil reservoirs. There are various chemical factors (such as high salinity, microorganisms, etc.), thermal factors (high temperature), and mechanical factors (such as high shear rate due to pumps and injection devices) that affect the viscosity and polymer system behavior.

Extensive studies have been conducted on the improvement of flow behavior and elastic properties of common polymer systems used in the applications of EOR. These include the copolymerization of synthetic and natural polymers, the use of cross-linking agents in the polymer structure, the application of nanoparticles in the polymer structure, and the introduction of non-ionic hydrophilic polymers [3, 13, 23, 28, 36, 55,57].

Some studies have shown that the use of hydrophobic or temperature-sensitive monomers improves the stability of polyacrylamide-based polymer systems at high temperatures and salinity, but due to the presence of acrylamide groups, these systems also deteriorate after a few days. Graft copolymerization of synthetic and natural polymers improves the viscosity, viscoelastic properties, and stability at high temperatures and salinity [2,3,4,8,23,25, 26, 35,47].

In this research, to improve shear resistance, thermal stability, and mechanical properties of HPAM and AM acrylamide based on gel system, we have investigated three methods such as interpenetrating polymer network (IPN), copolymerization, and graft copolymerization, that they have attracted much attention for the fabrication of hydrogel systems because of their ability to improve the properties of the polymers with a large range of applications owing to the combining of two or more polymers along with their desired properties [13, 44-49].

Therefore, the main objective of this study is to examine the feasibility of developing and improving the performance of hydrogel polymer systems based on HPAM/HPG by incorporating graphene-oxide as a high-thermal reinforcement nanoparticle-containing multifunctional group that is potentially used in EOR applications. To accomplish this objective, the experimental work was divided into three main phases:

Phase one: In this section, the effect of GO on semi-IPN nanocomposite structure based on HPAM/HPG hydrogel system to enhance nanocomposites hydrogel for EOR applications was evaluated. Thus, the purpose of this study is to investigate the influence of GO on the novel semi-IPN nanocomposite hydrogel in terms of:

- Viscosity, flow activation energy, temperature, long-term aging, viscosity loss, and thermal stability.
- FTIR, morphology, and electrical characterization of nanocomposite hydrogels

Phase two: Graphene oxide was prepared and synthesized using graphite, H_2SO_4, H_3PO_4 and $KMnO_4$. The characterization of GO and its effects on the development of a copolymer-based hydrogel system (AM-c-AMPS) as a rheology modifier were evaluated.

- The properties of synthesized GO were investigated by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD).

Phase three: synthesis and characterization of graft copolymer nanocomposite based on HPG-g-poly (AM-co-AMPS)/GO as a copolymer solution for developing the hydrogel system and its potential use in EOR application was evaluated. The main attention of this section of research is to investigate the dispersion effect of synthesized GO on graft copolymer nanocomposite as copolymer solution and develop a novel hydrogel system by using chromium triacetate to achieve the desired polymer hydrogel with adequate viscosity, gel strength, and thermal stability.

- The characterization of graft copolymer nanocomposite was evaluated by FTIR, XTD, TEM, and SEM
- The effect of the incorporation of GO on the rheological behavior of the nanocomposite hydrogel system in terms of viscoelastic behavior, long-term aging, viscosity loss, and thermal stability have also been investigated to determine the flow behavior in the reservoir.
- The affect of the graft copolymer nanocomposite and cross-linker concentrations, on viscosity, storage modulus, and strength of the hydrogel system were evaluated to determine an optimum gel formation in electrolyte media and EOR application.

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Chapter 2

Materials and Methods

2.1. Materials and methods

This chapter presents detailed descriptions of the methods and equipment used in attaining the purpose and objectives of this study. This research is an experimental based, which also embodies a qualitative pathway.

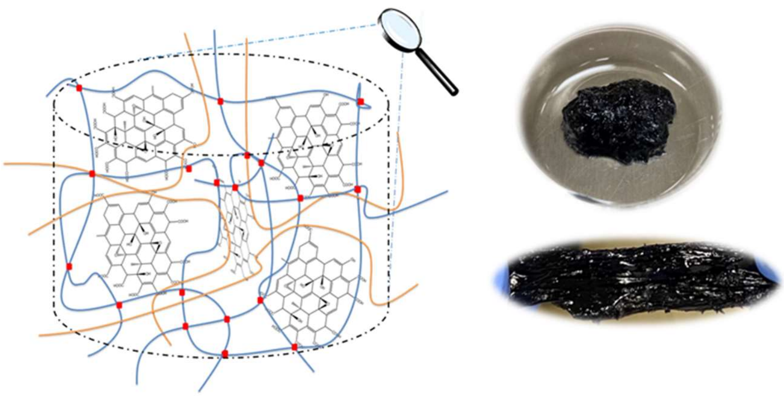
2.2. Chemicals and reagents

All chemicals were purchased from either one of the vendors such as Sigma Aldrich, Alfa Aesar, United nanotech innovation PVT Ltd, Shandong Shengyou cementing engineering & technology Co, SNF Co, and Carlo Erba. Solvents were purchased from Fischer Scientific. All chemicals were purchased in high purity and used without further purification.

2.3. Experimental procedure

2.3.1. Preparation of (HPAM/HPG/GO) IPN nanocomposite hydrogels

The IPN hydrogel and nanocomposite hydrogels were prepared and schematically shown in Scheme 1. First, 0.35 wt.% of HPAM as well as 0.35 wt.% of HPG powder were gradually added to the separate saline water and stirred regularly by a magnetic heater stirrer to obtain clear viscous solutions at room temperature and aged for 24 hr. Then the various amounts of GO (0.05, 0.1, 0.3, and 0.5 wt.%) were dispersed in saline water for 1 hr by a magnetic stirrer to form a stable dispersion. Afterward, the prepared HPG and HPAM were charged in GO solution, respectively and stirring was continued for another 1 hr using an overhead mixer (Heidolph RZR 2020). Then, 0.075 wt.% of the chromium triacetate as a crosslinker was prepared in water and added to the aqueous mixture while stirring gently. The reaction mixture was heated at 185°F (85°C) for approximately two hr to obtain a homogeneous solution. The final samples were dried in a vacuum oven for 24 hr at 158 °F (70 °C). The polymer concentration of all samples was 0.7 wt.%. The salinity of water is 7616 ppm.



Scheme 1: The schematic of structure HPAM/HPG/GO IPN nanocomposites hydrogel.

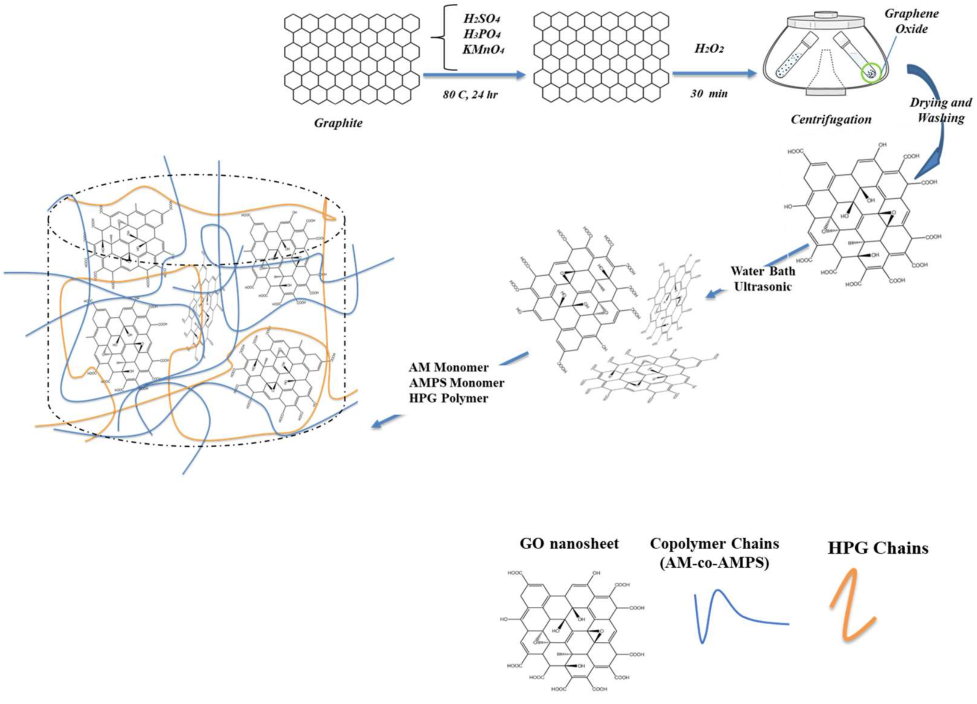
2.3.2. GO preparation

GO was prepared according to the following procedure, briefly 0.5 g of the graphite was mixed in 60 ml of H_2SO_4, and 6.6 ml of H_3PO_4 followed by stirring for 10 min. 1.5 g of $KMnO_4$ was then gradually added to the solution and the reaction was heated and stirred at 80°C for another 24 hr. Finally, 90 ml deionized water was added followed by 1 ml H_2O_2 into the solution which was then stirred for over 30 min. The final product was a bright yellow solution which was purified by centrifugation for around 60 min at 2500 rpm and washed several times with water to adjust pH to 7-8. The solution was centrifugated for an additional 60 min. The same step was repeated by changing water with ethanol. Finally, ethanol was removed by adding diethyl ether and the solution was poured onto a glass tray and the solvent was allowed to evaporate at room temperature. The sample was then dried in an oven at 80 °C for 24 hr and was milled with mortar.

2.3.3. Synthesis of the HPG-g-poly (AM-co-AMPS)/GO

The HPG-g-poly (AM-co-AMPS)/GO was synthesized by the free-radical copolymerization as shown in Scheme 2. Firstly, 1 g of HPG was added to a 250-mL three-necked flask and mixed until the mixture was homogenized. Then various concentrations (0, 0.05, 0.1, and 0.3 wt.%) of GO were interspersed in 20 mL distilled water and stirred in an ultrasonic bath

(Branson Co., 60 Hz, 80 W) to earn the good dispersion of GO solution. After that, GO added to the flask necked and allowed to mix. Subsequently, a 30 mL aqueous solution containing 8 and 2 g of AM and AMPS monomers was poured into the flask and was mixed for 45 min. Thereafter, 0.011 mol/L of APS as an initiator in 5 mL distilled water was added slowly and the pH of the reaction solution was adjusted to 7-8 with sodium hydroxide and hydrochloric acid. Later on, the reaction was continued to stir for another 3hr by soaring the temperature to 80°C, under an inert nitrogen gas atmosphere up to the viscous solution was engendered. The synthesized product was precipitated and washed with acetone to obviate any impurities Afterwards, it was dried in a vacuum oven for 6 hr up to achieve a stable weight, finally, it was powdered by a mortal pastel.



Scheme 2. The schematic of HPG-g-poly (AM-co-AMPS)/GO graft copolymer nanocomposite.

2.3.4. Preparation of nanocomposite hydrogel

The nanocomposite hydrogel is prepared by gradually adding different amounts (0.5, 0.7, 0.9, and 1.1 wt.%) of synthesized graft copolymer nanocomposite to the saline solution (NaCl: 15000 ppm) and stirred frequently by a magnetic stirrer to get viscous solutions and kept for 24 hr. After that, the different amounts (0.6, 0.8, 1, and 1.4 wt.%) of chromium triacetate as a crosslinker were provided in water and mixed with the graft copolymer nanocomposite solution. Finally, the reaction was done by heating to 85 °C for nearly 2 hr to produce a uniform gel solution.

2.4. Equipment and characterization used

A magnetic stirrer was used for making polymer solutions and mixing gellant solutions. A few of the techniques employed during different projects are enlisted below

2.4.1. Fourier transform infrared *(*FTIR)

FTIR spectra of dried samples were accomplished by Thermo is10 spectrometer and PERKIN ELMER-65 spectrometer, in the range of 4000-650 and 500 cm^{-1}. The resolution and the scanning number were 4 cm^{-1} and 16, respectively.

2.4.2. X-ray diffraction (XRD) characterization

Wide-angle XRD analysis of dried samples was carried out at room temperature using a Rigaku diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å) in the range $2\theta=5-70$.

2.4.3. Thermogravimetric analysis (TGA)

TGA was examined using Perkin Elmer, STA 6000. The dried samples were scanned from 30 °C to 500 °C at 10°C/min.

2.4.4. Morphology characterization

Scanning electron microscopy (SEM) was carried out by TESCAN Vega Model and also HITACHI, SUI 510 which was equipped with energy dispersive X-ray (EDX) by software X-MAX (Oxford instruments, 20 mm^2) for elemental analysis. The dried samples were coated by sputtering the thin layer of gold for good conductivity. Transmission electron microscope (TEM) of graft copolymer nanocomposite was obtained using a PHILIPS EM 208 S.

2.4.5. Rheological measurements

Rheological characterizations of the nanocomposite hydrogels were performed by a rheometer (Paar-Physica, MCR 301) at temperatures of 200 and 240°F (93 and 115 °C), which was equipped with parallel plate geometry and also a Peltier device for control of temperature. To inhabit the water loss, silicone oil was used at the outer surface. The strain amplitude was 1 % with the frequency in the range 0.01-100 rad/s.

The viscosity stability vs. time for the nanocomposite hydrogels was carried out using HT/HP **(**High temperature/High Pressure) fluid rheology tester (HT/HP Acid-resisting, GRACE M5600 Rheometer). The test of gellant samples was performed for 51 min under a pressure of 480 psi and at the shear rate of 100 1/s (API RP 39). The temperature of the samples was 200 °F and 240 °F.

2.4.6. Aging effect

Long-term aging by viscosity monitoring was performed and the samples were held in an oven at 200 and 240 °F, for 7 days, separately. The effect of the loss viscosity of these samples on long-term thermal stability was studied.

2.4.7. Electrical characterization

The electrical conductivity of IPN nanocomposite hydrogels was evaluated in conformity with ASTM D257 by Tara S cm^{-1} at 500 V by CEAST Co. The sheet samples (1mm thick) were prepared and coated with silver paint.

Chapter 3

Rheological and thermal stability of interpenetrating polymer network hydrogel based on polyacrylamide/hydroxypropyl guar reinforced with graphene oxide for application in oil recovery

3.1. Introduction

Polymers are often employed in oil recovery applications not only as gel polymers for water production control in-depth reservoir formation but also for oil displacement in polymer flooding. In this chapter, the effect of graphene oxide (GO) as a thermal reinforcer for improving the viscosity and thermal stability of hydrogel system based on HPAM/HPG was evaluated. The nanocomposite hydrogel was prepared by HPAM with a modifier of viscosity like hydroxypropyl guar HPG using the interpenetration polymer network (IPN) technique called IPN hydrogel in presence of the reinforcement effect of GO and the cross-linker chromium triacetate as a new admixture hydrogel with excellent properties for EOR applications in high temperature was studied.

3.2. Objectives

The main objectives of this section of research are as follows:

- The interactions between GO and polymer chains of the matrix at the interface, to improve IPN network strength were investigated.
- The influence of GO as reinforcement on the shear viscosity versus shear rate.
- The reinforcing effect of the GO for the formation of GO network structure on IPN hydrogel based on HPAM/HPG.
- The effect of GO on shear-thinning behavior and pseudoplastic fluid behavior.
- Effect of low and high shear rate on the dispersion of GO in nanocomposites.
- Relationship between viscosity stability of IPN versus time to evaluate the flowability of polymer with desired viscosity in the reservoir as porous media.
- The significant effect of temperature on the rheological behavior of IPN hydrogel.
- Noticeable effects of GO on electrical conductivity that it has been studied by electrical conductivity. And also, this effect helps to better understate the dispersion of GO in the matrix.

- The effect of GO on the improvement of the effect of the aging long term of IPN hydrogel as a polymer solution, during the shear rate and temperature.

3.3. Article 1

Rheological and thermal stability of interpenetrating polymer network hydrogel based on polyacrylamide/hydroxypropyl guar reinforced with graphene oxide for application in oil recovery

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3.4. Author’s contribution

Amir Narimani: Conceptualization of the project, visualization, and investigation of experiments, all mixing of polymers and experiments conducted, validation of methodology and curation of data, drafting the original manuscript.

Farid Kordnejad: Investigation in rheology study.

Dr. Prabhjyot Kaur: Writing- review, and editing.

Prof. Mahmood Hemmati: Investigation in EOR study.

Prof. Saeed Bazgir: Investigation in rheology study.

Prof. Adam Duong: Project administration, supervision, funding acquisition, writing-review, and editing.

Rheological and thermal stability of interpenetrating polymer network hydrogel based on polyacrylamide/hydroxypropyl guar reinforced with graphene oxide for application in oil recovery

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Abstract

The purpose of the present work is to enhance the thermal stability and rheological properties of semi-interpenetrating polymer network (IPN) hydrogel-based on partially hydrolyzed polyacrylamide/hydroxypropyl guar (HPAM/HPG) nanocomposite reinforced with graphene oxide (GO), at temperatures (200 and 240 °F) for use in oil recovery applications. FTIR spectra of the IPN nanocomposite hydrogels revealed interactions of GO with HPAM/HPG chains. An increase in the viscosity is also observed from the rheological study. Moreover, IPN and its nanocomposite hydrogels exhibited non-Newtonian behavior. The decline of viscosity of IPN nanocomposite hydrogels was observed with an increase in the temperature from 200 to 240 °F but was still higher than IPN hydrogel without GO. Dispersion of GO through the HPAM/HPG hydrogel matrix was evaluated by SEM morphology and electrical conductivity. The IPN nanocomposite hydrogels showed high viscosity stability, thermal stability, and flow activation energy as compared to IPN hydrogel without GO. Therefore, the addition of 0.1 wt.% of GO to the HPAM/HPG matrix is suitable to create a cross-linked polymer solution with improved properties which may be beneficial for use in oil recovery applications.

Keywords: Rheological behavior, graphene oxide, enhanced oil recovery, thermal stability, cross-linked hydrogel

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1. Introduction

Polymers are often applied in oil recovery applications not only as gel polymers for water production control in-depth reservoir formation but also for oil displacement in polymer flooding [1-2]. The hydrophilic polymers boost remarkably the viscosity of the injection water, and decrease the mobility ratio of water to oil, to enhance the sweep efficiency in the reservoir [3-4]. Polymer solutions present a suitable performance when their viscosity is maintained at the desired level. Therefore, rheological behaviors and properties of the polymer solution play a fundamental role in enhanced oil recovery (EOR) applications. The knowledge of these properties assists in the selecting, designing, and processing of the fluid into porous media like the oil reservoir [5-6]. Oil reservoirs have a heterogeneous structure with different natural fractures and these reservoirs are also different in terms of porosity and permeability [7], which affects sweep performance [8]. Furthermore, the flow rate corresponds to the shear rate of the polymer solution, which would alter from the well surface to the reservoir [7]. As well, harsh conditions of reservoirs such as salinity and high temperature affect the stability and viscosity of polymer solutions during the recovery process [9-11]. Therefore, all these factors can reduce the efficiency of oil recovery [12].

Polyacrylamide (PAM), partially hydrolyzed polyacrylamide (HPAM) [12] xanthan, [13] guar [14] are the most important water-dissolvable polymers, used in EOR applications such as polymer flooding, water shutoff, and also in drilling fluid [11,15]. HPAM with a cross-linker is mixed to create a gellant that is injected from the surface into the reservoir. Under the effect of temperature and time, HPAM and crosslinker react to make a three-dimensional network structure [16]. However, HPAM is sensitive to salinity and has poor shear resistance, as well as its molecular chains break while passing through the porous media at high speed [4,17]. HPAM is also not stable upon increasing the temperature, because of NH_2 group hydrolyzation [15,18] which results in a significant decrease in the viscosity and strength of hydrogel. Therefore, to overcome this drawback of hydrogel based on HPAM, mixing with natural polymers, like hydroxypropyl guar (HPG), along with using the chemical cross-linkers through interpenetrating polymer network (IPN) technique can be highly effective [19-20]. HPG is not only less sensitive to mechanical shearing but is also used as a high modifier in increasing the viscosity [21-22].

IPN technique is the admixture of two polymers, which have been cross-linked and/or synthesized to improve the new admixture polymer properties. Through this method, various polymer compounds can be prepared based on the desired properties of both polymers by changing their compositions [23-24]. In addition, when one polymer is cross-linked and the other polymer is not networked, a semi-IPN is created. In contrast, when both are cross-linked, a full IPN is created [25]. The present study is limited to the use of semi IPN hydrogel in the presence of the crosslinker as a cross-linked polymer hydrogel. This polymer gel system can flow while having a cross-linked structure in porous media. In fact, crosslinked gel systems can obviate the difficulty of high permeability zones in a non-homogenous reservoir and enhance control of water production. It can also be used due to the slow-motion of gels in zones with high permeability as an oil displacement by decreasing the mobility ratio as well as reducing the viscous fingering simultaneously [1,26-27]. However, the application of this sort of conventional IPN hydrogel as a polymer solution is somewhat limited, because of the low thermal stability of IPN hydrogel that causes reduction of hydrogel viscosity and mechanical performance, especially in reservoirs with high temperatures [10,12,19]. Therefore, the mechanical strength, thermal stability, and rheological performance of conventional IPN hydrogel in harsh reservoir conditions can be remarkably improved by the incorporation of nanoparticles owing to their excellent properties, including mechanical strength, salt tolerance, thermal stability, and elasticity [4,10]. In addition, adding nanoparticles to fluids enhances the effectiveness of oil recovery processes by causing a decline in the interfacial tension and changing the rock wettability [28-29]. More recently, GO has gained attention in this regard and is used as a thermal, electrical, and stiffness reinforcement nanoparticle for hydrogel polymer in harsh conditions [30-31]. GO is produced by chemically modifying graphene using $KMnO_4$, $NaNO_3$, and H_2SO_4 [32]. It has a large surface area, and also contains abundant functional groups including epoxide, carboxyl, hydroxyl, and carbonyl [33-34]. Because of its hydrophilic nature and functional groups, it is dispersible in an aqueous environment and is also compatible with some hydrophilic polymers as a modifier [31,35-36]. Hence the major concern to obtain IPN nanocomposites hydrogels with desired viscosity, strength, and thermal stability performance in electrolyte media under harsh reservoir conditions is the uniform dispersion of GO [1, 36-37].

In this study, IPN nanocomposite hydrogel based on HPAM/HPG, produced by incorporating GO in presence of chromium triacetate as a cross-linker has been studied. To the best of our knowledge, there is no report of the effect of GO on semi-IPN nanocomposite structure based on HPAM/HPG hydrogel system to improve the rheological behavior, thermal stability, and long-term aging of IPN nanocomposites hydrogel for EOR applications. Thus, the purpose of this study is to investigate the influence of GO on the novel semi-IPN nanocomposite hydrogel, in terms of viscosity, flow activation energy, temperature, long-term aging, viscosity loss, and thermal stability. In addition, FTIR, morphology, and electrical characterization of nanocomposite hydrogels have been evaluated.

