Synthesis of Hydrogel Nanocomposites Based on Partially Hydrolyzed Polyacrylamide, Polyethyleneimine, and Modified Clay

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ABSTRACT: Polymeric gels have been an important category for material scientists due to its versatile structural features. Hence, hydrogels are being used to reduce excess production water in oil reservoirs. In this work, cross-linked partially hydrolyzed polyacrylamide (HPAM) composite hydrogels impregnated with bentonite clay (Bent) and bentonite clay modified (Orgbentent) with the surfactant hexadecyltrimethylammonium bromide were synthesized and characterized as a sealing agent in high water producing permeable zones in the petroleum industry. The concept of utilizing hydrophobically modified clay as an inorganic additive in the hydrogel matrix emanates from the fact that this additive exhibit greater interaction with the polymer chains. These interactions can promote the inherent properties of the hydrogel. Polyethyleneimine (PEI) was chosen as the cross-linking agent. HPAM/PEI conventional hydrogels and HPAM/PEI/Bent and HPAM/PEI/Orgbent at 100 mg L\(^{-1}\) clay were synthesized. The developed hydrogels were characterized by a hybrid rheometer and Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) instruments. Rheological results reveal that the (HPAM/PEI/Bent-3 and HPAM/PEI/Orgbent-3) composite hydrogels showed higher elastic modulus (\(G'\)) and durability in the studied conditions (stable at 30 days) than conventional ones (HPAM/PEI), indicating the dispersion and reinforcing effect of clay. The functional groups of these hydrogels were confirmed by FTIR, and TGA demonstrated the structural reinforcement due to the presence of the clays, which had lower weight loss than the conventional hydrogel. The hydrogel morphologies were analyzed by SEM, and the results corroborated with those obtained by TGA, indicating better structural reinforcement when using organophilic clay.

1. INTRODUCTION

Water shut-off techniques are used for reducing water cuts in oil fields,\(^{1,2}\) which have drawn considerable attention recently due to extensive water production in mature oil fields.\(^{3}\) Reservoirs with induced fractures or high permeability channels, commonly called thief zones or streaks, are quite common in mature fields due to extensive water flooding.\(^{4,5}\) Consequently, this problem promotes low oil recovery and excessive early water production in these regions.\(^{5,6}\)

For the past decades, polymer gels have been shown as a remarkable category for material scientists because of their versatile structural characteristics, which have awakened many scientific researches involving development, evaluation, and application in the most diverse areas.\(^{7−11}\) Particularly, polymeric hydrogels are said to be hydrophilic semisolids whose three-dimensional (3D) structure involves a liquid part responsible by its elastic character.\(^{12}\) In general, it has (i) infinite molecular weight, (ii) are insoluble and not fusible, and (iii) has the ability to swell reversibly.\(^{11,13}\)

Because of these characteristics, hydrogels have been used to prevent and reduce the excessive water production in hydrocarbon reservoirs, and it is one of the most effective and practical techniques applied for this purpose.\(^{8,14−16}\) This chemical technique is capable of plugging fractures and high permeability zones, enhancing oil sweep efficiency, and achieving a successful conformance control.\(^{17}\) In this method, in situ gels are injected into the reservoir to form a 3D gel network structure under reservoir conditions (temperature, salinity, and pH) that will reduce permeability.\(^{18,19}\)

The major difficulties of this technique are related to the lack of control in gelation time, gelling dilution, components loss by adsorption on the rocks during injection, and, mostly, the destabilization due to severe conditions.\(^{6,16}\)
Therefore, the obstacles found for the application of gelling solution guide the need of adapting these materials for use. Thus, hydrogel nanocomposites have been widely studied because it has better properties compared to conventional ones. In addition, hydrogel nanocomposites present better thermal and mechanical stabilities, which improve the oil recovery efficiency.10,20–22