2. Experimental

2.1. Materials

HPAM, with 25 mol.% degree of hydrolysis, and 8×10^6 Dalton molecular weight was supplied from SNF Co. GO (research-grade, Few-Layer: 0.43 gr/cc, Purity:99%), was obtained from united nanotech innovation PVT Ltd, India. HPG with a molecular weight of 2×10^6 Dalton was obtained from Shandong Shengyou cementing engineering & technology Co., Ltd, China. Chromium triacetate was supplied from Carlo Erba, Italy. The total dissolved solids (TDS) of saline water is 7616 ppm.

2.2. Preparation of nanocomposite hydrogels

The IPN hydrogel and nanocomposite hydrogels were prepared and schematically shown in Figure 1. First, 0.35 wt.% of HPAM along with 0.35 wt.% of HPG powder were gradually added to the separate saline water and stirred regularly by a heater magnetic stirrer to obtain clear viscous solutions at room temperature and aged for 24 hrs. Then the various amounts of GO (0.05, 0.1, 0.3, and 0.5 wt.%) were dispersed in saline water for 1 hr by a magnetic stirrer to form a stable dispersion. Afterward, the prepared HPG and HPAM were charged in GO solution respectively, and stirring was continued for another 1 hr. using an overhead mixer (Heidolph RZR 2020). Then, 1.4 wt.% of the chromium triacetate as a crosslinker was prepared in water and added to the aqueous mixture while stirring gently. The reaction mixture was heated at 185°F (85°C) for approximately 2 hrs. to obtain a homogeneous solution. The final samples were dried in a vacuum oven for 24 hrs. at 158 °F (70 °C). The polymer concentration of all samples was 0.7 wt.%.

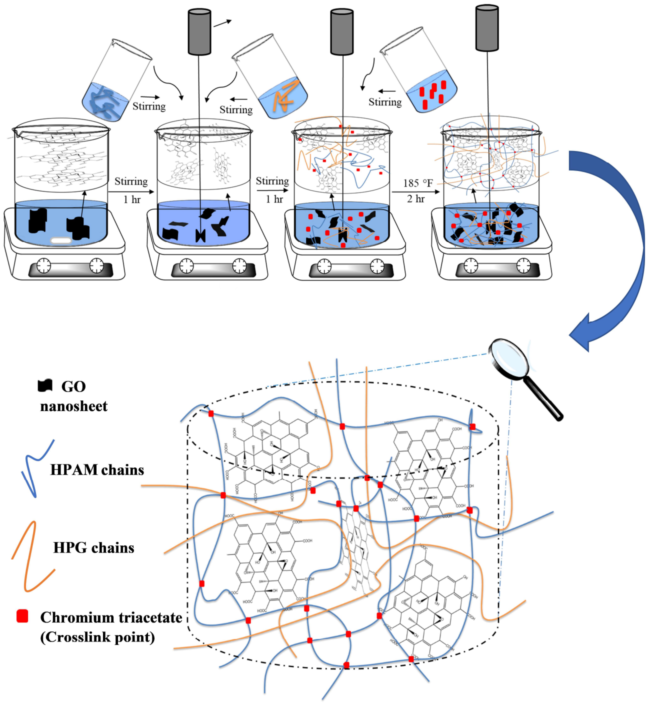

Figure 1. The schematic of the preparation procedure of HPAM/HPG/GO semi IPN nanocomposites hydrogel.

2.3. Characterization

2.3.1. FTIR characterization

Fourier transform infrared (FTIR) spectra were performed by PERKIN ELMER-65 spectrometer, using KBr pellets in the range of 4000-500 cm^{-1}.

2.3.2. Rheological characterization

Rheological characterizations of the nanocomposite hydrogels were performed by a rheometer (Paar-Physica, MCR 301) at temperatures of 200 and 240°F (93 and 115 °C), which was equipped with parallel plate geometry and also a Peltier device for control of temperature. To prevent the water loss, silicone oil was used at the outer surface. The strain amplitude was 1 % with the frequency in the range 0.01-100 rad/s.

The viscosity stability vs. time for the nanocomposite hydrogels was carried out using HT/HP **(**High temperature/High Pressure) fluid rheology tester (HT/HP Acid-resisting, GRACE M5600 Rheometer). The test of gellant samples was performed for 51 min under a pressure of 480 psi and at the shear rate of 100 1/s. The temperature of the samples was 200 °F and 240 °F.

2.3.3. Morphology characterization

Scanning electron microscopy (SEM) was accomplished by TESCAN Vega Model to study the morphology of HPAM/HPG/GO nanocomposite hydrogels. The fractured surface of samples was coated by sputtering the gold layer.

2.3.4. Electrical characterization

The electrical conductivity of IPN nanocomposite hydrogels was evaluated in conformity with ASTM D257 by Tara S cm^{-1} at 500 V by CEAST Co. The sheet samples (1mm thick) were prepared and coated with silver paint.

2.3.5. Aging effect

Long-term aging by viscosity monitoring was performed and the samples were held in an oven at 200 and 240 °F, for 7 days, separately. The effect of the loss viscosity of these samples on long-term thermal stability was studied.

3. Results and Discussion

3.1. FTIR characterization

FTIR was employed to evaluate the interaction between the IPN matrix and GO. As presented in Figure 2, the FTIR spectrum of GO displayed peaks at 3437,1720, 1623, 1396, 1224, and 1046 cm^{-1}, corresponding to the O-H hydroxyl group, C=O carbonyl stretching, C=C, O-H deformation vibration, C-OH, and C-O-C (epoxy) stretching respectively [38-39]. In the spectrum of IPN hydrogel, the peak at 3449 cm^{-1} is attributed to the overlap of the O-H bond of the hydroxyl group of HPG and the N-H band of the amide group of HPAM [21]. Besides, C-H stretching at 2825 cm^{-1} is observed. The peak near 1682 cm^{-1} is owing to the C=O stretching of the amide group of HPAM. CH_2 scissoring band appears at 1431 cm^{-1}. The peak at 1089 cm^{-1} is due to CH_2-O-CH_2 stretching vibrations. Meanwhile, the peak around 617 cm^{-1} is because of the N-H wagging vibration [21]. By comparing the FTIR spectrums of IPN hydrogel, with nanocomposite hydrogels at 0.1 and 0.5 wt.% of GO, it was observed that most of the characteristic peaks of IPN hydrogel shifted to a lower wavenumber for semi IPN nanocomposite hydrogels. The characteristic peak at 3449 cm^{-1} in HPAM/HPG hydrogel shifted to 3446 cm^{-1} and 3445 cm^{-1} in HPAM/HPG/GO for 0.1 and 0.5 wt.% of GO. It indicates that the interaction between GO and matrix occurs by the N-H bond of HPAM in the IPN hydrogel matrix and O-H deformation vibration of GO. The other peaks appear at 2823 and 2824 cm^{-1} for IPN nanocomposites at 0.1 and 0.5 wt.% of GO, indicating the stretching vibration of C-H. Moreover, the characteristic peak in IPN hydrogel moved from 1682 cm^{-1} to 1664 and 1662 cm^{-1} for IPN nanocomposites hydrogel at 0.1 and 0.5 wt.%

of GO which was related to C=O of the amide group. However, the peak at 1431 cm^{-1} in IPN hydrogel shifted to 1423 and 1422 cm^{-1} for IPN nanocomposite hydrogels at 0.1 and 0.5 wt.% of GO, due to C-H bending vibration. Also, there is the C-O-C stretching around 1085 cm^{-1} for IPN nanocomposites [12,40]. These results indicate the link between the HPAM/HPG chains and GO through hydrogen bonding [34-35,39].

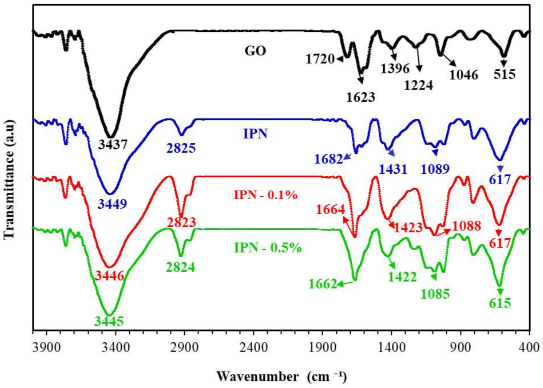

Figure 2. FTIR spectra of GO, IPN (0, 0.1 and 0.5) wt.% of GO.

3.2. Rheological behavior

Polymer flowability is a significant factor in EOR applications because high viscosity polymers solution cannot flow easily in the reservoir, while low viscosity polymers solution decreases polymer injection efficacy in the EOR [2]. To get an insight on this, the dependency of viscosity on the shear rate for IPN nanocomposite hydrogels at 200 and 240 ºF was evaluated. As shown in Figure 3, the viscosity was boosted by adding GO, which was remarkable at 0.1 wt.% of GO, at the low-shear rate, indicating the formation of physical interaction between GO and the matrix, which restrained the movement of polymer chains, resulting in a rapid rise in the viscosity [12,41]. In other words, a large surface area of GO nanosheets can act as a multifunctional cross-linker and interact with polymer chains of the matrix, along with the chromium triacetate which created further crosslinking in the polymer network. This leads to an enhancement in the strength of the network structure of nanocomposite hydrogels [35,42]. Moreover, nanoparticles tend to form agglomerates because of high interparticle interactions [10,38]. As a result, a slight raise of viscosity was also observed with increasing GO to 0.5 wt.%. According to figure 3, the viscosity of all samples diminished by a raise in the shear rate. However, the speed of this reduction is related to the GO contents. The nano samples with the addition of GO show better resistance to the increase of shear rate than neat IPN hydrogel, at both temperatures (200 and 240 °F). In fact, GO nanosheet gave greater strength to the IPNs, due to which, the network of IPN nano hydrogel could further withstand against stretch stress and deformation created by shearing fields [42].

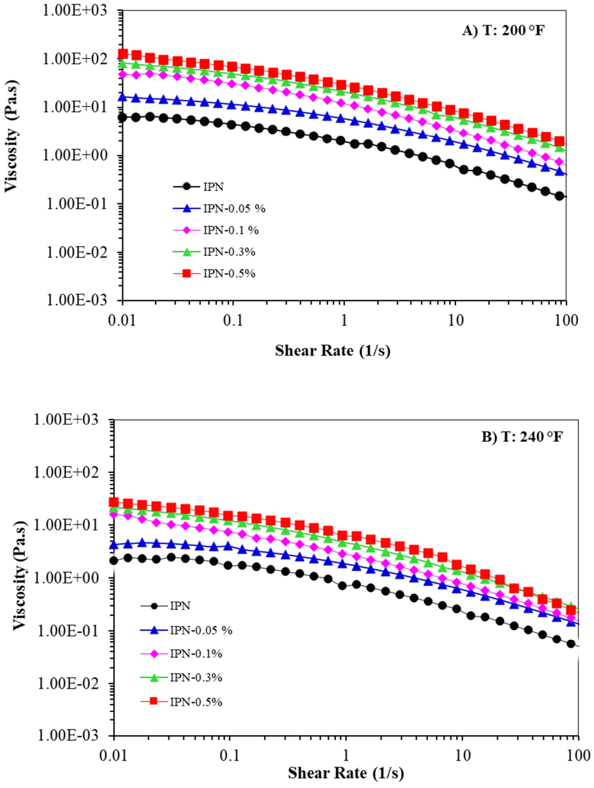

Figure 3. Viscosity vs. shear rate of IPN nanocomposite hydrogels at A) 200 and B) 240 ºF.

It was also found that all samples showed the non-Newtonian and shear thinning behavior, by soaring the shear rate, at both temperatures, which implied the dependency of the power-law to shear rate [11]. This was because of soaring the end-to-end distance as a consequence of unraveling the polymer chains, owing to shear fields. This causes a decrease in polymer viscosity, which implies the pseudoplastic fluid behavior [12]. The shear-thinning behavior displays the dependency of rheological properties on the viscoelastic characteristics of the polymer matrix [5].

Figure 4 depicts the influence of GO contents on the viscosity of semi IPN nanocomposite hydrogels for four different shear rates at 200 and 240 ºF. At low shear rates (0.1 and 1 1/s), the viscosity soared promptly by adding GO, which was noticeable at 0.1 wt.%, because of the good dispersion of GO into the polymer matrix to form the GO network structure. The viscosity continued to increase linearly with an increase in the GO to 0.5 wt.%. In contrast, at a high shear rate (100 1/s), viscosity was less sensitive to the augmentation of GO content. In other words, the reinforcement effect of GO nanosheet was more prevailing at a low shear rate compared to a high shear rate and also at both temperatures 200 and 240 ºF [43-44].

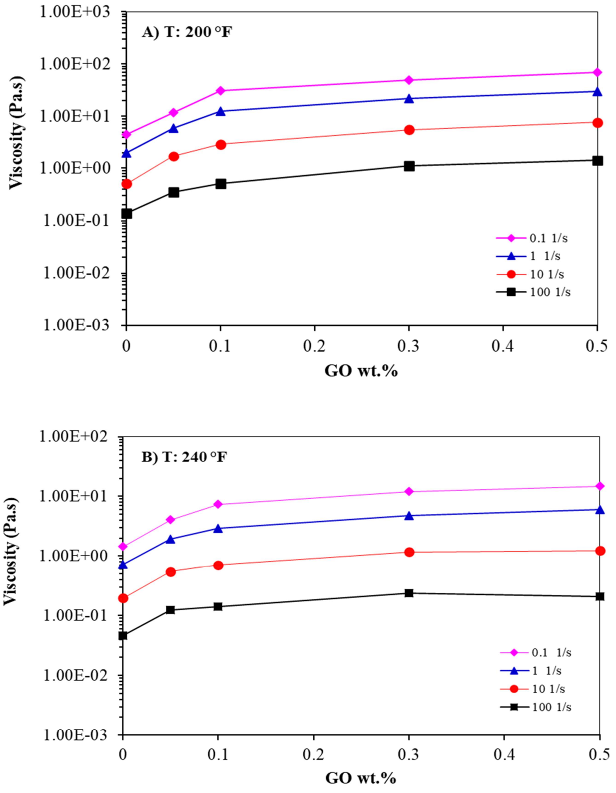

Figure 4. Viscosity versus GO contents at A) 200 and B) 240 °F.

For further understating the effect of GO on rheology behavior, the activation energy (*E*) was studied by the Arrhenius-Frenkel-Eyring equation to appraise the dependency of viscosity to temperature [45] and was computed by the equation (1) [46].

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{R}{E} \ln\left(\frac{\eta_1}{\eta_2}\right) \qquad (1)$$

Where η_1, η_2, T_1, T_2, and R were the viscosities, temperatures, and gas constant (8.315 J. gmol^{-1}. K^{-1}), respectively. As shown in Figure 5, the flow activation energy of the hydrogels was improved with the addition of 0.1 wt.% of GO. This was mainly attributed to cross-linking between GO as a bridge reinforcer with matrix, causing a resistance to the mobility of the polymer chains, and creating an energetic barrier for polymer chains [9,47]. In contrast, further increases in GO contents had no suitable effect on flow activation energy.

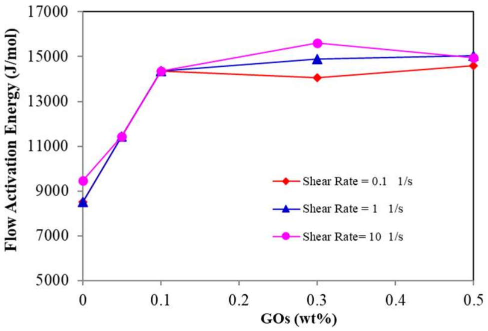

Figure 5. Flow activation energy versus GO contents.

The common types of polymer degradation are mechanical (shearing) and thermal degradation both of which affect the viscosity of the polymer. However, the effect of temperature is higher than the shear degradation [43]. Polymer solution will expose to diverse temperature gradients from the well surface to the reservoir. Because of this, the effect of temperature on the viscosity of semi IPN nanocomposite hydrogels was investigated. As illustrated in Figure 6, the viscosity diminished with an increase in the temperature from 200 to 240 °F, at all the shear rates. This behavior was due to an increase in chain mobility of polymers and the opening of entanglement of IPN hydrogel chains in the matrix. Moreover, the decrease in the number of cross-linking points into the IPN network at elevated temperatures, and, the undermined strength of the interaction between GO nanosheet and matrix, leads to slippage of polymer chains over GO sheet, causing a decline in the viscosity [5,10]. However, IPN nanocomposite hydrogel showed great strength, compared to a neat IPN hydrogel because of the GO effect. In other words, when the polymers and GO are dissolved in saline water, the GO as a strong thermal enhancer interacted with polymer chains of IPN hydrogel, to form a durable solution. In addition, functional groups in GO provide crosslinking strength in the hydrogel network. This reinforces the thermal stability of the hydrogel and also reduces the rapid network breakage of the hydrogel with increasing temperatures and shear rates [12,39]. Besides, the presence of chromium triacetate as a crosslinker can have a positive effect in improving the strength of the IPN network structure [1,27]. On the other hand, IPN hydrogel without the GO, despite the presence of a crosslinker, an increase in the temperature would weaken the polymer network, due to the poor strength of cross-linking points, compared to IPN nanocomposites. As a result, cross-linking between polymer chains debilitated, resulting in rapid breakage in its network structure, causing a decrease in the viscosity of the solution [40]. Therefore, GO nanosheets as strong thermal reinforcement can hinder the degradation process and defer the further thermal degradation of the polymer matrix by increasing temperature [31,36], which causes polymer solution to flow further in high permeability zones of a reservoir to ameliorate the oil recovery efficiency.

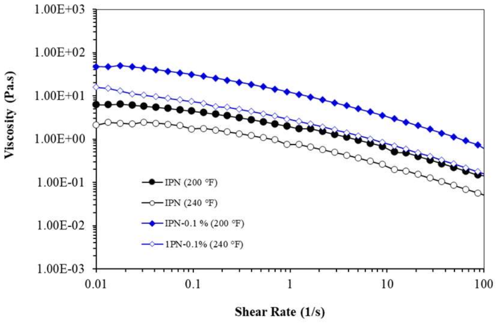

Figure 6. The dependency of the viscosity on the temperature of IPN nanocomposite hydrogels, at 200 and 240 ºF.

The viscosity stability of IPN nanocomposite hydrogels is another important rheological parameter in oil recovery and was determined at 200 and 240 °F, and at a constant shear rate of 100 1/s with the time, as shown in Figure 7 (a and b). Viscosity stability of IPN hydrogel and its nanocomposite hydrogels sharply decreased with time. The same effect was observed with an increase in temperatures until the arrival at the target temperature (200 and 240°F). After this, the viscosity remained constant and no significant decline of the viscosity was observed with time under constant shear rate. This viscosity stability was because of the creation of a strong network in the matrix at 0.1 wt.% of GO [48]. However, with a raise in the GO content to 0.5 wt.%, this effect was not significant.

It is also noteworthy from Figure 7(c) that, the decline in viscosity stability versus the time, at temperature 240 °F was greater than at temperature 200 °F. However, the viscosity stability of the cross-linked polymeric system containing HPAM and HPG hydrogel in presence of GO at 0.1 wt.% was higher than the HPAM/HPG hydrogel without GO. This behavior was due to the role of GO nanosheet as a reinforcing bridge, leading to an enhancement in the strength of the hydrogel [34,42]. As a result, the network structure of nanocomposite hydrogels displayed shear stability and also required more shear force and time to break its strength.

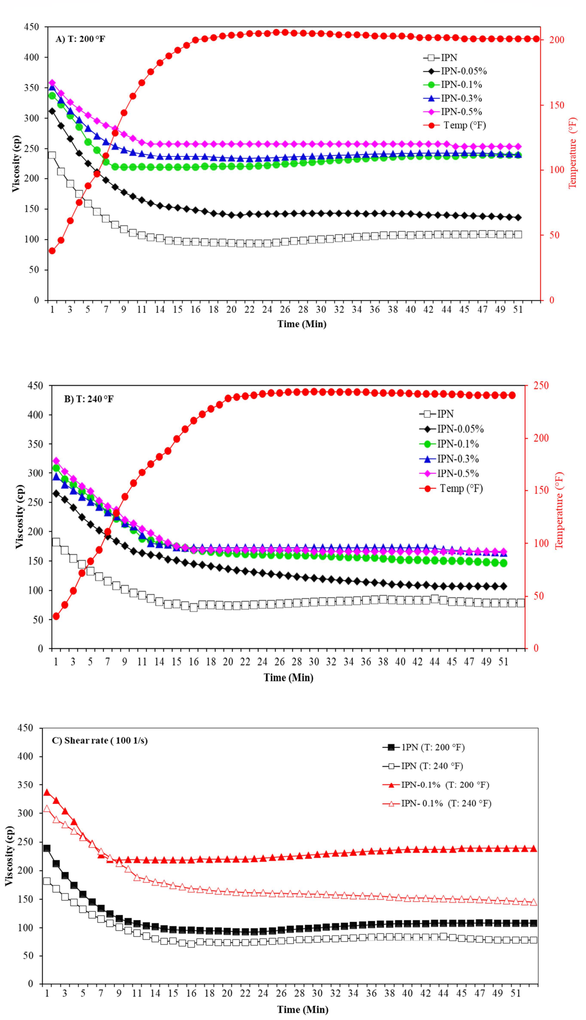

Figure 7. The influence of time on the viscosity stability of IPN nanocomposite hydrogels at A) 200 ºF, B) 240 ºF, and C) shear rate at 100 1/s.

3.3. Morphology characterization

To better understand the dispersion of GO for IPN hydrogels, the morphology of the nanocomposite hydrogels was evaluated by SEM. As observed in Figure 8 (a-c), GO is well dispersed in a mixture solution of HPAM and HPG and formed a uniform solution with the addition the 0.1 wt.% and somewhat uniform at 0.3 wt.% while some agglomerate of the GO particles was observed with the further increase in GO to 0.5 wt.%, as shown in Figure 8(d). This was due to the strong interparticle attraction of GO to form agglomerates in the matrix of IPN hydrogel [49-50]. In addition, GO particles trend the sedimentation in solution [18], which may cause plugging of the pores in the reservoir, due to nonuniformed dispersions and sedimentation of particles [51]. Therefore, the GO concentration is the key factor for the performance of the interpenetrated polymer network.

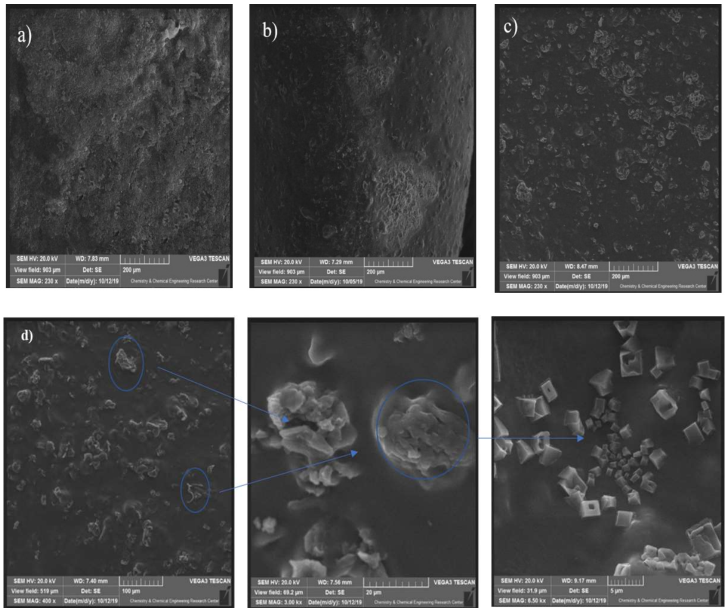

Figure 8. SEM images of IPN nanocomposites hydrogel; a) 0.1; b) 0.3; c) 0.5 wt.% of GO; and d) Agglomeration of GO particles at 0.5 wt.%.

3.4. Electrical characterization

For further evaluation of the dispersion of GO in the IPN hydrogel systems, the electrical conductivity of IPN nanocomposite hydrogels was also investigated. As can be observed in Figure 9, with the addition of GO up to 0.1 wt.%, the conductivity of nanocomposite increased, this change in electrical conductivity was due to the good dispersion of GO nanosheets within the IPN matrix, to form a strong network structure. As a result, a large number of the electrons are transported within the matrix, owing to the creation of the interconnecting conductive channels [31,50]. Moreover, this raise in electrical conductivity corresponded to the formation of stable conductivity paths [31]. However, electrical resistivity decreased when GO contents increased up to 0.5 wt.%. This may be due to poor GO dispersion and a decline in the distance between the GO sheets with increasing GO contents. This leads to a decrement in the passing of electrons through the matrix and hinders the formation of the electrical network, indicating an agglomerate of GO particles in the IPN matrix [52]. Therefore, the electrical conductivity of IPN nanocomposite hydrogels improved by reinforcing the effect of GO but up to 0.1 wt.% of GO. This behavior was also supported by morphology and rheological studies.

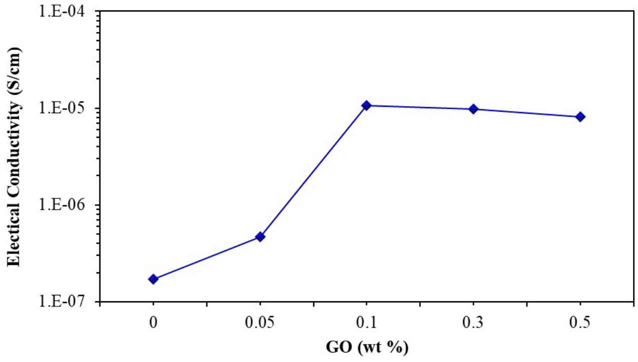

Figure 9. Electrical conductivity versus GO contents.

3.5. Aging effect

Viscosity loss of polymer solutions is a significant element in polymer injection, especially in long-term aging under harsh conditions of the reservoir in EOR applications. Because of this, the influence of thermal aging on the viscosity behavior of IPN nanocomposite hydrogels, at temperatures of 200 and 240 °F were investigated. As highlighted in Figure 10, the shear viscosity of all samples decreases remarkably by increasing shear rate and temperature. This reduction of viscosity was dependent on GO concentration. Indeed, the physical interaction between GO and matrix undermined significantly, resulting in a decrease in the strength of the IPNs network structure [11]. Interestingly, with the addition of GO to 0.1 wt.%, the sample displayed higher thermal stability than all samples. This behavior is because of the good dispersion of GO in the IPN hydrogel matrix and makes a potent physical interaction with HPAM and HPG chains [10,18]. Besides, the presence of chromium triacetate and HPG in the matrix further strengthens the IPN network and improves the shear stability [1,21-22]. In addition, the cross-linked network of polymer solutions caused decreasing accessibility of divalent cations such as Ca^{2+} and Mg^{2+} to the HPAM chains [2], and the polymer solution presented greater thermal stability. According to this result, the GO nanosheet as a reinforcing bridge enhanced the strength of the IPN network and boosted the thermal stability and viscosity stability of the polymer solution at high temperatures for the long term. In contrast, with an increase in the GO contents up to 0.5 wt.%, viscosity decreased. This effect could be due to the formation of the agglomerate of GO, which notably reduced the interaction between GO and matrix, because of a decline in the cross-linking in the network. This behavior was supported by morphology studies. Therefore, based on these results, IPN nanocomposite hydrogel by adding 0.1 wt.% of GO, showed less viscosity loss than the other samples at both temperatures, for long-term aging.

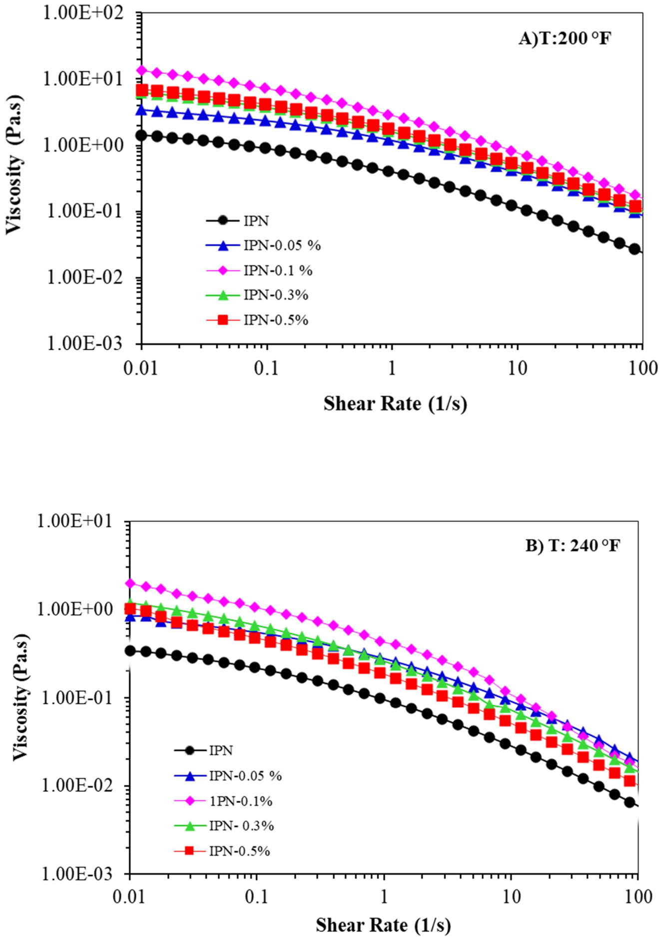

Figure 10. Viscosity vs shear rate of IPN nanocomposite hydrogels after aging at A) 200ºF and B) 240ºF.

4. Conclusion

Rheological and thermal aging of interpenetrating polymer networks based on partially hydrolyzed polyacrylamide (HPAM)/hydroxypropyl guar (HPG) reinforced by GO was investigated at various temperatures. The dependency of GO on improving the thermal and viscosity stability was relevant to the good dispersion of GO and its interaction with polymer chains. The interaction of GO with HPAM/HPG chains of IPN hydrogel was observed by FTIR spectra. The rheological studies demonstrated that the viscosity increased by increasing

GO contents, while it diminished with the rise in the shear rate, indicating the shear thinning behavior. GO enhanced viscosity stability of nano samples with an increase in temperature from 200 to 240°F, and improved the nanocomposite hydrogel effects, compared to the IPN hydrogel without GO. Flow activation energy elevated by adding 0.1 wt.% of GO. Rheological and morphology results were sensitive to the physical interaction between GO and matrix. SEM study showed the enhancement of the dispersion of GO in the matrix of the polymer (HPAM/HPG) at 0.1 wt.%. This effect is followed by electrical conductivity that improved at 0.1 wt.%. Nano samples exhibited viscosity stability behavior and mechanical strength, at both temperatures 200 and 240 °F, under constant shear rate. GO enhanced the thermal stability of HPAM/HPG/GO hydrogel in long-term thermal aging, compared to IPN hydrogel. Therefore, it can be concluded from these results that the PHPA/HPG/GO nanocomposite hydrogel presents suitable thermal and viscosity stability which may be beneficial for use in a high-temperature reservoir.

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Conflict of Interest- The authors have no conflict of interest to declare.

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3.5. Conclusion

The thermal stability and rheological properties have played a key role in the performance of hydrogel which was well established mostly in EOR applications. Understanding the effect of GO dispersion as a thermal reinforcer has led us to determine the properties and activities of the new hydrogel produced by the interpenetrating polymer network technique. This chapter focused on developing novel hydrogel nanocomposite based on partially hydrolyzed polyacrylamide/hydroxypropyl guar (HPAM/HPG) nanocomposite reinforced with graphene oxide (GO), at temperatures (200 and 240 °F) in presence of the chromium triacetate as crosslinker. The interactions of GO with HPAM/HPG chains of IPN nanocomposite hydrogels were investigated in this work. This work can motivate the researchers in developing a new class of hydrogel systems that can well serve as promising candidates for EOR applications. GO improved viscosity stability of nano samples by increasing in temperature from 200 to 240°F, and improved the nanocomposite hydrogel effects, compared to the IPN hydrogel without GO. In addition, the IPN nanocomposite hydrogels displayed great viscosity stability, and thermal stability as compared to IPN hydrogel without GO. The mechanical strength and rheology properties of cross-linked hydrogel structure were improved by GO which may be beneficial for use in oil recovery applications

Chapter 4

Synthesis and preparation of poly (AM-co-AMPS)/GO nanocomposites hydrogel as a rheology modifier and fluid loss controller for use in oil well cementing

4.1. Introduction

Hydrogels are a sort of hydrophilic polymers with a network structure, which can be constituted by physical and chemical crosslinking with water-soluble monomers, and they can absorb and hold a large volume of water or other aqueous fluids for several hours while being under pressure. It can be applied as a suitable fluid loss controller along with a rheology modifier in oil well cementing, and also as a polymer solution to enhance oil recovery in water or brine solution. The interesting prospects of the previous chapter inspired us to incorporate the synthesized GO for developing the acrylamide base copolymer hydrogel system. In this chapter, we have synthesized the copolymer nanocomposites hydrogel based on acrylamide (AM) and 2-acryloamido-2-methylpropane sulfonic acid (AMPS) in the presence of the N, N-methylene-bis-acryl-amide (NMBA) as a crosslinker by the free radical copolymerization technique as a rheology modifier along with fluid loss controller. The influence of GO on the strength and structure of the copolymer hydrogel system was investigated. Characterization of the synthesized poly (AM-co-AMPS)/GO was conducted using various methods. In addition, its effect on the improvement of the rheological properties, the fluid lost, free water, and compressive strength of cement slurry as a viscosity modifier and fluid loss controller was studied for use in oil well cementing.

4.2. Article 2

Synthesis and preparation of poly (AM-co-AMPS)/GO nanocomposites hydrogel as a rheology modifier and fluid loss controller for use in oil well cementing

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4.3. Author’s contribution

Amir Narimani: Conceptualization of the project, visualization, and investigation of experiments, all synthesis of monomer and experiments conducted, validation of methodology and curation of data, drafting the original manuscript.

Farid Kordnejad: Investigation in rheology study.

Dr. Prabhjyot Kaur: Writing- review, and editing.

Ferhi Najmeddine: Assistance in preparation of graphene oxide

Prof. Mahmood Hemmati: Investigation in compressive strength study.

Prof. Japan Trivedi: Investigation in fluid loss and rheology study

Prof. Adam Duong: Project administration, supervision, funding acquisition,writing- review, and editing.

Synthesis and preparation of poly (AM-co-AMPS)/GO nanocomposites hydrogel as a rheology modifier and fluid loss controller for use in oil well cementing

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Abstract

The aim of the present work is to evaluate the influence of graphene oxide (GO) on copolymer nanocomposites hydrogel structure based on acrylamide (AM) and 2-acryloamido-2-methylpropane sulfonic acid (AMPS) in the presence of the N, N-methylene-bis-acryl-amide (NMBA) by the free radical copolymerization technique. The influence of poly (AM-co-AMPS)/GO as a rheology modifier along with fluid loss controller on the rheological and mechanical properties of brine cement slurry was also investigated. The characterization results confirmed the synthesis of AM monomer and AMPS and showed their grafting with GO surface. The poly (AM-co-AMPS)/GO hydrogel improved the rheological properties of the cement slurry as compared to conventional cement slurry. Furthermore, free water and fluid loss of cement slurry declined by adding the copolymer nanocomposites hydrogel at elevated temperatures. Moreover, not only the thickening time of cement slurry dropped but also, the compressive strength increased with a rise of nanocomposites hydrogel concentrations. However, the nanocomposite hydrogels showed a great effect on early compressive strength than the final compressive strength. The results of this investigation revealed the excellent performance of crosslinked structure of copolymer nanocomposites hydrogel due to the linking of sulfonated AMPS and AM on the surface of GO nanosheet in the attendance of NMBA. This renders greater stability to the cement slurry against salinity and temperature changing of well formations during cementing operation. Thus, poly (AM-co-AMPS)/GO as a suitable rheology modifier and property enhancer can be applied in oil well cementing.

Keywords: Oil well cementing, copolymer nanocomposites hydrogel, graphene oxide, rheological property, compressive strength

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1.Introduction

The cementing of oil and gas well is a significant operation to create a suitable barrier between the formations and the well casing by making a good cement bonding between formation and casing [1-2]. In the cementing operation, the cement slurry is pumped into the wellbore through the casing to start filling the annular space between the formations and the well casing and return it to the surface [3-4]. The main goals of well cementing are the protection of the casing, the formation zonal isolation, well integrity, no fluid leakage, and endurance against the formation stress, not only throughout drilling operations but also during the lifetime of production of the well [2,5]. The cement slurry must retain its properties during cement operation [4]. Therefore, the performance of production wells greatly appertains to the quality of the cement job and the design of cement slurry in each hole section of the well [3,6-7]. The excessive fluid loss along with the low viscosity of cement slurry can jeopardize cementing operation [8] and cause weaker cement bonding between the formation and casing creating pathways or channels. As a result, the parts of the formation layers remain as a permeable zone, leading to the migration of underground fluids and/or gas to the surface through these pathways or zones [1,9]. Hence, the fluid loss control (FLC) and rheology modifier additives based on the water-soluble polymers are widely used to decline the fluid loss and enhance the rheology properties of cement slurry. These polymers have functional groups in their structures, that can readily adsorb water of slurry [10]. FLC can control water loss and also hinder premature dehydrating of cement slurry [11]. The performance of these fluid loss and rheology modifier additives also depends on the downhole conditions of the well [8]. In fact, as the well depth increases, thermal resistance becomes a feature that must be considered at elevated temperatures and pressures. Moreover, the well lithology and complexity of underground layers must also be investigated. Besides the existence of poor strength layers of formation along with the presence of salt environment affects the viscosity, stability, and performance of water-soluble polymer as a modifier and fluid loss controller in the cement slurry [9,12-13]. Thus, it is important to select the appropriate polymer as a rheology modifier and a control agent that can control the fluid loss and create sufficient viscosity, gel strength, and salt tolerance while retaining the thermal stability for cement slurry during pumping operations [8,14]. As a consequence, numerous studies have been done to develop polymer materials as a modifier with suitable performance in oil well cementing according to the well conditions [7,10-12,15-17]. For example, Guo et al. [7] synthesized new quaternary polymer AMPS/AM/NDMA/MA that demonstrated good dispersing power, fluid loss control ability, thermal resistance, and salt tolerance ability. Xin et al. [8] reported that a synthetic polymer based on AMPS/AM/AA exhibited great FLC performance. Liu et al. [11] described three types of copolymers, by free-radical copolymerization: AMPS with AM, DMAM, and DEAM. AMPS/DMAM showed suitable water-retaining capacity at a high temperature. Zhu et al. [17] synthesized a superabsorbent composite, poly (AMPS-co-AM)/kaolin, by using a method of radical polymerization. This hydrogel showed good water and salt solution absorbency at a high temperature. In general, hydrogel polymers containing specific functional groups have been readily adsorbed on cement particles. Hydrogels are a sort of hydrophilic polymers with a network structure, which can be constituted by physical and chemical crosslinking with water-soluble monomers, and they can absorb and keep a large volume of water or other aqueous fluids for several hours while being under pressure [17-19]. Amongst the water-soluble polymers, acrylamide-based homopolymer or copolymer, as a rheology modifier or thickener is used in the oil well cementing, drilling fluid, and enhanced oil recovery [11,20]. However, acrylamide (AM) based polymer has poor shear and salt resistance and low thermal stability [21-22]. It is also not stable against elevated temperatures, due to hydrolyzation of the functional NH_2 group [23]. To overcome these drawbacks, the acrylamide-based polymer gel is usually copolymerized with at least one comonomer as a modifier [24]. AMPS as an ionic comonomer has been observed to ameliorate the rheological, and mechanical properties of AM monomers. AMPS is a type of sulfonated monomer with suitable shear resistance, stability, strong absorbing units, high salt tolerance, and good thermal stability [10,15-16]. This property can be attributed to its highly ionized sulfate groups [25]. AM copolymer with a monomer containing the sulfonate groups can provide high solution stability and salt tolerance, which can be used as a suitable FLC along with rheology modifier in fluid drilling and oil well cementing in water or brine solution [7,10,26-27]. However, current conventional copolymer gel has somehow been limited in oil well-cementing application because of the low gel strength, particularly in the swollen state, and poor ability to withstand layer formation pressure, especially at high well temperatures. Cement slurry is exposed to different temperature gradients and pressures starting from the well surface to the downhole of the well, therefore, the newly developed hydrogel copolymer gel is required to achieve the desired properties of FLC along with being a rheology modifier while sustaining against the downhole conditions [17-18, 28-30].

To ameliorate the strength and thermal stability of conventional copolymer hydrogel structure, nanoparticles like graphene oxide (GO) can be incorporated, because of their outstanding mechanical, thermal, and unique strengthening enhancer properties [18,30-31]. Interestingly, GO shows a positive effect on the mechanical properties of cementitious materials [32]. It is produced by the chemical modification of graphite [33-34]. GO has a great surface area, with plenty of oxygen functional groups such as epoxide, hydroxyl, on its surface, and carboxyl, carbonyl on its edges [33,35] These provide a wide range of active sites on the surface, causing a better crosslinking with the polymer chains and cement particles [36-37]. Furthermore, the hydrophilic groups of GO result in better dispersity in an aqueous solution [35,38] that can help in improving the mechanical strength of polymer hydrogels and cement composites [36]. Although the addition of GO, increases the cost of materials a little bit but all the advantages associated with GO, make it worth it. GO nanosheets, tend to form agglomerates with increasing concentration which reduces their reinforcing effect [38]. Therefore, the most important challenge is to achieve the uniform dispersion of GO in the copolymer matrix and to study its effect on the network structure of hydrogel and cement-based materials [30,32]. According to the best of our knowledge, there is no report so far on the use of poly (AM-co-AMPS)/GO nanocomposite hydrogel as a rheology modifier along with fluid loss controller for use in oil well cementing and electrolyte media. The aim of this research work is to investigate the influence of GO on the strength and structure of copolymer hydrogel system based on acrylamide and 2-acryloamido-2-methyl propane sulfonic acid in the presence of the N, N-methylene-bis-acryl-amide as a crosslinker. The characterization of this copolymer nanocomposites hydrogel was performed. In addition, its effect on the improvement of the rheological properties, the fluid lost, free water, and compressive strength of cement slurry as a viscosity modifier and fluid loss controller was studied for use in oil well cementing in electrolyte media.

2.Materials and Methods

2.1. Materials

Acrylamide (AM), N, N-methylene-bis-acryl-amide (NMBA), graphite powder, ammonium persulfate (APS), and hydrochloric acid (HCl, 37%) were provided from Sigma-Aldrich. 2-acryloamido-2-methyl propane sulfonic acid (AMPS, 98%) was obtained from Alfa Aesar, Canada. Sulfuric acid (H_2SO_4, 95%), potassium permanganate ($KMnO_4$), phosphoric acid (H_3PO_4), hydrogen peroxide (H_2O_2), diethyl ether, and acetone were supplied by Fisher Scientific, Canada. Sodium hydroxide (NaOH, pellet model) was purchased from Anachemia, Canada. Well cement class "G" was provided from Cement Kerman Co. The retarder, micro block, dispersant, antifoam was provided from Shandong cementing engineering Co., China.

2.2. GO preparation

GO was prepared by a modified Hummers' method according to the following procedure, 0.5 g of the graphite was mixed in 60 ml of H_2SO_4, and 6.6 ml of H_3PO_4 followed by stirring for 10 min. 1.5 g $KMnO_4$ was then gradually added to the solution and the reaction was heated and stirred at 80°C for another 24 hr. Finally, 90 ml deionized water was added followed by 1 ml H_2O_2 into the solution which was then stirred for over 30 min. The final product was a bright yellow solution which was purified by centrifugation for around 60 min at 2500 rpm and washed several times with water to adjust pH to 7-8. The solution was centrifugated for an additional 60 min. The same step was repeated by changing water with ethanol. Finally, ethanol was removed by adding diethyl ether and the solution was poured onto a glass tray and the solvent was allowed to evaporate at room temperature. The sample was then dried in an oven at 80 °C for 24 hr and was milled with mortar.

2.3. Synthesis of copolymer nanocomposites hydrogel

The copolymer nanocomposites hydrogel (AM-co-AMPS)/GO were formed by free-radical crosslinking copolymerization. At first, various amounts of GO (0, 0.05, 0.1, and 0.3 wt.%) were dispersed in 20 ml deionized water by ultrasonic water bath (Branson Co., 60 Hz, 80 W) for 30 min to obtain homogenous dispersions which were then transferred to a 250 ml three-necked flask. Then 8 g of AM, 2 g of AMPS, and 0.008 mol/L of NMBA respectively were added into the three-necked flask, (the ratio of AM/AMPS was constant, 80%: 20%).[26] After 10 min, 0.011 mol/L of APS as initiator was dissolved in 5 ml of water and added to the mixture solution. The pH of the reaction was regulated to 7-8 by the addition of HCl and NaOH. The reaction was stirred for another 3 hr by increasing the temperature to 80°C, under inert nitrogen gas and stirring until the viscous solution was produced. This was followed by cooling the reaction mixture to room temperature and precipitating the product by acetone. After that, it was dried in a vacuum oven for 6 h, until it arrived at a constant weight. Finally, it was powdered by a mortar and pestle. The poly (AM-co-AMPS) copolymer hydrogel and poly (AM-co-AMPS)/GO copolymer nanocomposites hydrogel have been named as CPH and CPNHG, respectively in this study. The schematic of the copolymer nanocomposite hydrogel structure shows in Figure1.