In order to improve the performance of these sealant agents, studies have been developed through the insertion of reinforcing fillers in the structures of these materials. Among the most mentioned are carbon nanotubes,31–33 nanosilica,10,28–31 coal fly ash,9,22,32,33 and clays.13,34–41 Chen et al.31 observed that nanosilica decreased the gelation time and increased the rigidity of the polyacrylamide/polyethyleneimine hydrogels. The same was observed by Aalaie et al.13 when developing hydrogels with montmorillonite clay. The polymer chains aggregate the clay surface in order to interact with single clay platelets at several points of their extension. As a consequence, the formation of a single polymer–clay structure promotes changes in the characteristics of the materials.42

The use of organic modified fillers was mentioned by Helvacioglu and co-workers,35 which were used to improve the performance of polyacrylamide hydrogels, while Rezaei et al.43 used similar organic fillers in partially hydrolyzed polyacrylamide polymer dispersions (HPAM), where improvements were observed in their fluid properties.

The present work introduces a hydrogel nanocomposite synthesized from partially hydrolyzed polyacrylamide (HPAM), polyethyleneimine (PEI) as a cross-linker, and modified or unmodified bentonite clay as fillers. Moreover, the effects of cross-linker and modified and unmodified bentonite clay concentrations were investigated in salinity and temperature reservoir conditions. Finally, rheological tests were performed to determine the strength of the hydrogel nanocomposites.

2. EXPERIMENTAL PART

2.1. Materials. Partially hydrolyzed polyacrylamide (HPAM) with an average molecular weight of 8 × 10⁶ g/mol (hydrolysis degree of 30%) was provided by SNF FLOERGER, with trade name FP330S. Branched polyethyleneimine (PEI) with an average molecular weight of 25,000 g/mol was purchased from Sigma-Aldrich to work as an organic cross-linker. The clay used in this work was sodium bentonite clay (Na⁺-Bent), predominately montmorillonite, with a trade name of Argel-40, provided by Bentonit Uniao Nordeste Indústria e Comercio Ltda. Argel-40 is a natural sodium bentonite with high mineralogical purity with a cation exchange capacity (CEC) of 110 meq/100 g. Table 1 presents the physical and chemical properties of the bentonite clay.

Hexadecyltrimethylammoniumbromide with ≥98% purity was also used, provided by Sigma-Aldrich (SP, Brazil), and used as received.

2.2. Chemical Modification of Bentonite Clay. The sodium bentonite clay has metallic ions occupying the interlayer space. With the addition of hexadecyltrimethylammonium bromide surfactant, these ions were replaced by surfactant molecules. This methodology was based on Calderon et al.44 and Ezquerro et al.45 Initially, 5 g of sodium bentonite was dispersed in 500 mL of deionized water under continuous stirring (25 °C) over 24 h. Then, an aqueous solution of quaternary ammonium salt was added to the suspension containing sodium bentonite at a concentration equivalent to 100% CEC and kept under stirring for 24 h. After that, the suspension was filtered and washed several times with distilled water to remove bromide residues. The organophilic clay was then dried at 50 °C for 72 h, milled, and stored at room temperature. The clays were milled and sieved to 200 mesh and used without purification.

Table 1. Physical and Chemical Properties of Bentonite Clay

| physical and chemical properties (average values) |
|-----------------------------------------------|
| appearance | light yellow |
| water content | 9.0–13.0% |
| swelling capacity (2.0 g/100 mL) | 35 |
| pH (2.0 g/100 mL) | 7.5 |
| cation exchange capacity (CEC) | 110 meq/100 g |

| chemical analysis (average values) |
|-----------------------------------|
| SiO₂ | 62% |
| Al₂O₃ | 19% |
| Fe₂O₃ | 3% |
| MgO | 2% |
| CaO | 2% |
| Na₂O | 2.5% |
| TiO₂ | <1% |
| K₂O | <1% |

The bentonite clay was characterized after the modification to determine the efficiency of this procedure using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The hydrogel samples were evaluated at 1, 7, 15, and 30 days as follows: gel strength was determined through the bottle test described at Table 4,46 rheological behavior, FTIR, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) analysis.