2.4. Cement slurry preparation

The cement slurry design with an addition of various concentrations of copolymer nanocomposite hydrogel (CPNHG) with GO at 0.1 wt.% is listed in Table 1. Cement slurry was prepared by a blender (The Model 20 Constant Speed Blender, 1 Liter). At first, the different amounts of CPNHG in 50 ml saline water were stirred by a magnetic stirrer and kept for 24 hr. Then CPNHG solution was fed into a blender containing saline water and stirred for 2 min at a low speed (4000 rpm). Subsequently, micro block, dispersant, retarder, and antifoam were charged into the mixer.

The mixture was then stirred for 1 min. The cement powder was added gradually to the mixture slurry, and it was mixed for another 2 min at 12000 rpm. The neat cement (CMT) and CMT/CPNHG slurries were measured according to API RP 10B standard. The saline water was considered with total dissolved solids (TDS) of 7616 mg/L.

2.5. Characterization of copolymer nanocomposite hydrogel

2.5.1. Fourier transform infrared *(*FTIR) characterization

FTIR spectra of dried samples were accomplished by Thermo is10 spectrometer, in the range of 4000-650 cm^{-1}. The resolution and the scanning number were 4 cm^{-1} and 16, respectively.

2.5.2. X-ray diffraction (XRD) characterization

Wide-angle XRD analysis of dried samples was carried out at room temperature using a Rigaku diffractometer with Cu-Kα radiation (λ = 1.5418 Å) in the range 2θ=5-70.

2.5.3. Thermogravimetric analysis (TGA)

TGA was examined using Perkin Elmer, STA 6000. The dried samples were scanned from 30 °C to 500 °C at 10°C/min.

2.5.4. Morphology characterization

Scanning electron microscopy (SEM) was carried out by HITACHI, SUI 510 which was equipped with energy dispersive X-ray (EDX) by software X-MAX (Oxford instruments, 20 mm^2) for elemental analysis. The dried samples were coated by sputtering the thin layer of gold for good conductivity.

2.6. The cement slurry systems

2.6.1. Slurry density determination

Slurry density was determined by a 4-scale metal mud balance, OFITE company. The density measurement range is 49 - 172 lbs/ft^3.

2.6.2. Rheological measurements

Rheological properties of cement slurry (yield point (YP), plastic viscosity (PV), and the gel strength) were evaluated by viscometer "OFITE MODEL 900" OFITE company, through the measurement of the reading value at a shear rate of 300 and 100 rpm. The cement slurry was preheated for 20 min by an atmospheric consistometer at 196°F before adding the viscometer cup. Viscometer reading values as shear stress (lb/100 ft^2) were also measured at shear rates of 300, 200, 100, 6, and 3 rpm. At the end of the test, the sedimentation of slurry particles in the bottom of the rheology cup was evaluated.

$$PV = (\theta_{300} - \theta_{100}) \times 1.5$$

$$YP = \theta_{300} - PV$$

2.6.3. Free water and stability measurements

Cement slurry was preheated for 20 min in an atmospheric consistometer (model 1200, chandler engineering company) at 196 ^{0}F. Preheated cement slurry was poured into a 250 (cc) graduated cylinder and was allowed to rest at ambient temperature in static conditions. Accumulated free water on top of the cylinder and particles sedimentation of cement slurry were monitored and recorded for 2 hr.

2.6.4. Fluid loss (FL) measurements

The fluid loss test was performed by filter press model 171-01-C, OFITE company. Cement slurry was preheated for 20 min in an atmospheric consistometer (model 1200, chandler engineering company) at 196 ^{o}F. Then, the preheated slurry was added to the filter press, to consider to "blowout" before 30 min under a pressure of 1200 psi and at 196 ^{o}F. FL is calculated by the following equation.

$$FL= 2\ V_t \sqrt{}\ 30/t$$

V_t is the volume of water at the time blow (millimeters), t is the time (minutes).

2.6.5. Thickening time test

Slurry thickening behavior was performed using Model 7322 HPHT consistometers chandler engineering Co at temperature 196 ^{o}F and bottom hole pressure of 5946 psi. The thickening time at 30 Bc (Bearden units of consistency) is considered as the time at which the cement slurry is in an unpumpable state and a thickening time of 70 Bc indicates that the cement slurry cannot be pumped anymore. Hence, 70 Bc is considered as the appropriate thickening time.

2.6.6. Compressive strength

There are two methods for the evaluation of cement compressive strength. The first method is known as the crushing method and the second method is by using the ultrasonic cement analyzer measurement (UCA). Cement strength by crushing is performed at atmospheric pressure for 24 hr at temperature 196 °F, by using water bath model WB1130C-1, Thermo Scientific company. The cube samples were crushed and measured by a hydraulic press model 3853, Carver company. For each sample, an average of 3 cubic specimens was made for compressive strength measurements. UCA was performed by the model 4265, chandler engineering company, to determine the strength of a cement sample at 196 ^{0}F and 3000 psi pressure conditions for 24 hr.

3. Results and Discussion

3.1. The characterization of synthesized copolymer nanocomposites hydrogel

Fourier transform infrared (FTIR) analysis of AM, AMPS, GO, CPH, and CPNHG was done to evaluate the interaction between copolymer chains with GO and was shown in Figures 2 and S1. As shown in Figure 2a, the FTIR spectra of AM show peaks at 3337 and 3163 cm^{-1} which are due to the stretching vibration of N–H. In addition, the peaks at 2812, 1663, 1610, 1424, and 1135 cm^{-1} correspond to CH_2, the stretching vibration of C=O, C=C, C-N, and bending and stretching of C–N in AM, respectively [39]. As shown in Figure 2b, AMPS spectra show the peaks at 2986, 1667, 1612, 1372, 1232, and 941 cm^{-1} which are related to the C-H vibration, C=O, C=C stretching vibration, bending vibration of C-N, stretching of C-N, and S-O stretching [14,39-40]. In Figure 2c, FTIR spectra of CPH displays peaks at 3339 and 3193 cm^{-1} which are ascribed to the stretching vibrations of N-H and O-H. In addition, absorption peaks at 2933 cm^{-1} owing to the C-H stretching are also observed. It also shows a strong peak at 1649 cm^{-1} indicating the stretching vibrations of the C=O and a weak peak at 1451 cm^{-1} due to the vibration bond of C=O. The bending vibration of C-N of AMPS emerges at 1321 cm^{-1}, and the peak at 1039 cm^{-1} is owing to the symmetric S=O stretching of the sulfonate group [11,17,26-27]. This result shows that AM and AMPS are successfully synthesized, and a copolymer has been formed [17].

As highlighted in Figure S1a, in the GO spectra, peak around 3406 cm^{-1} is assigned to the hydrogen-bonded hydroxyl group (O-H). The peak at 2954 cm^{-1} is related to the C-H stretching while the peak at 1646 cm^{-1} is due to C=C [37]. Whereas the peak that emerged at 1422 cm^{-1} is associated to the functional group of the O-H. Moreover, the two peaks at 1287 and 1021 cm^{-1} are associated to C-OH bonds and C-O-C stretching respectively [18,37]. As compared to the copolymer hydrogel spectrum with its nanocomposite, as shown in Figure S1(b-e), all the characteristic peaks of CPNHG appeared at lower wavenumber with increasing GO concentrations. However, increasing the GO to 0.3 wt.% has no significant effect on the FTIR spectra of poly (AM-co-AMPS)/GO hydrogel. It is clear from Figure S1d, the absorption peaks at 3336 and 3190 cm^{-1} are related to the stretching vibrations of amide groups. The peak at 2930 cm^{-1} is due to the C-H vibration, while the one at 1647 cm^{-1} corresponds to bonding between the stretching vibrations of carbonyl groups and amide N-H and C=C of GO. Additionally, peaks at 1450 and 1320 cm^{-1} are attributed to the bending vibrations of CH_2 and CH respectively. Another peak at 1039 cm^{-1} corresponds to the stretching vibrations of S=O [30,37]. Hence, it can be concluded that the linking occurs between AM and AMPS and with the surface of GO, through hydrogen bonding to form cross-linked network structure hydrogel [19,28,37,41].

XRD was carried out to evaluate the dispersion of GO in copolymer nanocomposite. Figure 3(a-b) shows the XRD spectra of AM, AMPS, GO, CPH, and CPNHG. As presented in Figure 3 (a), the XRD spectrum of AM, AMPS revealed that the characteristic peak was located at $2\theta=18$-20^{o} and in the range of 15-30^{o} respectively. As can also be observed from Figure 3(a and b), CPH depicted a diffraction peak in the range $2\theta=18$-$20°$ and 20-30^{o}. Moreover, it can be also seen in Figure 3(b), the XRD spectrum of prepared GO displayed that the main characteristic peak at $2\theta=10.25^{o}$ and d-spacing was calculated to be 8.61 A^{o} which indicated the attendance of hydrophilic oxygen-containing functional groups on the sheet of GO [35,37]. However, after intercalation of the GO with poly (AM-co-AMPS), the XRD spectrum revealed that the intensity of characteristic peaks decreased sharply in comparison to GO, which indicates the uniform dispersion of the GO nanosheet in the copolymer matrix [37,41]. Furthermore, the broad peaks for copolymer hydrogel nanocomposites, in the range of 2θ=15-20°, and 20-25° were observed, which correspond to the amorphous nature of AM and AMPS in copolymer hydrogel structure [19,37]. According to these results, GO acts as a crosslinking point and is dispersed uniformly in the copolymer matrix chains, thus assisting in improving the strength and structure of nanocomposites hydrogel.

One of the main challenges regarding the copolymer hydrogel feature is its thermal stability. Hence, the thermal stability of copolymer hydrogel and its nanocomposites hydrogel with different GO concentrations were studied and are presented in Figure S2. As depicted in this figure, thermograms of CPNHG at 0.05, 0.1, and 0.3 wt.% of GO are similar to those of the samples without GO. In the first stage of thermal decomposition, dissociation occurs in the temperature range of 100°C, owing to interlayer water loss in the sample. In the second stage, the weight loss at around 100°C-250°C is related to the dissociation of the low molecular weight copolymer chains, and the functionalities of GO, thus causing a slight decline in the strength of the network structure. The presence of GO along with AMPS resulted in preventing the fast hydrolysis of the amide group in the copolymer network as compared to the sample without GO [42]. The third degradation stage at around 250°C-350°C is owing to the elimination of amide and sulfonic acid groups of copolymers in addition to the functional groups on the GO, which further results in the weakening of the network structure of copolymers hydrogel [26]. The last decomposition that occurs at a temperature above 350 °C is owing to the degradation of the copolymer backbone chains, and decomposition of the GO structure, resulting in complete degradation of the network structure [37,39]. In addition, it was also found from this figure that the weight loss percentage of the copolymer nanocomposite hydrogel was much lower than the copolymer hydrogel without GO. This is likely to be due to the role of the thermal effect of GO in the copolymer hydrogel structure, which has a strong interaction with AM and AMPS chains of the copolymer matrix [30]. When the amount of the GO further increased to 0.3 wt.%, there isn't any noticeable change in the thermal stability. This is because an increase in GO results in its agglomeration in the matrix of the copolymer and hence weakens the physical interaction of GO with the polymer chains, leading to a weak hydrogel network structure [19]. Therefore, it can be concluded that the GO acts as a multifunctional crosslinker and thermal enhancer when grafted with the AM and AMPS copolymer chains. Besides, the presence of the NMBA improves further the crosslinking density in copolymer network hydrogel and thus improves the strength and thermal stability of the nanocomposite.

The morphology of the GO and copolymer nanocomposites hydrogel with various percentages of GO to better understand the dispersion effect of GO in poly (AM-co-AMPS)/GO was investigated by SEM, as presented in Figures 6 and 7. As observed in figure 4a, GO showed the wrinkled and flake-like sheets. Figure 4b shows the energy X-ray spectroscopy (EDX) pattern indicating the presence of C, O, and S, all of which are the major elements for GO [2,19,35,37]. As depicted in Figure 5, the surface of poly (AM-co-AMPS) hydrogel was in the form of discontinuous sheets, which may be related to the structure of the porous network [17]. In contrast, with an addition of the of GO to 0.1 wt.%, CPNHG showed a compact and dense surface with less wrinkles and folding regions which indicates the homogeneous dispersion of GO sheets in the polymer matrix. With an increasing concentration of GO to 0.3 wt.%, the surface morphology of the nanocomposite hydrogel was rougher and denser with high folding regions, indicating a weak surface interaction between GO and copolymer network, which might be due to the poor dispersion of GO in the copolymer network matrix [19,32]. This behavior is supported by the XRD and TGA results. Furthermore, because of the large surface area of GO, particles of GO tend to stack upon each other resulting in aggregation in the matrix with increasing GO concentration as shown in Figure S3 [28,30,36]. To further describe CPH and CPNHG at 0.1 wt.%. of GO, EDX analysis is shown in Figure S4. It can be seen that C, O, Na, and S elements were dispersed in both copolymer and its nanocomposites hydrogel [37], along with the presence of N in nanocomposites hydrogel. However, the carbon atom concentration in poly (AM-co-AMPS)/GO was higher than in the sample without GO. According to this result, it can be concluded that the GO, AM, and AMPS copolymer chains interacted by hydrogen bonds. Moreover, it highlights the fact that GO is well dispersed in the polymer matrix up to 0.1 wt.% and can be considered as a crosslinker agent.

Therefore, according to the above results, GO acting as a crosslinker agent can improve the strength and thermal stability of the copolymer hydrogel based on poly (AM-co-AMPS). Furthermore, CPNHG with optimum GO concentration at 0.1 wt.%, has been chosen as a rheology modifier and fluid loss controller in cement slurry in this research.

3.2. The influence of synthesized copolymer nanocomposites hydrogel on cement slurry systems

The rheology of cement slurry plays a key role in the performance of cement operations. In addition, the viscosity is an effective parameter in cement slurry design, in a way that the cement slurry with low viscosity can be pumped easily. On the other hand, the cement slurry with suitable viscosity can greatly increase the ability of slurry to mud displacement and to create the turbulent flow as a mud cake removal, especially in the wells with high mud viscosity [5]. Indeed, the residual mud on the surface of the formation can prevent the good cement bonding between formations and casing. Therefore, achieving the optimum viscosity is a highly important factor in the design of cement slurry. To get an insight into this, the effect of incorporation of CPNHG with GO at 0.1 wt.%, as a rheology modifier on rheological properties of the cement slurry based on the Bingham fluid model [1,43] was studied and listed in Table 2.

As can be observed from the results of Table 2, the weight of cement slurry increased slightly at high CPNHG concentrations i.e., 1.5% and 2%. It might have been due to the absorbency effect of CPNHG at higher concentrations. In addition, it was found that the incorporation of CPNHG improves the gel strength properties and the stability of cement slurry (at 10 seconds and 10 minutes) because of the effect of CPNHG on the sedimentation inhibition by causing a soar in the suspending ability of the cement particles in the slurry environment [4,9,43-44]. On the other hand, there is no sedimentation, and settling between cement particles and other additives in the slurry at the bottom cup of the viscometer after 10 min with the addition of 1.5 wt.% of CPNHG. Indeed, the cement specific gravity is around 3.14 which is more than an aqueous environment, which causes the cement particles to settle and segregate resulting in an inhomogeneous cement behind the casing [43]. However, the slurry tends to further thicken with an increase in CPNHG concentrations due to the extreme absorbency capability of CPNHG. As a result, the viscosity and gel strength of the liquid phase escalated significantly, which would create a higher amount of gel in the cement slurry, leading to the instability of cement slurry. In addition, the particles settling were observed at the bottom cup of the rheology test after 10 min by increasing the CPNHG, particularly at 2 wt.% [2,9]. Therefore, the rheological properties of CMT/CPNHG should be optimized by choosing the suitable CPNHG concentration as a rheology modifier, to prevent the sudden increase in gel which causes cementing failure during and after the pumping process. It was noteworthy from Table 2 that the plastic viscosity and the yield point tend to rise remarkably from 25.5 cp to 76.5 cp, and 6.5 to 39.5 Ib/100ft^2 as the CPNHG concentrations increase from 0 to 2 wt.%, respectively. This behavior has also been shown in Figure S5. It can be explained by the fact that CPNHG acts as an effective suspension agent which soars the cohesive forces between particles and hinders the sedimentation of cement and other additives to form a stable slurry with less free water and fluid loss [2]. Therefore, CPNHG not only can assist the ability of cement slurry to displace the mud, particularly for the high mud viscosity but also has the great ability to suspend the cement particles. This results in viscosity stability, during the pumping process, thus forming uniform cementing behind the casing [5]. However, an optimum concentration of CPNHG is necessary for this role which is at 1 wt.%. A further increment in the concentration of CPNHG results in an increase in the yield point creating a highly ineffective gel in the cement slurry, thus making the pumping of cement slurry difficult. It is also interesting to note that all the samples show greater yield point and plastic viscosity compared to cement slurry without CPNHG. Thus, the role of the CPNHG, as a rheology modifier, enhances the stability of cement slurry.

Figure 6 depicts the dependency of the shear stress on the shear rate for CMT/CPNHG that was measured at 196 ºF. As shown in this figure, the shear stress rises with the addition of CPNHG. This enhancement was also prompted by increasing the shear rate. This increase was mainly ascribed to the interaction between the functional groups of GO and the copolymer chains with the surface cement particles, which causes the resistance to mobility [11,45].

Figure S6 displays the effect of CPNHG on the shear stress of nanocomposites hydrogel at three different shear rates. As can be seen from the figure, the shear stress magnifies with the CPNHG concentrations. It is due to the structure of copolymer nanocomposites, which improves the interaction with cement particles. Also, an enhancement in shear stress of samples was observed as compared to the cement slurry without CPNHG [40,45]. Therefore, these results, show that the fluidity and strength of cement slurry are sensitive to CPNHG concentration. CPNHG gives more strength to the cement slurry, which can provide greater resistance to the force and deformation created by shear fields.

The high fluid loss and free water cause a weakening of the cement bonding between formation and casing, which makes a channel in the cement sheath. This channel provides a path for the migration of fluid or gas during the wait of cement to the surface, especially from the bottom of the well [1,9]. Based on these problems, the effect of CPNHG concentration on the free water and fluid loss of the cement slurry has also been evaluated as shown in Figure 7. Fluid loss of the samples reduces notably by adding the CPNHG concentrations, as compared to neat cement slurry at temperatures as high as 196 ^{o}F and under the pressure of 1200 psi. This result can be explained by crosslinking between the functional groups of the GO and AM and AMPS copolymer chains, to form stable hydrophilic network hydrogel. This network structure can keep higher brine water under pressure and temperature, which can decrease the amount of free water in the brine slurry [7,10,12,46]. On the other hand, the presence of NMBA as a crosslinker agent in the copolymer hydrogel structure boosts the strength of the CPNHG network structure and provides an improvement in fluid loss control performance at temperature as high as 196 ^{o}F and pressure of 1200 psi [40]. Therefore, by increasing the CPNHG, the water absorption ability of hydrogel rises, which leads to a decrease in the fluid loss and increased viscosity of the CMT slurry. Besides, it can be seen from Figure 7 that free water loss tends to be close to zero with increasing the CPNHG concentrations [12,46]. It was also found from the sedimentation test that there is no free water separation in the cement slurry during 2 hr, compared to the cement slurry without CPNHG. In addition, cement slurry without CPNHG shows settling behavior [43]. This behavior was also observed in the rheological results. Consequently, the poly (AM-co-AMPS)/GO acts as a unique fluid loss controller with multipoint of absorption in its structure due to the existence of plenty of oxygenated functional groups on the GO surface along with the sulfonic acid group (SO_3H) of the AMPS in AM base copolymer network hydrogel. This renders the CPNHG to be highly stable under pressure of 1200 psi and at a temperature as high as 196 ^{0}F. The thermal stability effect of GO, presence of salt, and shear resistance of AMPS in main chains of the copolymer nanocomposites hydrogel, results in high absorption at the surface of cement particles. This causes a reduction in the liquid loss in the brine cement slurry [7,12,16,19,46].

The thickening time is one of the key parameters in cement design and can be defined as the duration for which the cement slurry will remain liquid as a pumpable fluid during cement operation [14]. Because of this, the effect of the incorporation of CPNHG on the thickening time as a function of the time of slurry pumping is investigated as shown in Figure 8. In this test, the temperature and pressure increase gradually up to 196 ^{0}F and 5946 psi, respectively for an early 42 min, and then they remained constant till the end of the test. The thickening time of cement slurry drops with the addition of CPNHG concentrations, compared to neat cement slurry as presented in Figure 8a. It declines from 342 to 301, 279, 262, and 245 minutes for the samples with 0, 0.5, 1, 1.5, and 2 wt.% of CPNHG with GO at 0.1 wt.%, respectively, at 70 Bc. This observation can be ascribed to the fact that CPNHG results in more absorption of brine water in slurry causing an increase in viscosity, thereby accelerating the hydration process. This leads to a decrease in the thickening time and in the time of the pumping process [1,7,47]. It was also found from Figure 8b, that the transition time (time between 30 to 70 Bc) was short which can be probably effective in controlling the fluid or gas migration during and after cement displacement [48]. CPNHG creates a stable solution in the cement slurry. In addition, the presence of GO as a thermal enhancer along with AMPS and NMBA as a modifier monomer and a cross-linker in copolymer network soars greatly the thermal stability in cement slurry which causes it to withstand elevated temperature and pressure [8,14].

The compressive strength of cement slurry is another basic feature in cement design for determining the cement integrity and its sustainability against the imposed stresses from formations before continuing the drilling operation or the well production time [5]. Therefore, the influence of the addition of copolymer nanocomposites hydrogel on the compressive strength properties of the cement slurry is determined. The results based on the crushing method are shown in Figure S7. Compressive strength boosted slowly from 803 psi to 1032 psi, compared to neat cement slurry, which is likely due to the linking between cement particles with a large surface area of GO in copolymer matrix. This strengthens the calcium silicate hydrate (C-S-H) structure in the cement matrix and enhances the cement strength by decreasing the volume of pores between the cement matrix [2,4,32,36].

Figure S8 shows the compressive strength test by using UCA, which measures the early and final compressive strength which are vital for cementing at 24 hr. This time is known as a wait of cement (WOC) which is a critical time for strengthening the cement slurry before resuming the drilling operations [49]. In this test, the temperature and pressure increase gradually up to 196°F and 3500 psi, respectively for 42 min, and then they become constant at the target temperature for 24 h. The compressive strength starts to develop slightly with the addition of CPNHG during the increasing time. It shows an augmentation from 816 to 1010 psi as the CPNHG concentrations increase from 0 to 2 wt.%, respectively after 24 hr. This effect is mainly due to the linking between GO along with copolymer in the matrix with the cement particles [32-33,47]. In other words, it may be due to the load transferring from cement matrix to GO and copolymer matrix through the distribution of surface stress [13], resulting in an enhancement of the compressive strength of cement slurry. However, no noticeable effect on compressive strength is observed at 2 wt.% concentration of CPNHG. The obtained results from this test showed that the compressive strength of all the cement slurry with CPNHG is higher than the sample without CPNHG. Interestingly, it was found from the results of the rheological and compressive strength, that CPNHG displays a great performance as a rheology modifier and a fluid loss controller than as a strengthening enhancer on the brine cement slurry. It can be also observed from figure S8 that the early compressive strength increased slightly during the first 5 hr although, the most significant increase of compressive strength was observed between 5 to 10 hr. After this, the compressive strength continues to increase slightly for up to 24 hr but this time showed less effectiveness on final compressive strength. In other words, CPNHG has a great effect on early compressive strength than the final compressive strength. This early development of compressive strength is a key parameter in ensuring the appropriate support of zonal isolation by cementing operation [5]. Consequently, the period between 5 to 10 hr is an important time of WOC for strengthening of CMT slurry and for the better determination of the timeline of cementing operation [48]. This observation is followed by thickening time results. According to these results, the copolymer AM and AMPS in presence of the GO improve the mechanical and compressive strength of cement slurry at temperatures as high as 196 ^{0}F. Based on these observations, it seems that the synthesis of crosslinked copolymer hydrogel nanocomposite based on poly (AM-co-AMPS)/GO has a significant positive effect on the improvement of the viscosity and fluid loss control as well as stability of the cement slurry while pumping as compared to that with other polymers synthesized from similar monomers [7-8,11-12,17]. However, since these nanocomposite hydrogels are novel materials for use as a rheology modifier and fluid loss controller in oil well cementing and electrolyte media, it is essential to further evaluate them during the development and routine testing for field applications.

4. Conclusions

The influence of GO on the structure strength of copolymer nanocomposites hydrogel based on poly (AM-co-AMPS) was evaluated. Also, the performance of poly (AM-co-AMPS)/GO as a rheology modifier and fluid loss controller on the mechanical, compressive strength, and rheological properties of the cement slurry were investigated. The XRD, FTIR, and TGA results indicated that the AM monomer and AMPS were synthesized and grafted on the GO surface. This led to improved thermal stability and strength of copolymer network hydrogel which was related to the good dispersion of GO and its interaction with copolymer chains. In addition, the presence of NMBA boosts the strength of the copolymer hydrogel network structure. The morphology results showed the uniform GO dispersion by 0.1 wt.% in the AM and AMPS copolymer matrix. The results showed that the 1 wt.% of CPNHG including 0.1 wt.% GO improved viscosity properties, control fluid loss value, compressive strength of cement slurry at a temperature as high as 196 ^{0}F, as compared to cement slurry without CPNHG. This was because of the existence of plenty of functional units on nanocomposite copolymer structure. The rheological properties of cement slurry were enhanced with an addition of the CPNHG. Besides, CPNHG due to the presence of functional groups on its network structure showed great ability in control of fluid loss and diminished the free water. The poly (AM-co-AMPS)/GO decreases the cement thickening time. And also, the improvement of the cement strength was observed which is due to the linking between cement particles and the large surface area of GO in the copolymer matrix. Results of the rheological, fluid loss controller, and compressive strength showed that the crosslinked nanocomposite hydrogel has a great performance as a rheology modifier and a fluid loss controller than as a strengthening enhancer on cement slurry. Therefore, based on these results, poly (AM-co-AMPS)/GO hydrogel was found as a good rheology modifier along with a fluid loss controller with great thermal and salt stability which can be a suitable additive candidate for use in oil well cementing.

Statements and Declarations

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Table 1. The compositions of CMT/CPNHG

Sample Code	CMT	CMT/ CPNHG 0. 5 %	CMT/ CPNHG 1%	CMT/ CPNHG 1.5%	CMT/ CPNHG 2%
Well Cement Class G (bbl/SK)	0.3775	0.3775	0.3775	0.3775	0.3775
Dispersant (Ib/SK)	0.3	0.3	0.3	0.3	0.3
Micro Block (gal/SK)	0.5	0.5	0.5	0.5	0.5
Antifoam (gal/SK)	As needed	As needed	As needed	As needed	As needed
Saline Water (bbl/SK)	0.239	0.239	0.239	0.239	0.239
Retarder (Ib/SK)	0.1	0.1	0.1	0.1	0.1

lb/SK: pounds per sack; gal/SK: gallon per sack; bbl/SK barrel per sack

Table 2. Rheological properties of CMT/CPNHG

Sample	Slurry Weight (PCF)	Plastic Viscosity (cp)	Yield Point (lb/100ft^2)	Gel Strength 10 Sec (lb/100ft^2)	Gel Strength 10 min (lb/100ft^2)
CMT	98	25.5	6.5	8.3	10
CMT-CPNHG 0.5%	98	45	20	12	32
CMT-CPNHG 1%	98	57	28	25	53
CMT-CNPHG 1.5%	99	67.5	34.5	33	69
CMT- CNPHG 2%	100	76.5	39.5	44	88

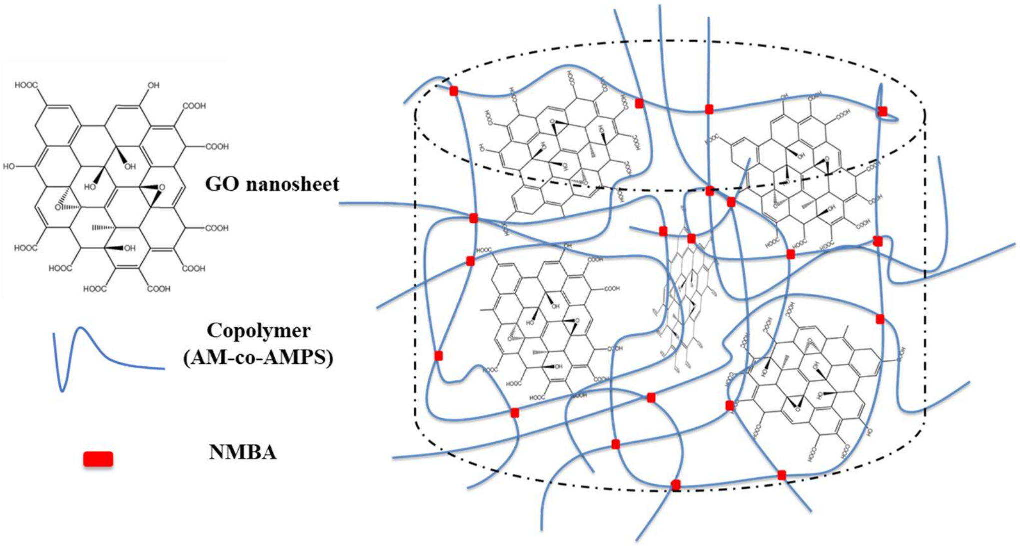


Figure 1. The schematic of the copolymer nanocomposite hydrogel structure.

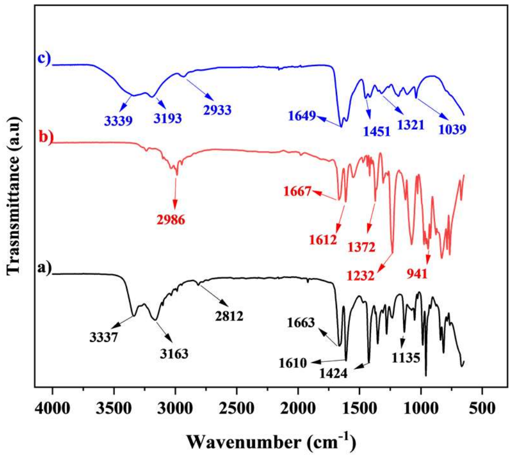


Figure 2. FTIR spectra of a) AM, b) AMPS and c) CPH.

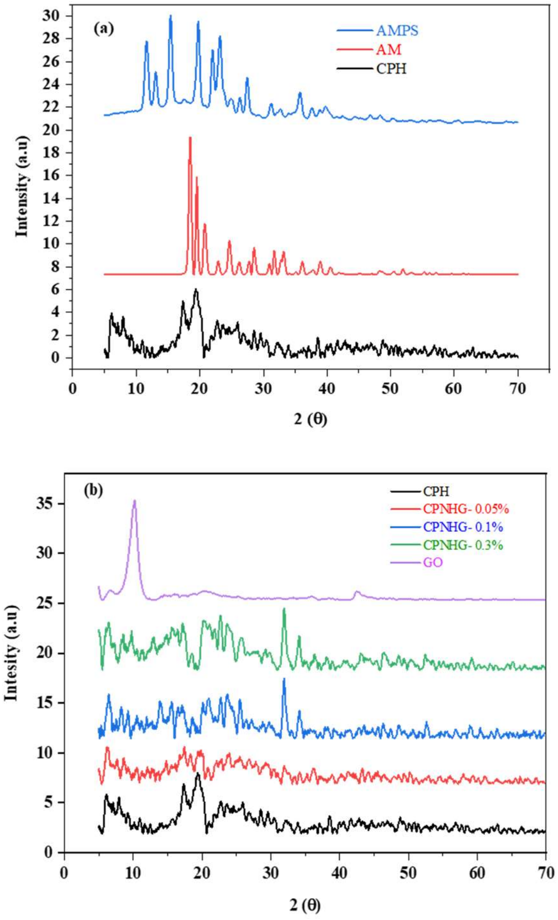


Figure 3. XRD of (a) AM, AMPS, CPH, and (b) GO, CPNHG with (0.05; 0.1; 0.3 wt.%) of GO.

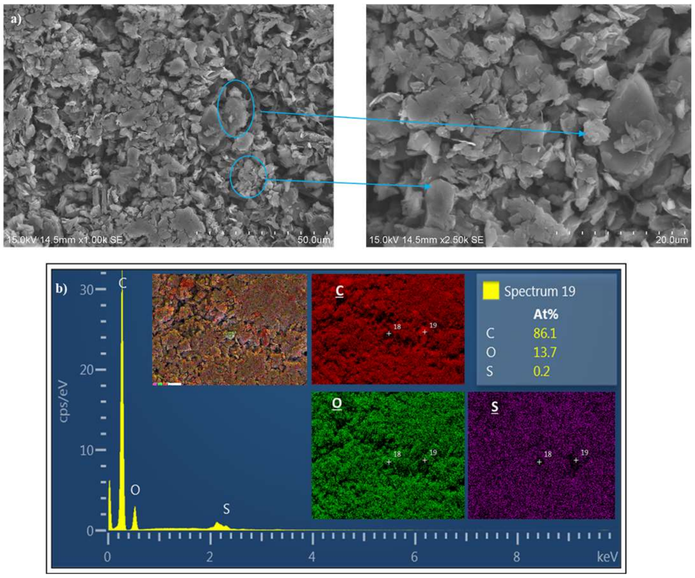
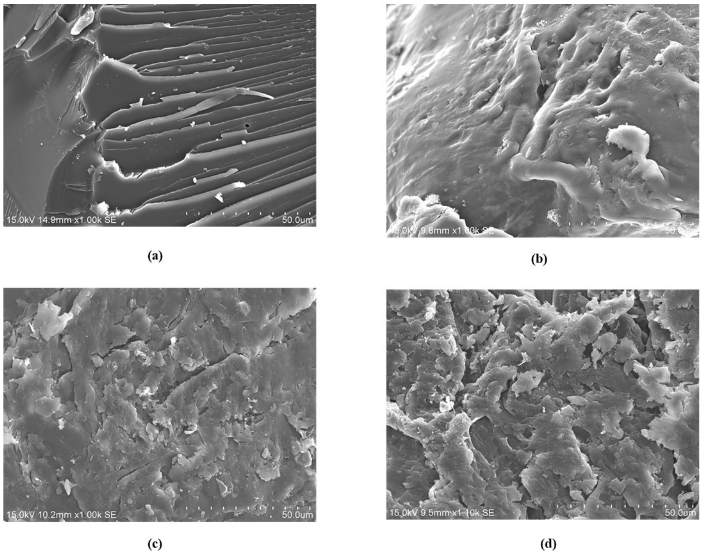


Figure 4. (a) SEM images of GO and (b) EDX of GO.



(a) (b)

(c) (d)

Figure 5. SEM micrographs of (a) CPH and CPNHG with (b) 0.05, (c) 0.1 and (d) 0.3 wt.% of GO.

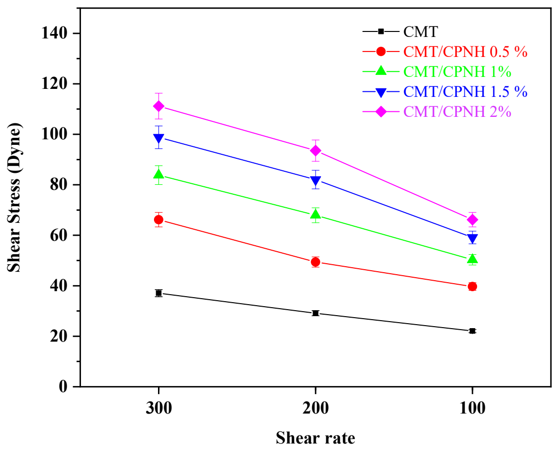


Figure 6. Shear stress vs shear rate of CMT/CPNHG.

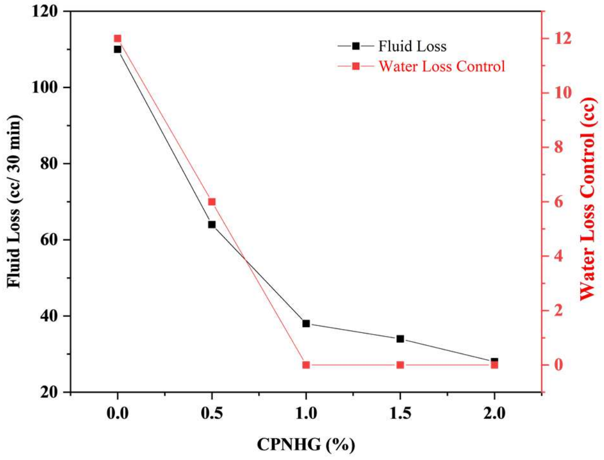


Figure 7. Influence of CPNHG concentrations on the free water and fluid loss of cement slurry.

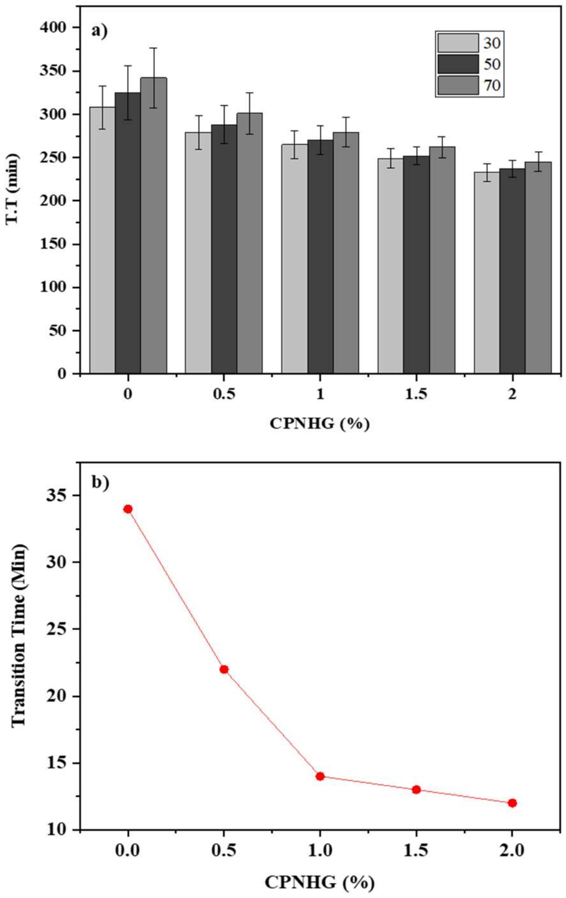


Figure 8. Effect of copolymer nanocomposites hydrogel a) on the thickening time and b) transition time of cement slurry.

4.4. Supporting information

Supporting Information

Synthesis and preparation of poly (AM-co-AMPS)/GO nanocomposites hydrogel as a rheology modifier and fluid loss controller for use in oil well cementing

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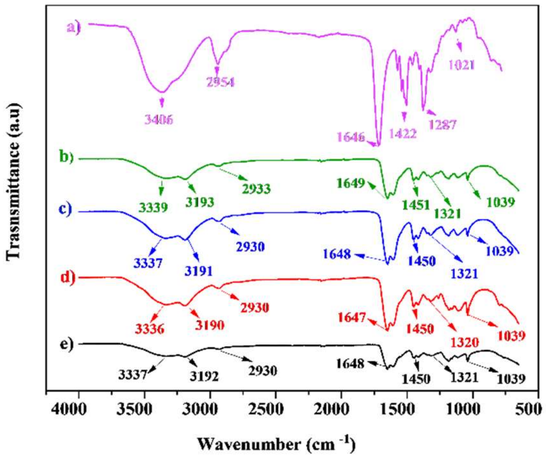

Figure S1. FTIR spectra of a) GO, b) CPH, and CPNHG with c) 0.05; d) 0.1; e) 0.3 wt.% of GO.

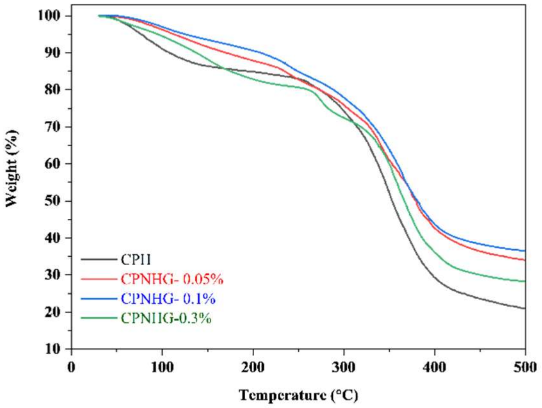

Figure S2. Thermal stability of CPH and CPNHG with (0.05 to 0.3) wt.% of GO.

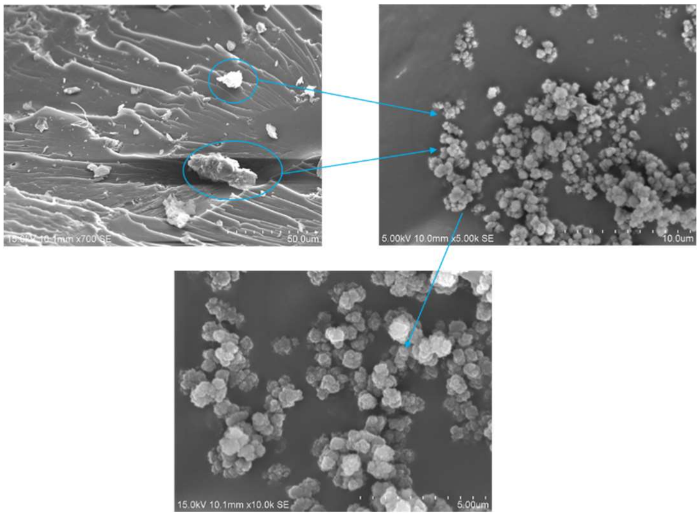

Figure S3. SEM micrographs agglomeration of CPNHG with GO at 0.3 wt.%.

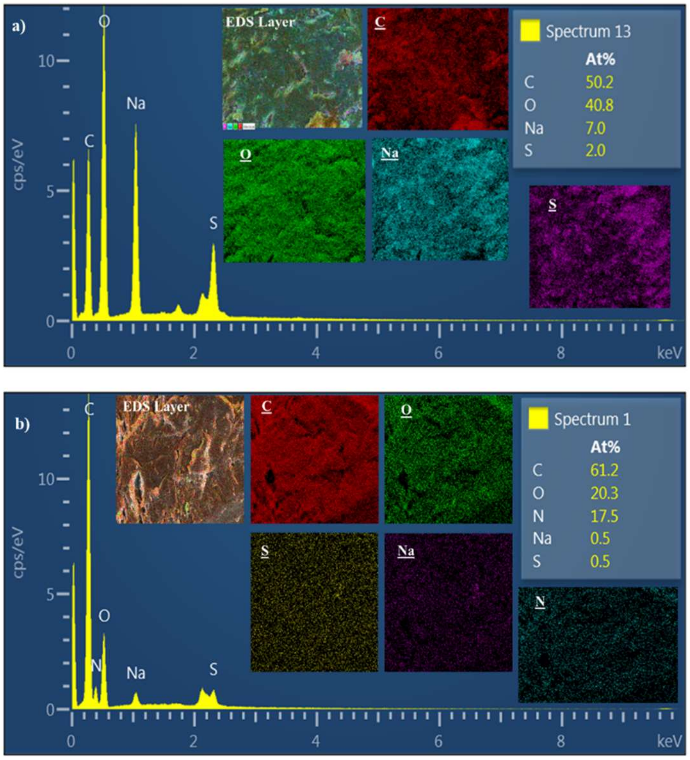

Figure S4. EDX spectrum and element mapping of a) CPH and, b) CPNHG with 0.1 wt.% of GO.

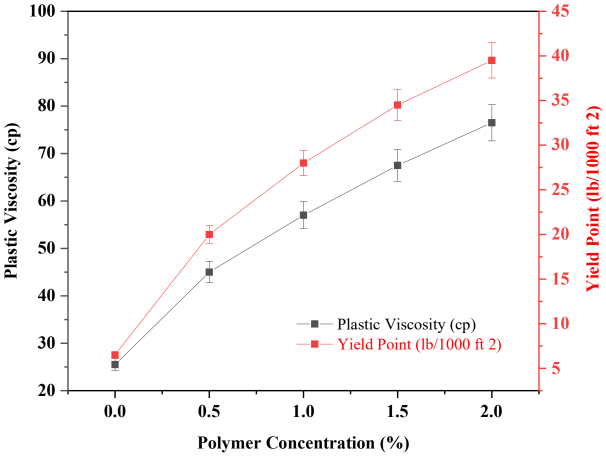

Figure S5. Influence of CPNHG concentrations on the PV and YP of cement slurry.

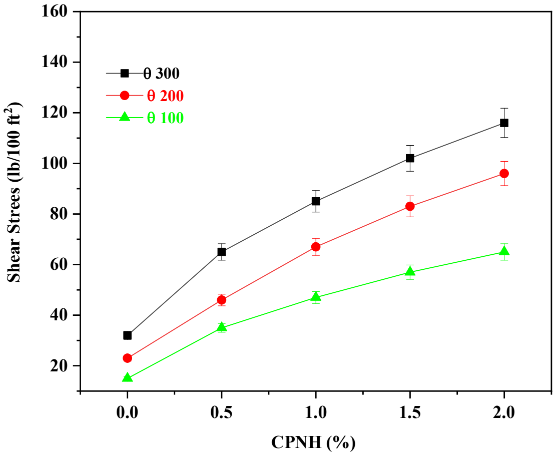

Figure S6. Shear stress vs CPNHG concentrations.

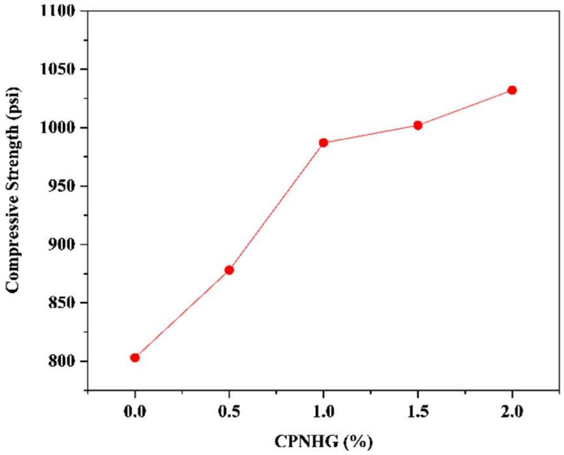

Figure S7. Compressive strength vs CPNHG concentrations at 196 °F.

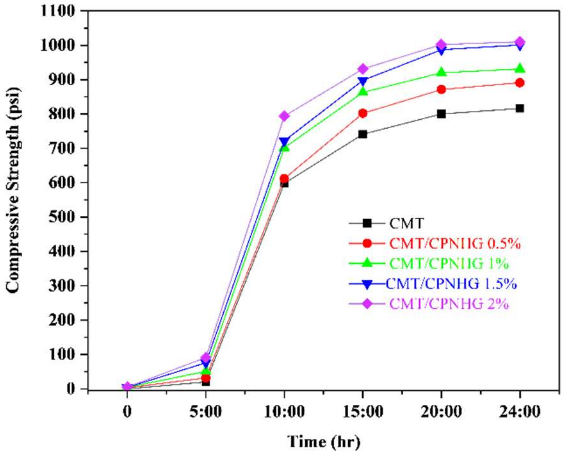

Figure S8. UCA compressive strength of cement slurry at 196 °F as a function of time.

4.5. Conclusion

Inspired from the works of chapter 3, we synthesized the poly (AM-co-AMPS)/GO nanocomposite hydrogel which was further used to oil well cementing and its possibilities in EOR applications to develop a novel AM-based hydrogel with plenty of functional units on nanocomposite copolymer structure. In addition, we synthesized and characterized the GO by XRD, EDX, and SEM in this chapter. This work gives an insight into the ability to use the functional groups of GO that react with copolymer chains through hydrogen bonds to form crosslinked hydrogel networks with great thermal and salt stability. The influence of synthesized GO on the strength structure of copolymer nanocomposites hydrogel based on poly (AM-co-AMPS) was evaluated. The advantage of this cross-linked hydrogel is the ability to absorb and keep a large volume of water or other aqueous fluids for several hours while being under pressure. The characterizations of this copolymer nanocomposites hydrogel were also investigated. All nano samples exhibit high thermal stability, as determined by TGA. The success of this approach highlights the potential of using it as a rheology modifier in designing and engineering fluids in oil well cementing. The work also opens wider access for developing a new hydrogel system.

Chapter 5

Synthesis, characterization and rheological behavior of HPG graft poly (AM-co AMPS)/GO nanocomposite hydrogel system for enhanced oil recovery

5.1. Introduction

Excessive water extraction becomes one of the serious challenges pending the life of production wells and oil recovery in mature oil fields that leads to a decline in the oil production efficiency. Hence, several techniques are associated with enhanced oil recovery (EOR) methods to decline unwanted water from the reservoirs. The water shut-off treatment with cross-linked polymer systems is one of the major treatments in this regard. In this chapter, by inspiring from chapters 3 and 4, we synthesized GO and its effect on the hydrogel network structure of graft copolymer nanocomposite based on hydroxypropyl guar (HPG) graft acrylamide (AM) and 2-acryloamido-2-methyl propane sulfonic acid (AMPS) which was reinforced with graphene oxide (GO), and its suitability for the development of the copolymer-based hydrogel systems by chromium triacetate crosslinker to use in EOR applications in electrolyte media, in terms of viscoelastic behavior, viscosity loss, long-term aging, and thermal stability have also been evaluated to specify the flow behavior in the reservoir. Characterizations of graft copolymer were also studied. Finally, the effect of the graft copolymer nanocomposite and cross-linker concentrations, on viscosity, storage modulus, and strength of the hydrogel system were investigated to optimize the gel formation in electrolyte media.

5.2. Article 3

Synthesis, characterization, and rheological behavior of HPG graft poly (AM-co-AMPS)/GO nanocomposite hydrogel system for enhanced oil recovery

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5.3. Author's contribution

Amir Narimani: Conceptualization of the project, visualization, and investigation of experiments, all synthesis of monomer and experiments conducted, validation of methodology and curation of data, drafting the original manuscript.

Farid Kordnejad: Investigation in rheology study.

Prof. Mahmood Hemmati: Investigation in EOR study.

Prof. Adam Duong: Project administration, supervision, funding acquisition, writing-review, and editing.

Synthesis, characterization, and rheological behavior of HPG graft poly (AM-co-AMPS)/GO nanocomposite hydrogel system for enhanced oil recovery

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Abstract

The purpose of this study is to investigate the synthesis of graft copolymer nanocomposite based on hydroxypropyl guar (HPG) graft acrylamide (AM) and 2-acryloamido-2-methyl propane sulfonic acid (AMPS), reinforced with graphene oxide (GO), and study its suitability for the development of the copolymer-based hydrogel systems by chromium triacetate crosslinker to use in oil recovery applications. The characterization outcomes acknowledged the grafting of AM and AMPS onto HPG in the attendance of the GO. The uniform dispersion of GO at 0.1 wt.% was observed in the morphology analysis. Moreover, not only the viscosity but also, the storage and loss modulus of graft copolymer nanocomposites hydrogel improved by adding GO. The effect of graft copolymer nanocomposite and crosslinker concentrations on the performance of hydrogel was also evaluated and optimized by a rheological test. These results showed the outstanding performance of crosslinked hydrogel structure of HPG-g-poly (AM-co-AMPS)/GO, owing to the linking of AM with AMPS and grafting on the HPG chains and the surface of GO in attendance of chromium triacetate. This makes the copolymer hydrogel system more stable against salinity, shearing, and high temperature. Therefore, this nanocomposite hydrogel system is potentially useful for oil recovery applications.

Keywords: Graft copolymer nanocomposite, graphene oxide, thermal stability, gel system, enhanced oil recovery

1. Introduction

Excessive water extraction becomes one of the serious problems during the life of production wells and oil recovery in mature oil fields that leads to a decline in the oil production efficiency [1-2]. The main reason for water production is the high permeability layers owing to the existence of fractures in the reservoir rocks, which leaves large oil fields without oil production [3-5]. Therefore, various techniques are associated to reduce unwanted water from the reservoirs, including mechanical separation, cement injection, and water shut-off treatment with cross-linked polymer systems [6]. Among the available techniques, an injection cross-linked polymer system comprising of a polymer or copolymer solution and a water-soluble crosslinker is extensively employed in water control treatments [2,7]. Under the temperature and time, polymer chains are linked together by a crosslinker as a bridging agent to generate a three-dimensional hydrophilic network structure. This hydrogel acts as a flow blocking or diverting agent [8-9]. Indeed, a gel polymer system can avoid water production by obstructing the high permeability zones and diverting to the low permeability zones in the reservoir. As well, owing to the slow movement of this sort of gel, it can be employed as a viscosity modifier for oil displacement, by increasing the viscosity of the fluid which helps to decrease the mobility ratio [10-11]. Gel polymer represents a convenient performance when their viscosity stability, gel strength, and thermal stability are at the desired level. Hence, rheological behaviors and thermal properties of the gel polymer solution play an important key in EOR applications [12-13]. As a result, the proper selection of gel polymer system is a key point and it depends on the reservoir conditions including lithology of formation, salinity, water hardness, and temperature [1,3, 14]. All these factors would cause the reduction of the durability and viscosity of hydrogel solutions pending the recovery process [14-15]. Consequently, based on these factors, several studies have been performed to develop an adequate polymer solution and also polymer gel system with suitable performance in EOR with regards to the harsh conditions of the reservoir [2, 5, 6, 12, 16-18]. For example, Mohammadi et al. [2] described the inverse emulsion copolymerization of AMPS and AM to make a high-weight nanostructure polymer mixed with chromium (III) acetate using EOR application. Singh et al. [6] synthesized a graft polymer nanocomposite hydrogel system, based on poly (AM -g-starch)/clay, by using a method of radical polymerization. Alvand et al. [12] reported an improvement in the behavior of sulfonated polyacrylamide with the addition of laponite and chromium (III) as a weak hydrogel system. Li et al. [18] synthesized a new hydro soluble sulfonated copolymer AMPS/DMAEMA/MA that demonstrated good shear and thermal resistance and salt tolerance ability in EOR applications.

Water-soluble polymers are highly applied in EOR applications such as control of water production and polymer flooding [19-21]. Therefore, acrylamide-based homopolymer or copolymer are common polymer solutions for gel systems [14]. In recent years, acrylamide (AM) is widely used, due to its properties to control the excess water production in the EOR process. However, the molecular chain of AM is easy to break when passing through the porous rocks. Moreover, it has poor shear resistance and salinity and it is easily degraded thermally, resulting in a substantial decline in the strength and viscosity of the hydrogel [22-23]. To prevail over these drawbacks of polymer gel based on acrylamide, AM monomers copolymerized with one or two monomers as a modifier have been employed [24]. AMPS as a monomer modifier has the potential to improve the chain stability of AM in harsh conditions of the reservoir [3,24]. The introduction of the sulfonic acid group into AM enhances the salt tolerance ability of AM monomer. Indeed, AMPS is a sort of vinyl monomer including sulfate groups with high durability, and also great salt tolerance which will result in the provision of high molecular weight copolymers that is desirable for EOR applications [25-26-27]. On the other hand, the use of the hydroxypropyl guar (HPG) as a natural polymer is beneficial as it is not only less sensitive to shearing but is also a great viscosity modifier, particularly in hydraulic fracturing [10, 28-29]. HPG chains can be grafted by AM monomer which causes a further increase of shear resistance in the copolymer structure [28-29]. HPG has an outstanding ability to carry the solid particles within the created mechanical fracture in the reservoir during the fracture operation. These particles help to keep the fractures open so that the oil can easily egress from the deeper reservoir to the well surface [30].

The use of methods such as interpenetrating polymer network, copolymerization, and graft copolymerization including natural and functional synthetic polymers has attracted much attention for the fabrication of hydrogel systems because of their ability to improve the properties of the polymers with a large range of applications owing to the combining of two or more polymers along with their desired properties [6, 10, 16-17, 31]. The graft copolymer as a polymer solution reacts with various crosslinkers to make the hydrogel with great thermal, salt, and shear stability, owing to the linking of AM with an ionic comonomer in its matrix and grafted with natural polymer in the backbone [6, 32]. However, this conventional hydrogel is limited, owing to the low network strength when passing into porous media which leads to the reduction of hydrogel viscosity [6,15,31], especially in reservoir conditions. Therefore, introducing nanoparticles into the polymer structure of hydrogel due to their outstanding properties such as improved strength, thermal stability, and salt tolerance [15] enhances the properties of conventional hydrogels [14-15, 19]. Recently, GO has been highly considered and employed as a thermal and mechanical strength enhancer for hydrogel polymer systems in harsh conditions [33-35]. Due to the hydrophilic nature of the GO and its abundant oxygen functional groups comprising epoxide, hydroxyl, carboxyl, and carbonyl, it can be dispersed in an aqueous solution and employed with hydrophilic polymers as a reinforcer [36-38]. The main attention of this research is to investigate the dispersion effect of GO on graft copolymer nanocomposite as copolymer solution and develop a novel hydrogel system to achieve the desired polymer hydrogel with adequate viscosity, gel strength, and thermal stability. To the best of our knowledge, there is no report for HPG-g-poly (AM-co-AMPS)/GO as a graft copolymer nanocomposite hydrogel system in EOR application and electrolyte media at elevated temperatures. Therefore, in this study, a novel hydrogel was prepared by crosslinking the chromium triacetate as a crosslinker with graft copolymer nanocomposite as a copolymer solution. The HPG-g-poly (AM-co-AMPS)/GO graft copolymer nanocomposite was synthesized by the graft copolymerization of AM and AMPS onto the chains of HPG, with the incorporation of the GO, and its characterization was studied. Then, the effect of the incorporation of GO on the rheological behavior of the nanocomposite hydrogel system in terms of viscoelastic behavior, long-term aging, viscosity loss, and thermal stability have also been investigated to determine the flow behavior in the reservoir. Finally, the effect of the graft copolymer nanocomposite and cross-linker concentrations, on viscosity, storage modulus, and strength of the hydrogel system was evaluated to determine an optimum gel formation in electrolyte media and EOR application.

2. Experimental

2.1. Materials

AM, graphite, ammonium persulfate (APS), and hydrochloric acid were purchased from Sigma-Aldrich. HPG was supplied by Shandong engineering & technology Co., China. AMPS was purchased from Alfa Aesar, Canada. Chromium triacetate was supplied from Carlo Erba, Italy. Sulfuric acid (H_2SO_4, 95%), potassium permanganate ($KMnO_4$), phosphoric acid (H_3PO_4), hydrogen peroxide (H_2O_2) and acetone were provided from Fisher Scientific, Canada. Sodium chloride (NaCl), and sodium hydroxide were obtained from Anachemia, Canada.

2.2. Preparation of graphene oxide

GO was prepared by a modified Hummer's method. In brief, 0.5 g of the graphite was mixed with 60 ml of H_2SO_4, and 6.6 ml H_3PO_4 then stirred for 10 min. 1.5 g of $KMnO_4$ was then gently added to the mixture and the reaction was continued at 80°C for 24 hr. Thereafter, 90 ml deionized water was added and mixed by dropping 1 ml of H_2O_2 into the solution for over 30 min. The obtained solution was purified by centrifugation for nearly 60 min at 2500 rpm. The specimen was washed many times by water to regulate pH between7-8 and was finally dried in an oven at 80 °C for 24 hr.

2.3. Synthesis of the HPG-g-poly (AM-co-AMPS)/GO

The HPG-g-poly (AM-co-AMPS)/GO was synthesized by the free-radical copolymerization. Firstly, 1 g of HPG was added to a 250-mL three-necked flask and mixed until the mixture was homogenized. Then various concentrations (0, 0.05, 0.1, and 0.3 wt.%) of GO were interspersed in 20 mL distilled water and stirred in an ultrasonic bath (Branson Co., 60 Hz, 80 W) for good dispersion of GO solution. After that, these concentrations were added to the three-necked flask and allowed to mix. Subsequently, a 30 mL aqueous solution containing 8 and 2 g of AM and AMPS monomers was poured into the flask and was mixed for 45 min. Thereafter, 0.011 mol/L of APS as an initiator in 5 mL distilled water was added slowly and the pH of the reaction solution was adjusted to 7-8 with sodium hydroxide and hydrochloric acid. The reaction was stirred for another 3hr by increasing the temperature to 80°C, under an inert nitrogen gas atmosphere up to the formation of a viscous solution. The synthesized product was precipitated and washed with acetone to obviate any impurities Afterwards, it was dried in a vacuum oven for 6 hr up to achieving a stable weight and was finally powdered by a mortar pestle.

2.4. Preparation of nanocomposite hydrogel

The nanocomposite hydrogel is prepared by gradually adding different amounts (0.5, 0.7, 0.9, and 1.1 wt.%) of synthesized graft copolymer nanocomposite to the saline solution (NaCl: 15000 ppm) and stirred frequently by a magnetic stirrer to get viscous solutions and kept for 24 hr. After that, the different amounts (0.6, 0.8, 1, and 1.4 wt.%) of chromium triacetate as a crosslinker were provided in water and mixed with the graft copolymer nanocomposite solution. Finally, the reaction was done by heating to 85 °C for nearly 2 hr to produce a uniform gel solution.

2.5. Instruments and characterizations

X-ray diffraction (XRD) analysis of dried graft copolymer and its nanocomposite was carried out using a Rigaku diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å) in the range $2\theta=5$-70. Fourier transform infrared (FTIR) spectra of dried graft copolymer and its nanocomposites were done by Thermo is10 spectrometer, in the range of 4000-650 cm^{-1}. Scanning electron microscopy (SEM) was done using a HITACHI, SUI510 that was equipped with energy dispersive X-ray (EDX) software X-MAX (Oxford instruments, 20 mm^2) for elemental analysis. Transmission electron microscope (TEM) of graft copolymer nanocomposite was obtained using a PHILIPS EM 208 S.

2.6. Rheological measurements

The rheological behavior of the nanocomposite hydrogel was measured using a rheometer (Paar-Physica, MCR 301) at 115 °C, for both steady and viscoelastic properties, in 25 mm parallel plate geometry and 1 mm gap with a Peltier device for temperature control. The strain amplitude was 1 % with the frequency in the range of 0.01-100 rad/s. To prevent water dissipation, silicone oil was applied to the outer surface. The viscosity stability vs. time for the nanocomposite hydrogel was performed using high temperature/high pressure, GRACE M5600 Rheometer at 115 °C for 51 min and a constant shear rate of 100 1/s and a pressure of 480 psi. Long-term aging of the nanocomposite hydrogels was done by viscosity monitoring. The gel specimens were kept in an oven at 115 °C, for 7 days. Thereafter, the influence of the loss viscosity of specimens on long-term thermal stability was investigated.

2.7. Thermal stability measurement

Thermogravimetric analysis (TGA) of dried hydrogels was evaluated with the Perkin Elmer, STA 6000. Specimens were heated from 30 to 700 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

3. Results and Discussion

3.1. Characterization of graft copolymer nanocomposite

Figure 1 depicts the synthetic route to the preparation of graft copolymer nanocomposite as a copolymer solution for fabricating the hydrogel system, by grafting copolymerization of AM and AMPS monomers onto HPG chains with the incorporation of GO as a multifunctional crosslinker agent and reinforcer along with the APS as an initiator. In fact, APS is decomposed by heating to engender the sulfate radicals then it initiates to develop chains between AM and AMPS monomers with the HPG chains. During chain propagation, GO acts as a crosslinking agent through the strong hydrogen bond formation among the GO functional groups and graft copolymer chains to form a three-dimensional network [33, 39].

The structural characterization of GO, HPG-g-poly (AM-co-AMPS), and HPG-g- poly (AM-co-AMPS)/GO was performed by XRD to investigate the dispersion of GO in graft copolymer as highlighted in Figure 2. XRD spectrum of GO reveals that the principal characteristic peak is located at $2\theta=10.25$, and an interlayer spacing at 0.86 nm, corresponding to the presence of oxygen-comprising functional groups on the sheet of GO [40-42]. In the case of the graft copolymer, the XRD pattern showed a diffraction peak shift in the range of $2\theta=20-25^o$ which is related to the amorphous characteristic of graft copolymer structure. However, after the incorporation of GO with HPG-g-poly (AM-co-AMPS), the characteristic diffraction peak declined compared to GO, implying a good dispersion of the GO in the graft copolymer network [37, 39-40]. Moreover, the broad peaks of the amorphous structure were apperceived in the range of $2\theta=20-25^o$ [40, 43]. According to these results, (i) graft copolymer nanocomposite was synthesized, (ii) GO was uniformly dispersed in the graft copolymer matrix, and (iii) it could act as a crosslinking point, then helping in enhancing the strength and structure of graft copolymer nanocomposite.

Figure 3 displays the FTIR spectra of GO, HPG-g-poly (AM-co-AMPS), and HPG-g- poly (AM-co-AMPS)/GO to study the interaction between graft copolymer chains with the functional group of GO. As highlighted in the Figure 3, GO exhibited bands at 3407, 2952, 1647, 1422, 1281, and 1021 cm^{-1}, are related to O-H hydroxyl groups, C-H, C=C, O-H, C-OH, and C-O-C respectively [34, 40], indicating the creation of the multifunctional groups on GO surface to enhance the dispersion and interaction of GO with copolymer matrix. [44] In the spectrum of the graft copolymer, the bands at 3388 cm^{-1} and 3225 cm^{-1} are attributed to the O-H bond of the hydroxyl group of HPG and N-H of the amide group [28]. In addition, C-H stretching is apperceived at 2956 cm^{-1}. The band at 1653 cm^{-1} is assigned to the C=O stretching and also the CH_2 band emerged at 1421 cm^{-1}. Moreover, the band observed at 1319 cm^{-1} is ascribed to the N-H vibration of AM and C-N of AMPS. Meanwhile, the band at 1067 cm^{-1} is due to the S=O of the sulfonate group [18, 26, 28, 45]. These observations indicated the grafting of AM and AMPS on the HPG backbone, demonstrating the formation of the network structure in which the graft copolymer was successfully synthesized [28,45-46]. In comparison to the graft copolymer nanocomposites, the graft copolymer without GO, revealed a lower wavenumber in spectra, which can be explained by the formation of interaction between GO and chains of graft copolymer matrix. It can be seen from FTIR spectrums of graft copolymer nanocomposite with 0.1 wt.% of GO, the characteristic peaks at 3381 and 3216 cm^{-1} were observed that implied the hydrogen bonding between GO and graft copolymer chains occurred by N-H of the amide group and O-H deformation vibration of GO [36,44]. The other peak emerged at 2955 cm^{-1}, implying the stretching vibration of

CH_2. Furthermore, the characteristic peak at 1650 cm^{-1} corresponds to the amide N-H and C=C of GO. As well, there are peaks at 1421 cm^{-1}, due to the C-H bending vibration, and C-O-C stretching around 1057 cm^{-1} for graft copolymer nanocomposite [14, 47]. An increment of the GO to 0.3 wt.% shows no substantial influence on the FTIR spectra of graft copolymer nanocomposite. However, the broad peaks at about 1645 and 1588 cm^{-1} were observed which shifted to a lower wavelength [39]. Therefore, obtained results confirmed that the monomers grafted onto HPG chains, and the linking occurred between chains of graft copolymer with the functional groups of GO surface, by hydrogen bonding to make the three-dimensional structure [37, 40, 42-43].

The morphology of prepared GO, HPG-g-poly (AM-co-AMPS), and HPG-g-poly (AM-co-AMPS)/GO to study the dispersion of GO in graft copolymer nanocomposite were studied by SEM and TEM. As shown in Figures 4a and b, GO demonstrated the wrinkle and flake-like sheets. Figure 4c displays the EDX pattern which implies the attendance of C, O, and S, which are the main elements for GO [40-43]. SEM image of the graft copolymer nanocomposite is shown in Figure 5 (a-c). Compared to the morphologies of the nano samples with the sample without GO, a compact and dense surface was observed for the nano sample with 0.1 wt.% of GO, which was ascribed to the interaction between graft copolymer chains with oxygen-containing groups of the GO, resulting in an improvement of network strength [33,43]. However, with soaring GO concentration to 0.3 wt.%, the morphology of the nanocomposite surface was denser and rougher with great fold areas, implying the poor interaction between GO and the graft copolymer chains [31,39,43]. This is also acknowledged by the TEM image of the HPG-g- poly (AM-co-AMPS)/GO at 0.3 wt.% of GO in Figure 6. It was obvious from Figure 6 that by increasing GO up to 0.3 wt.% GO, the poor dispersion of GO was observed which indicates that excess GO tends to agglomerate in the matrix [6, 42, 44]. To further evaluate the elemental composition of synthesized HPG-g-poly (AM-co-AMPS)/GO with 0.1 wt.% of GO, the EDX analysis is highlighted in Figure 7. It demonstrated the presence of C, O, N, Na, and S elements map, thus suggesting the presence of nanoparticles in the graft copolymer matrix, indicating the sample was synthesized [40]. As a result, GO is well dispersed up to 0.1 wt.% in the graft copolymer matrix and it interacts with chains of graft copolymer matrix. Indeed, the graft copolymer chains were most likely located on the GO surface [47]. According to the above results, graft copolymer nanocomposite of AM and AMPS onto HPG chains with an attendance of GO was synthesized to engender a graft copolymer nanocomposite solution with a strong multifunctional network structure. Hence, HPG-g-poly (AM-co-AMPS)/GO with 0.1wt.% of GO can be potentially used as a copolymer solution of hydrogel system in EOR application at elevated temperatures.

3.2. Rheological behavior of nanocomposites hydrogel

The rheology of polymer gel solutions plays an essential role in hydrogel performance, especially in porous media like oil reservoirs. Polymer gel solution with low viscosity can be injected easily but, it might lead to lower efficiency. On the other hand, the polymer gel solution with high viscosity may be pumped with difficulty and cannot flow easily in the porous media of the reservoir. Therefore, achieving the desired viscosity with suitable gel strength is highly important in the design and performance of cross-linked gel systems [10,12]. According to this, the effect of incorporation of GO on the viscosity behavior versus shear rate for hydrogels was evaluated at 115 ^{o}C. In these experiments, graft copolymer nanocomposite, and cross-linker concentration for hydrogel samples are kept constant at 0.7

and 0.8 wt.%, respectively. As shown in Figure 8a, the viscosity was improved with an addition of the GO, at a low-shear rate. This enhancement was noticeable as the concentration of GO increases up to 0.1 wt.%. This increment was likely ascribed to the linking between GO with the chains of the graft copolymer matrix, owing to the uniform dispersion of GO in the graft copolymer matrix, which improves the resistance to the mobility of graft copolymer chains, leading to an enhancement in the viscosity [14, 48-49]. In fact, the large surface area of GO, can act as a physical crosslinking agent to improve the strength of nanocomposite hydrogel structure [37, 50]. However, a slight increase in the viscosity was also shown with an augmentation of GO to 0.3 wt.%, because the nanoparticle tends to agglomerate [15]. In addition, the nanocomposites hydrogel shows less dependency of viscosity to shear rate as compared to hydrogel without GO. These outcomes display that the network strength of polymer gel solutions is sensitive to GO loading. GO nanosheets give greater strength to the network of graft nanocomposites hydrogel to form the stable structure to resist stretch stress and deformation generated by shearing fields as compared to the hydrogel without GO [49]. It was also observed from Figure 8a, that all samples of gel systems displayed the non-Newtonian and shear thinning behavior, with an increasing shear rate, implying the pseudoplastic fluid behavior [12, 21]. An increase in the shear rate and temperature at 115 °C leads to the disentanglement of the graft copolymer nanocomposite chains and their easier movement, resulting in a lower viscosity [14]. It means that the graft copolymer nanocomposite chains are oriented further along with the flow [14, 49].

The properties of hydrogels are intermediate between viscous and elastic liquids which shows viscoelastic behavior [7]. Therefore, the viscoelastic behavior of the graft copolymer nanocomposite hydrogel in this study was also evaluated. Figure 8 (b-c) displays the influence of GO on the storage and loss modulus for the hydrogel system composed of the 0.7 wt.% of graft copolymer nanocomposite and 0.8 wt.% of the crosslinker with the applied frequency. The storage and loss modulus of nanocomposite hydrogel is enhanced with an addition of GO, by increasing the angular frequency. This behavior can be explained by the fact that at low frequency, the polymer chains had enough time to unwind and to form the network structure. Thus, a vast amount of relaxation occurred, leading to an enhancement in the rheology behavior of samples. However, at high frequency, this action time was shorter, and the disentanglements of matrix chains increased [48]. This enhancement was noticeable with the addition of 0.1 wt.% GO, which was owing to the uniform dispersion of GO in the graft copolymer matrix [47]. This reinforces the strength of the three-dimensional structure of nanocomposite hydrogel, thereby improving the viscoelastic properties [7,33,36]. However, this effect was not remarkable with the rise of GO contents to 0.3 wt.%. Therefore, a high concentration of GO causes the agglomeration of GO particles that make non-uniform dispersion in the graft copolymer matrix, resulting in a decreased strength of the hydrogel network and the elastic behavior [51]. Interestingly, from this Figure 8, the storage modulus (G') value is greater than that of the loss modulus (G"), implying that the elastic nature is dominant over its vicious nature. It means that the gel formation may have already commenced in the system. Hence, these obtained results revealed that polymer gel has great rubbery nature at concentrations 0.1 wt.% of GO, at low frequencies [16, 49, 52].

As shown in Figure 8, an improvement in the viscoelastic properties of nanocomposite hydrogels was observed as compared to the neat hydrogel at all the shear rates. This enhancement was mainly owing to the hydrophilic functional groups of GO that cross-linked with chains of graft copolymer matrix, by hydrogen bonding, causing the nanocomposites hydrogel to display good strength and rheological characteristics in electorate media [11, 37]. Likewise, not only neat hydrogel but also nanocomposite hydrogels exhibited terminal behavior, indicating the rheological behavior of materials to transition from liquid-like at low frequencies to solid-like at high frequencies [11,14,50]. Hence, according to these results, AM-based graft copolymer hydrogel showed a strong crosslinked structure with good rubbery behavior in an electrolyte media with a salinity of 15000 ppm, thereby incorporating HPG and AMPS into its matrix that is linked with the GO surface, to increase its salt tolerance and shear stability. As a result, HPG-g-poly (AM-co-AMPS)/GO hydrogel with 0.1 wt.% of GO renders great performance as a polymer gel system in the EOR process.

The viscosity stability of hydrogel is a significant rheological factor in EOR, which is defined as the ability of a polymer gel solution to keep its viscosity to the shear rate with respect to time [2]. For this purpose, the viscosity stability of nanocomposite hydrogels was examined and compared with the sample without GO at a temperature as high as 115 °C. The graft copolymer nanocomposite and cross-linker concentration for all hydrogel samples are held constant at 0.7 and 0.8 wt.%, respectively. It can be seen from Figure 9, the viscosity stability of both the samples reduced with time, particularly in the early 15 minutes. The same effect was shown with increasing temperature to reach the target temperature. Afterward, the viscosity became steady and no remarkable reduction in viscosity was apperceived with time. By comparing the viscosity stability of samples, it can be observed that the nanocomposite hydrogel with GO had greater viscosity stability and gel strength than hydrogel without GO in electrolyte media, which is likely due to the linking of GO with graft copolymer chains. It highlights the fact that the attendance of GO as a multifunctional crosslinker accompanied with AMPS and HPG as a sulfonated monomer and viscosity modifier in the network structure of the acrylamide-based copolymer nanocomposite hydrogel, results in an improvement of the viscosity stability against the created shear fields in salinity environment [10, 49].

Loss of viscosity of polymer gel solutions is the main factor in the EOR process, particularly in long-term aging under harsh reservoir conditions. Hence, the impact of long-term aging on the viscosity behavior of conventional hydrogel was investigated and compared with its nanocomposite hydrogel, in an electrolyte media and is shown in Figure 10. The graft copolymer nanocomposite and cross-linker concentration for all hydrogel samples are kept constant at 0.7 and 0.8 wt.%, respectively. According to this figure, the shear viscosity lessens with increasing shear rate. However, nanocomposite hydrogels show higher viscosity and thermal stability as compared to the hydrogel without GO. This improvement was noticeable for hydrogel with 0.1 wt.% of GO compared to all other samples. It can be explained by the attendance of chromium triacetate and GO as crosslinkers in hydrogels which strengthen the network structure by increasing the crosslinking density and preventing the rapid degradation of acrylamide molecules [15,53]. This enhancement in the nanocomposite hydrogel network causes a reduction in the accessibility of divalent cations including Ca^{2+} and Mg^{2+} in the AM chains [10, 12]. Consequently, GO, as a thermal enhancer, improves greatly the viscosity of loss in the polymer gel solution for long terms aging. Therefore, this result presents the HPG-g-poly (AM-co-AMPS)/GO hydrogel system can be highly stable at high temperatures.

3.3. Thermal stability of nanocomposite hydrogel

The thermal stability of the hydrogel system is another main factor in the EOR process, which affects the viscosity and stability of hydrogel performance. Based on this issue, the thermal stability of HPG-g-poly (AM-co-AMPS) hydrogel (0.7 wt.% graft copolymer and 0.8 wt.%

of crosslinker) was studied and compared with HPG-g-poly (AM-co-AMPS)/GO nanocomposite hydrogel (0.7 wt.% graft copolymer nanocomposite (containing 0.1 wt.% GO) and 0.8 wt.% of crosslinker). As highlighted in Figure 11, the thermogram of the HPG-g- poly (AM-co-AMPS) hydrogel displays five essential decomposition steps. The first step of weight loss appeared up to 100 °C, owing to water evaporation. The second step emerged from 100 to 240 °C, which is likely related to the thermal dissociation of amide and carboxylate side groups, and also decrease in the linking of graft copolymer chains with a crosslinker, causing a reduced network structure strength. However, the presence of AMPS in the copolymer chain assists in impeding the quick hydrolysis of the amide group in the hydrogel network [17, 52]. Another weight loss step occurred between 240 to 350 °C, which suggested the amide and sulfonic acid groups of the copolymer network were degraded [2, 18]. Then, the decomposition step, between 350-500 ^{o}C was observed due to the breakage of the graft copolymer chains. The last dissociation stage, above 500 ^{o}C, indicates the complete decomposition of the graft copolymer network and also the destruction of the crosslinked structure [18, 40, 45]. In contrast, the thermogram of the graft copolymer nanocomposite hydrogel demonstrates a noticeable extension of degradation temperature. It is mainly due to the grafting of AM monomer and sulfonated group AMPS onto HPG and also the homogeneous dispersion of the GO. GO acts as a thermal crosslinking agent in the graft copolymer matrix and creates a strong network structure which causes the great enhancement of the strength and thermal stability of network nanocomposite hydrogel as compared to hydrogel without GO [32-33,39, 44]. This behavior was supported by the loss of viscosity. According to these results, it appears that the synthesized graft copolymer nanocomposites hydrogel has a notable impact on improving thermal and viscosity stability during pumping in porous media. Although further evaluation can be essential during routine expansion and testing for fields operations.

3.4. Effect of graft copolymer nanocomposite and crosslinker concentrations on hydrogel system

The optimization of polymer and crosslinker concentrations are key parameters in the gel system that can affect the performance of polymer gel solution during pumping into the reservoir [6]. Based on this, the effect of graft copolymer nanocomposite concentrations on viscosity, and storage modulus of hydrogel was also examined and are shown in Figures 12 (a and b). Samples were prepared with various percentages (from 0.5 to 1.1 wt.%) of graft copolymer nanocomposite (containing 0.1 wt.% of GO), at a constant concentration of cross-linker (0.8 wt.%) at four shear rate and frequency. It is observed from Figure 12a that gel viscosity increased remarkably with the growing the graft copolymer nanocomposite concentration to 0.7 wt.% and then continued to further soar up to 0.9 wt.%. This is mainly because of the greater availability of negative charge sites of graft copolymer nanocomposite chains, which leads to an enhancement in the number of links between Cr^{3+} ions of crosslinker and graft copolymer nanocomposite chains; causing the increment of viscosity and an improvement in the gel strength [5, 9, 17]. On the other hand, these results also revealed that when the graft copolymer concentration increases in the gel network, caused by soaring the functional groups in the network and an increase in physical entanglement of graft copolymer nanocomposite chains. This restricts the polymer chains mobility, resulting in a further increase of the viscosity, and decrease in the gelation time [16, 51]. However, by increasing the shear rate, the viscosity of the hydrogel decreased, suggesting the hydrogel system displays pseudoplastic behavior [6]. Therefore, hydrogel samples including the graft copolymer nanocomposite at 0.7 and 0.9 wt.% showed greater strength and viscosity versus shear rate than all others, that can resist against deformation force when it passes through the slender paths of the reservoir [3,6]. It was also found from Figure 12b that at a lower concentration of graft copolymer nanocomposites (0.5 wt.%), there is no increase in the storage modulus. This is because of the existence of insufficient molecules of graft copolymer nanocomposite that can react with chromium triacetate, resulting in free chromium in the system [51]. In contrast, with the growing of graft copolymer concentration to 0.9 wt.%, there is a high number of available crosslinking sites and functional units for reaction with a crosslinker resulting in the increasing of storage modulus, suggesting further elastic behavior of hydrogel [5,19]. Also, higher storage modules were obtained at a higher concentration of graft copolymer nanocomposite at 1.1 wt.%. This was due to increasing intermolecular entanglements, and hydrogen bonds between the graft copolymer nanocomposite chains, resulting in a reduction in the gelation time of the hydrogels [1], which causes difficulties during gel injection and pumping into the porous rock.

Figure 13 represents the effect of different crosslinker concentrations (0.5, 0.8, 1, and 1.4 wt.%) by keeping constant the graft copolymer nanocomposite (containing 0.1 wt.% of GO) at 0.7%, on viscosity and gel strength of hydrogel system at four shear rates. As shown in Figure 13, viscosity augments with an increase in the crosslinker to 1 wt.%. It can be explained by the fact that by increasing the crosslinker, the number of links between the Cr^{3+} ions of the crosslinker and the graft copolymer nanocomposite chains rises [9,51]. As a result, further crosslinker points reacted to form a stable network structure, resulting in an increase in gel strength and it declines the gelling time [4]. On the contrary, an increment in the viscosity of hydrogel samples was decreased by further soaring in crosslinker to 1.4 wt.%. It is interesting to note that hydrogel with a cross-linker at 1.4 wt.% displays instability in its network structure. This behavior may be due to the attendance of extra Cr^{3+} ions, which results in greater constriction forces of crosslinking than the expansion forces in the gel network, causing the volume of the polymer gel and copolymer chains to reduce and the gel network to collapse [2, 4, 9]. Therefore, it is evident that an enhancement in viscosity depends on crosslinker concentration. Therefore, based on these results, the variations between these two parameters lead to a variety of hydrogel systems. It seems that the storage and viscosity of nanocomposite hydrogel increased by growing the graft copolymer nanocomposite and crosslinker concentrations thus, the 0.7 wt.% of graft copolymer nanocomposite containing GO and the cross-linker 0.8 wt.% can be selected as optimum values to enhance the strength performance of cross-linked copolymer hydrogel for injection into the reservoir.

4. Conclusion

The HPG-g-poly (AM-co-AMPS)/GO was synthesized by graft copolymerization of AM and AMPS onto HPG in presence of GO and its ability as a copolymer nanocomposite gel system using chromium triacetate was investigated in EOR applications. The obtained results from XRD and FTIR indicated the AM monomer and AMPS in presence of GO were copolymerized and grafted onto HPG chains. The morphology results displayed the uniform GO distribution at 0.1 wt.% in the graft copolymer matrix. As well, the impact of GO on the improvement of the graft copolymer network strength was connected to good dispersion of GO and its linking with graft copolymer chains. Rheological results revealed that all hydrogel samples were sensitive to the interaction between GO concentration with chains of the graft copolymer. Moreover, GO enhanced viscosity and thermal stability of nanocomposite hydrogel at a temperature as high as 115 ºC, and improved its rheological performance, compared to the hydrogel without GO. Besides, the loss viscosity of nanocomposite hydrogel was lesser, compared to the sample without GO. Furthermore, the rheology behaviors of the gel system were highly affected by the concentrations of graft copolymer nanocomposites and crosslinker. As well, the novel nanocomposite hydrogel system showed a high strength network, due to the abundance of functional units on graft copolymer nanocomposite structure to react with the crosslinker. Hence, according to these results, HPG-g-poly (AM-co-AMPS) /GO hydrogel was found as a suitable hydrogel system with great viscosity and thermal stability which can be beneficial for use in enhanced oil application.

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Disclosure statement

The authors state that there is no competing interest in this article.

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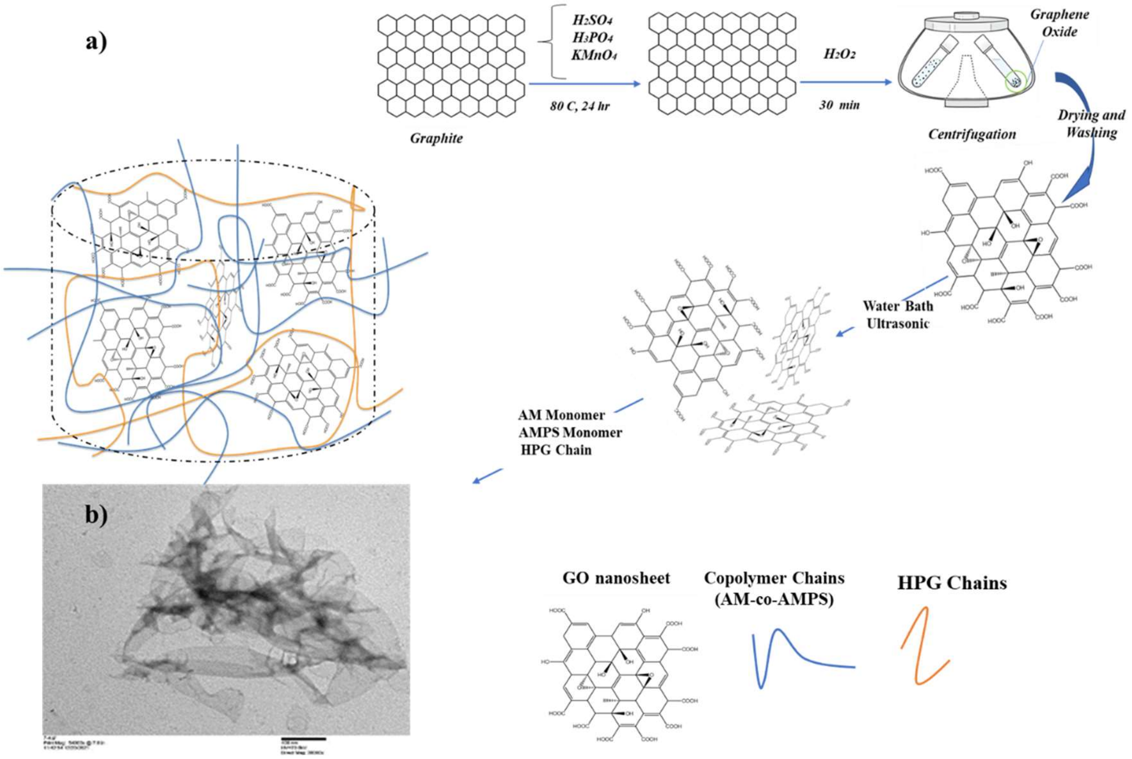

Figure 1. a) Schematic of the preparation procedure of HPG-g-poly (AM-co-AMPS)/GO; b) TEM of HPG-g-poly (AM-co-AMPS)/GO at 0.1 wt.% of GO.

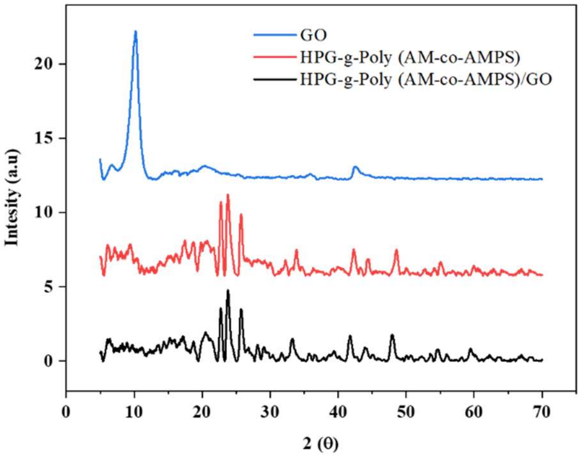

Figure 2. XRD of GO, graft copolymer, and graft copolymer nanocomposites.

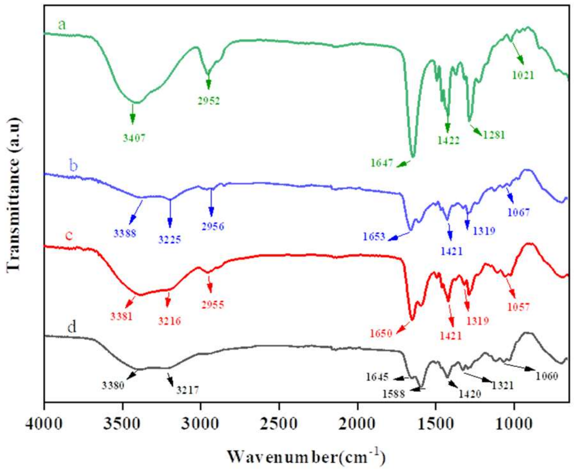

Figure 3. FTIR spectra of a) GO, graft copolymer nanocomposite b)0; c) 0.1 and d) 0.3 wt.% of GO.

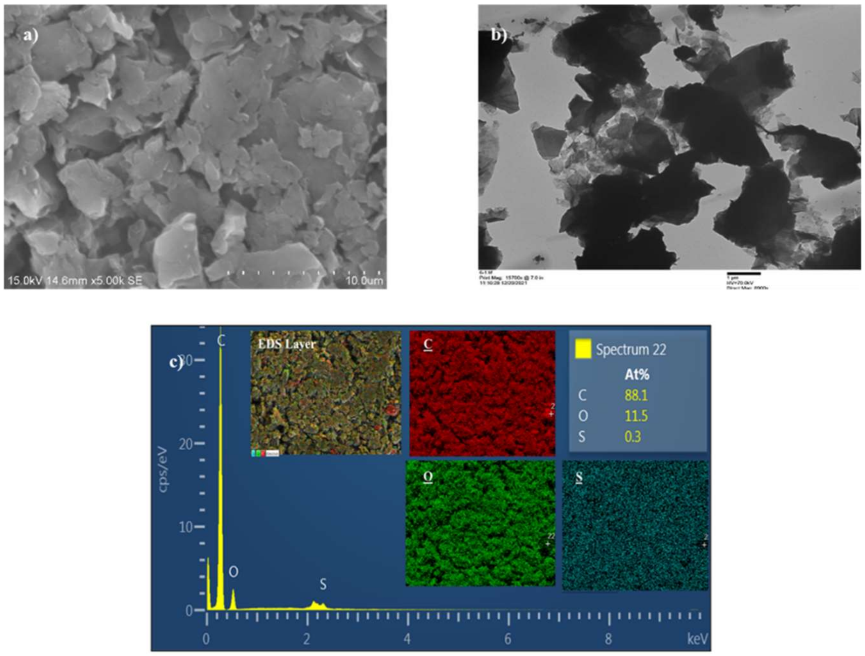

Figure 4. (a) SEM, (b) TEM and (c) EDX of graphene oxide.

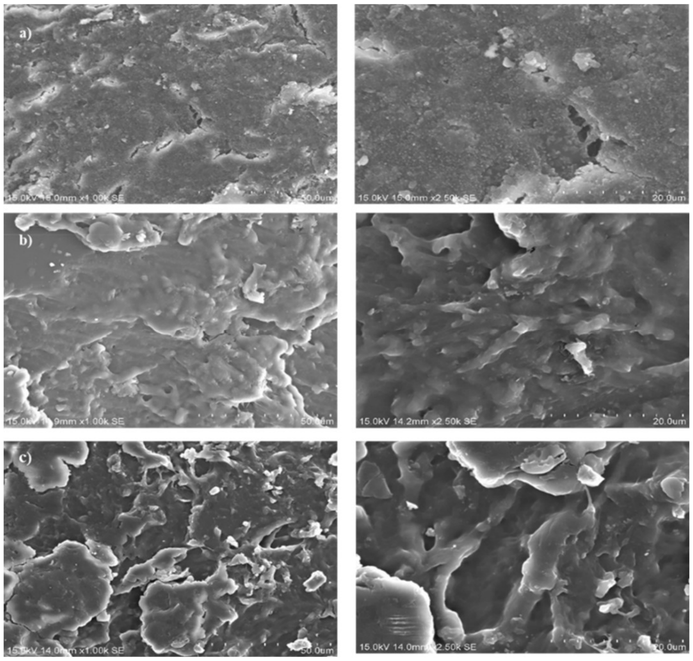

Figure 5. SEM images of HPG-g- poly (AMPS-co-AM)/GO a)0; b) 0.1; c) 0.3 wt.% of GO.

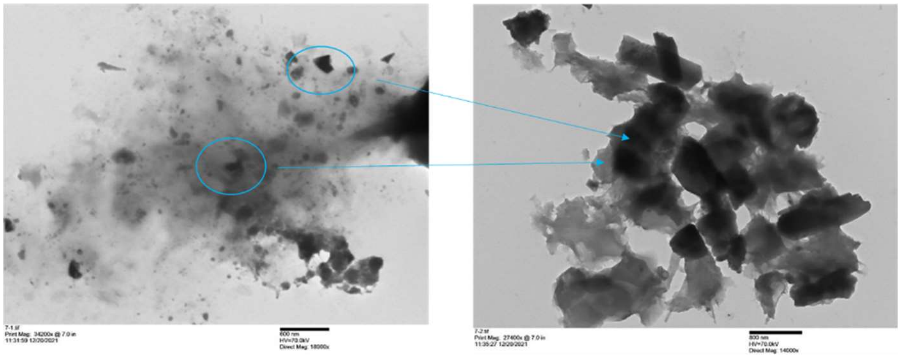

Figure 6. TEM images of HPG-g- poly (AMPS-co-AM)/GO at 0.3 wt.% of GO.

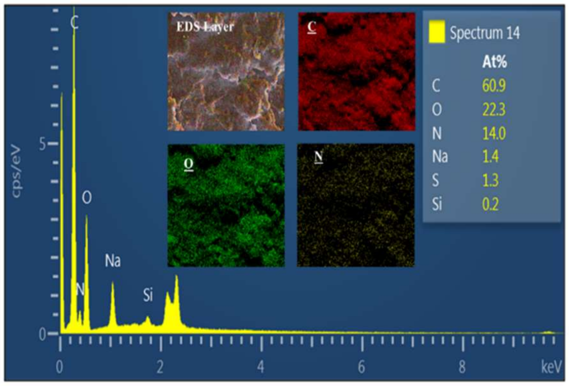

Figure7. EDX spectrum and element mapping of HPG-g- poly (AMPS-co-AM)/GO.

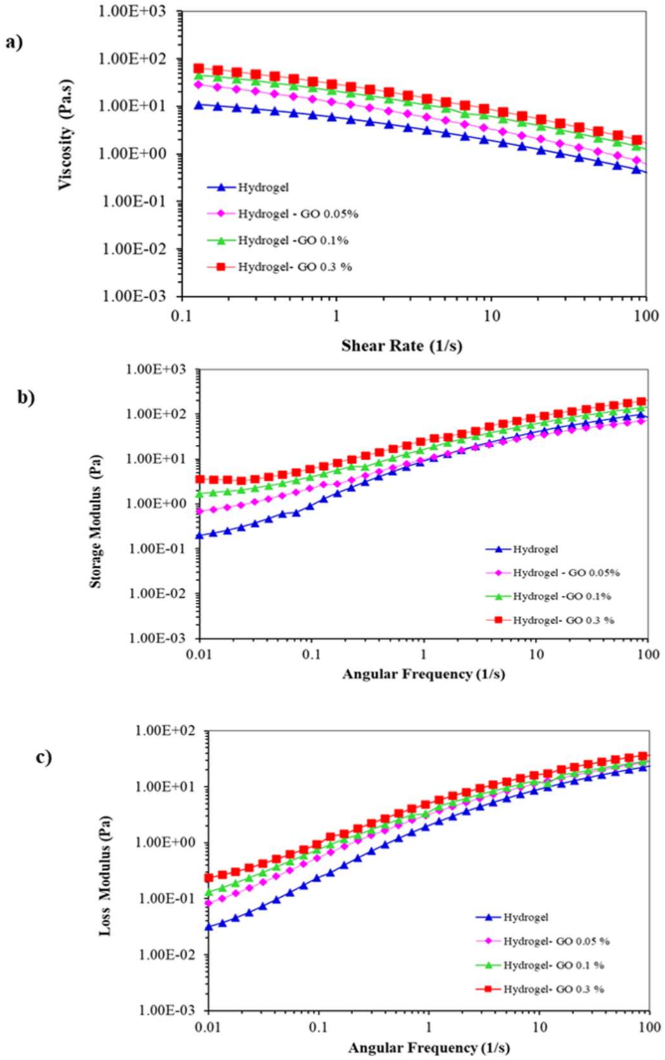

Figure 8. Influence of GO on a) viscosity vs. shear rate of hydrogels; b**)** storage and c) loss modulus vs. frequency.

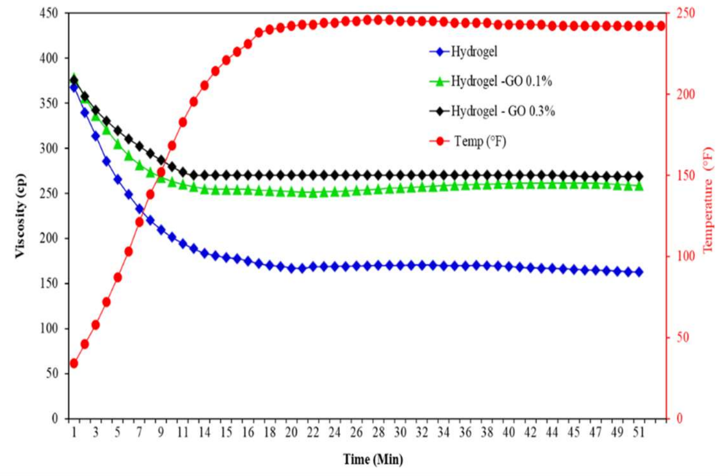

Figure 9. The influence of time on the viscosity stability.

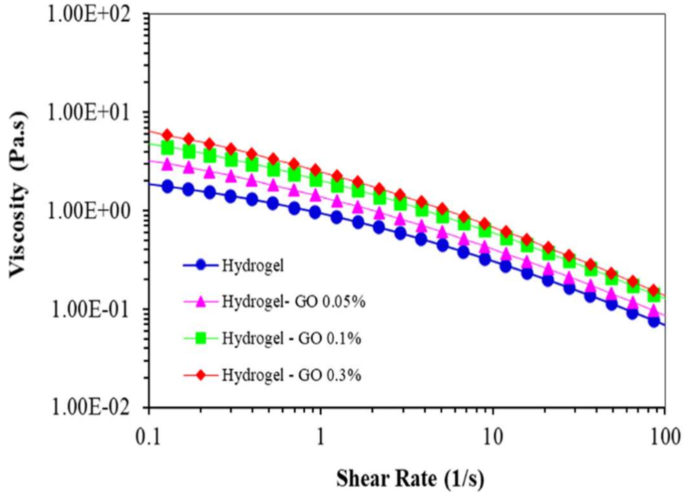

Figure 10. Viscosity vs shear rate of hydrogel after aging.

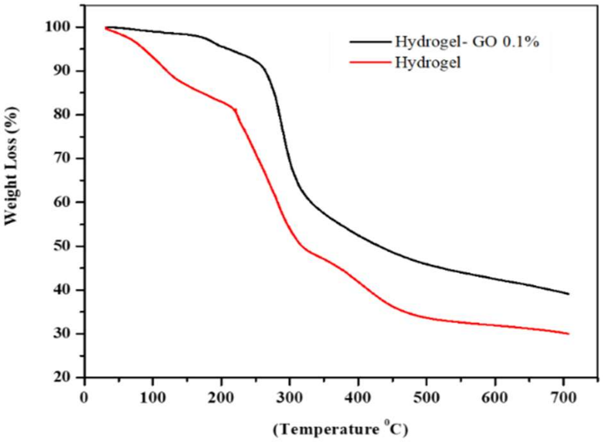

Figure 11. Thermal stability of hydrogel and nanocomposite hydrogel.

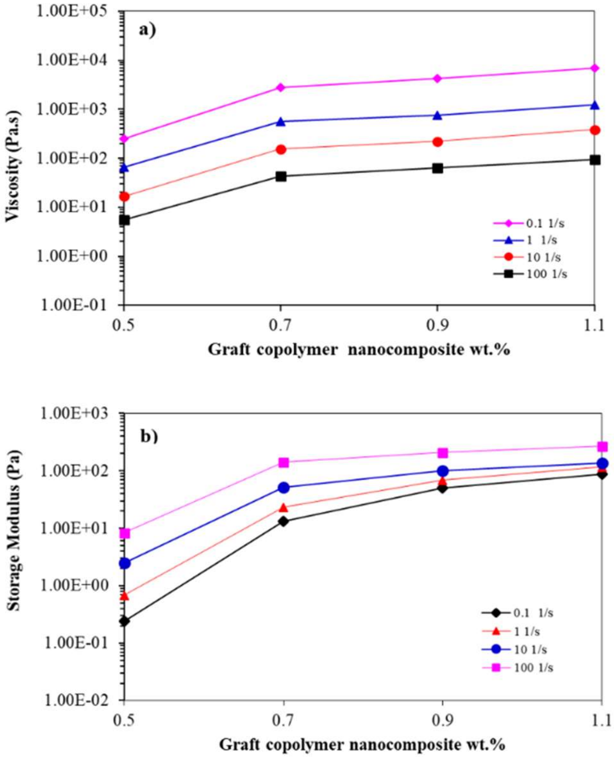

Figure 12. Effect of graft copolymer nanocomposites concentration on a) gel viscosity and b) on the storage modulus.

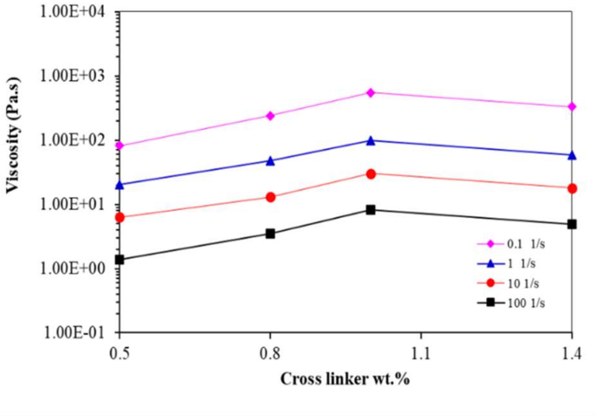

Figure 13. Influence of cross-linker concentration on gel viscosity.

5.4. Conclusion

In this chapter, the study serves a dual purpose (i) investigate the synthesis of graft copolymer nanocomposite based on hydroxypropyl guar (HPG) graft acrylamide (AM) and 2-acryloamido-2-methyl propane sulfonic acid (AMPS), reinforced with graphene oxide (GO) and (ii) study its ability for the development of the copolymer-based hydrogel systems by crosslinker to use in EOR applications. The existence of GO nanosheet and its uniform distribution throughout the graft copolymer nanocomposite was also determined using XRD, FTIR, SEM, EDX, and TEM. The rheological results presented the great performance of crosslinked hydrogel structure of HPG-g-poly (AM-co-AMPS)/GO, due to the linking of AM with AMPS and grafting on the HPG chains and the surface of GO in presence of chromium triacetate. Thermal stability results revealed a greater enhancement of the resistance to temperature for HPG-g-poly (AM-co-AMPS)/GO hydrogel as compared with the sample without GO by TGA. The influence of graft copolymer nanocomposite and crosslinker concentrations on the performance of hydrogel was also studied and optimized. This work enlightens the design of a novel graft copolymer hydrogel system with high shearing stability and temperatures in EOR applications.

Chapter 6

Conclusions and Perspectives

6.1. Conclusions

Intense research has been focused on the development of hydrogel systems for the advancements in EOR technology. This steep rise in demands can be perceived due to the exponential growth in global demand and shortage of availability of current energy sources. Energy crisis being the most affected sector, new materials and systems need to be developed to harvest and store energies efficiently. Among the various classes of materials used, gel polymer is one of the great materials to address these issues due to its versatility in structural engineering. In the thesis, this approach has been applied to expand various novel hydrogel nanocomposite characterization and properties of HPAM/HPG by IPN technique in presence of GO and also AM-based hydrogel system by graft copolymerization of AM with AMPS grafted on HPG chains and GO surface that introduces the desired properties of the strength and viscosity stability in harsh condition of the reservoir. The performance of all nano hydrogels was also evaluated by rheological tests at high salinities and temperatures. Chapter 1 introduced definitions, a brief literature review on previous works of literature and the project overview, including the general aim and specific objectives. This chapter give an idea of the objectives that are focused on the various projects undertaken in this thesis. These include (i) design an approach on addressing the issues such as enhanced oil recovery and its applications, (ii) interpenetrating polymer network and graft copolymerization technique for fabricating the polymer solution, (iii) construction of hydrogel polymers to prove the concept of forming three-dimensional structure using water-soluble polymers and cross-linker, (iv) development of AM-based gel system using the modifier monomers or natural polymers in presence of chromium triacetate for the extent of a new class of cross-linked hydrogel polymer, (v) synthesis of a GO nanosheet which consists of multifunctional sites, (vi) development of strength and viscosity of gel polymers based on nanoparticles for using in EOR applications. Chapter 2 presented the materials and methods required for the development of the project.

6.1.1. HPAM/HPG/GO semi IPN hydrogel system

To fulfill these objectives, adequate strategies were implemented to construct hydrogel systems with specific properties desired. For the semi IPN hydrogel systems in chapter 3, the mixing and reaction were employed between HPAM and HPG chains in attendance of GO as a thermal reinforcer by chemical cross-linker through hydrogen bonds. GO was selected depending on the desired properties. The obtained results have demonstrated the dependency of GO on improving the thermal and viscosity stability that was relevant to the good dispersion of GO and its interaction with polymer chains. FTIR results showed the interactions of GO surface with chains of HPAM/HPG matrix by hydrogen bonding to form the network structure**.** Understanding the uniform dispersion in the hydrogel matrix was performed by SEM. The conductivity test for further understanding of uniform dispersion of GO in the matrix to form a network structure of GOs was also done. The GO should be uniformly dispersed in the matrix to ensure the stability and homogeneity of nanofluids, resulting in an increase in the shear viscosity of the IPN hydrogel. It was observed that the addition of 0.5 wt.% of GO, did not cause much improvement in the rheology behavior of the HPAM/HPG solution. The increased temperatures caused a decrease in the viscosity of all the samples. However, the IPN nanocomposite hydrogel showed higher thermal stability than the sample without GO. The shear viscosity of HPAM/HPG/GO, after 51 min was stable, at both temperatures 200 and 240 °F, which suggests the potential applicability of semi-gel polymeric systems for oil recovery applications. Long-term aging of the nano samples was improved as compared with the sample without GO, particularly at 0.1 wt.% of GO. Therefore, it can be concluded from these results that the HPAM/HPG/GO nanocomposite hydrogel presents suitable thermal and viscosity stability which may be beneficial for use in a high-temperature reservoir. This chapter gives an insight to the scientific community on HPAM/HPG hydrogel with the helping of GO as a multifunctional agent which can be used to prepare a new class of gel polymers.

6.1.2. Poly (AM-co-AMPS)/GO copolymer nanocomposite hydrogel systems

Most of the gel polymer solutions known to date have been mainly made with acrylamide. However, its application is imitated in harsh conditions such as high temperature, salinity and shear stability. Hence, it is necessary to modify its structure to overcome such limitations/drawbacks. In order to investigate the potential of AMPS as one of the sulfonated monomer modifiers together with GO for thermal and strength enhancement, a novel copolymer nanocomposite hydrogel based on poly (AM-co-AMPS)/GO was synthesized. The synthesized copolymer hydrogel system was described in chapter 4.

This chapter mainly focuses on the synthesis and characterization of the novel hydrogel as a fluid loss controller and rheology modifier for use in oil well cementing. In addition, the influence of GO on the strength structure of copolymer nanocomposites hydrogel based on poly (AM-co-AMPS) was evaluated. The XRD, FTIR, and TGA results indicated that the AM monomer and AMPS were synthesized and grafted on the GO surface. In addition, the attendance of NMBA as a cross-linker boosts the strength of the copolymer hydrogel network structure. The morphology results showed the uniform GO dispersion in the AM and AMPS copolymer matrix. Thermal analyses were also performed on all the samples synthesized by TGA. Moreover, the results displayed that the addition of the 1 wt.% of copolymer nanocomposite hydrogel as a rheology modifier improved viscosity property, control fluid loss value, compressive strength of cement slurry, as compared to cement slurry without nanocomposite copolymer hydrogel. However, obtained results of the rheological, fluid loss controller, and compressive strength display that the crosslinked nanocomposite hydrogel has a great performance as a rheology modifier and a fluid loss controller than as a strengthening enhancer on cement slurry. This study has opened a new door for the research on synthesized GO in hydrogel copolymer systems based on AM and AMPS, making it a promising candidate for gel polymers. Abundant functionality group in hydrogel structure makes great performance in the EOR.

6.1.3. HPG-g-poly (AM-co-AMPS)/GO graft copolymer nanocomposite hydrogel system

The next objective of the thesis was to focus on the effect of prepared GO and its performance in novel hydrogel polymers systems. Chapter 5 discusses the development of the network structure of hydrogel system based on HPG-g-poly (AM-co-AMPS)/GO via graft polymerization technique using graft copolymerization of AM and AMPS onto HPG in presence of GO, and the study of its ability as a copolymer nanocomposite gel system using chromium triacetate was investigated in EOR applications. The synthesized GO was selected as a thermal reinforcer and multifunctional crosslinker. The structure and morphology of the prepared GO were characterized by scanning electron microscopy, scanning, transmission electron microscopy, FTIR and XRD. The frequency sweep tests showed that graft copolymer nanocomposite hydrogel has a predominant elastic behavior over the whole frequency range. The addition of GO improved the elastic response of the graft copolymer solution, whereas increasing GO showed an opposite effect. Differences in behavior corresponded to the interactions between the surface of the GO and the chains of the hydrogel matrix. GO nanosheet led to the formation of a gel structure, which was confirmed by the dominant storage modulus over the loss modulus (G'>G'') in the frequency range. The reduction in the incremental viscosity stability observed with the increased GO concentrations corresponded to the formation and aggregation of GO and weaken the interaction between GO and graft copolymer chains. As expected, GO enhanced viscosity and thermal stability of nanocomposite hydrogel at a temperature as high as 115 ^{0}C, and improved its rheological performance, compared to the hydrogel without GO. Furthermore, these results encouraged us to investigate the optimized gel formation in electrolyte media, then the rheology behaviors of the gel system were highly affected by the concentrations of graft copolymer nanocomposites and crosslinker. According to the results, it is concluded that HPG-g-poly (AM-co-AMPS) /GO hydrogel was developed in this study as potential injection agents which can enhance oil recovery owing to its greater viscosity and thermal stability at high temperatures.

6.2. Perspectives

This research has focused on various aspects, such as the development of a new class of polymeric materials, viscosity stability in electrolyte media and high temperature that address issues related to hydrogel systems for EOR applications. However, the following recommendations can be made for further study on the use of surface modification and developing the gel polymer system in oil recovery.

- Inspired by the novel full IPN hydrogel, synthesis of novel extended AM and AMPS with crosslinker and HPG with borate as a crosslinker can be accomplished. These new full IPN hydrogel can be an asset for the replacement of semi IPN thereby improving the desired properties of the material developed in EOR applications.

- The copolymer solution developed in chapter 5 can be further investigated for its other properties using the NMBA as a preformed particle gel. The work highlights that the network structure enhances by graft copolymerization AM and AMPS with HPG. Thus, an effort on developing new hydrogel as a copolymer solution can also be focused upon to attain various other interesting properties and can be applied in polymer flooding and also hydraulic fracturing with low concertation.
- More research is required to find the effective particle size, concentrations by using the reduced graphene oxide and its effect on the IPN or graft copolymer hydrogel structure to achieve the great cross-linked hydrogel structure with high multifunctional groups on the structure to absorb and hold a large volume of water or other aqueous fluids for several hours while being under pressure.
- In order to further develop hydrogel systems, some other interesting cross linker can also be applied with novel HPG-g-poly (AMPS-co-AM)/GO as a polymer solution. One such promising cross linker is to use the organic crosslinker-like polyethyleneimine (PEI) through covalent bonds that have interesting mechanical strength along with a suitable gel time for reservoirs of more than 125 ^{0}C to ensure proper treatment of the deeper zone of producing water.
- Another interesting class of nanoparticles that can be developed gel polymer system in the high-temperature application is to apply GO-g-modified CNT as a great thermal and multifunctional crosslinker. The degree of dispersion of GO/CNT in the polymer solution and its interfacial interaction play an important role in enhancing the properties of the polymer nanohybrids.

- One interesting area for future study consideration is the use of combinations of nanostructured materials including GO/CNT-based fluids with high thermal stability for hydrate formation. This will be of benefit to the oil and gas industry.
- However, more research is required to further understand the effect of these sorts of nanocomposite hydrogels in the reservoir in terms of operation by core flow testing, compatibility tests and contact angle test.
- The effect of oil composition and the content of divalent cations on the performance of the hydrogel require investigation.