2.4. Characterization Methods. The bentonite clay was characterized after the modification to determine the efficiency of this procedure using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The hydrogel samples were evaluated at 1, 7, 15, and 30 days as follows: gel strength was determined through the bottle test described at Table 4,46 rheological behavior, FTIR, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) analysis.

2.4.1. Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra of the samples were obtained by a Frontier FTIR/FIR spectrometer in the range of 4000 to 400 cm⁻¹ using

Table 2. Chemical Composition of Injection Water

| composition | concentration (mg·L⁻¹) |
|-------------|-----------------------|
| Na⁺/K⁺     | 11,309                |
| Ca²⁺       | 117                   |
| Mg²⁺       | 109                   |
| SO₄²⁻       | 5                     |
| HCO₃⁻       | 64                    |
| Cl⁻         | 17,756                |
| total       | 29,360                |
the KBr pellet method for clays and attenuated total reflectance method (ATR) for the hydrogels dried after 15 days of aging. Spectra were taken with a resolution of 4 cm⁻¹.

2.4.2. X-ray Diffraction (XRD). XRD analyses were performed with a Diffrac Plus v1.01 model (Bruker) wide-angle X-ray diffractometer (XRD) with Cu anode running at 40 kV and 30 mA, scanning from 4° to 20° at 2° min⁻¹.

2.4.3. Gel Strength Code. The bottle test was used to obtain a semiquantitative analysis of the gelation time, final consistency, and strength reached by the hydrogel over the aging time. In this work, the gel characterization was denoted by alphabetic codes from A to G.¹⁰,¹⁹

In this context, “code A” refers to a fluid state solution without changes in initial viscosity, and the advancement of these codes indicates changes in the state of this solution. For example, “code B” indicates a highly flowing gel, “code C” indicates a few flowing gel, “code D” a moderately flowing gel where a portion of the gel (about 5–15%) does not flow to the bottle cap upon inversion, “code E” shows a barely flowing gel where a small portion of the gel stays at the bottom at inversion, “code F” is an indication of a highly deformable nonflowing gel, and “code G” is a moderately deformable nonflowing gel.

2.4.4. Rheological Analysis. (i) Injectivity: The viscosity of gelling solutions was obtained to evaluate the injection capacity of the solutions in application conditions, where the shear rate was between 1 and 400 s⁻¹ at a temperature of 30 °C.

(ii) Viscoelastic behavior: Dynamic oscillatory measurements were used, varying the frequency from 0.1 to 100 Hz, with a fixed deformation of 1% at 70 °C to obtain the viscoelastic behavior of hydrogels samples. The rheometer used was the Discovery Hybrid Rheometer-3 from TA Instruments with parallel-plate geometry. Previous studies demonstrated that this geometry offers better measurement reproducibility of viscous modulus and elastic modulus for polymer gels.

2.4.5. Thermogravimetric Analysis (TGA). TGA curves were realized using a TGA Q500 V6.7 Build 203 in a nitrogen atmosphere up to 700 °C at a heating rate of 10 °C/min.

2.4.6. Scanning Electron Microscopy (SEM). The surface morphology of the dried hydrogels was observed by scanning electron microscopy (SEM) by the Hitachi TM3030Plus instrument at 15 kV voltage.

3. RESULTS AND DISCUSSION

3.1. Characterization of Bentonite Clay and Organo-clay. 3.1.1. X-ray Diffraction (XRD). Figure 2 shows the XRD patterns of the bentonite clay before and after modification with hexadecyltrimethylammonium bromide surfactant where it was observed that, after modification of the clay, the main diffraction peak shifts to smaller angle values, proving the intercalation of organic cations between silicate layers.

For the unmodified bentonite, two diffraction peaks are seen in the low angle region: the main one is at 2θ = 6.85°, and the other at 2θ = 13.48° referring to a smaller crystalline phase. For the modified bentonite, only one peak was observed at 2θ = 4.98°, showing that the modification contributed to a structural

Table 4. Gel Strength Code for the Samples Evaluated as a Function of Aging Days

| samples           | HPAM (mg·L⁻¹) | PEI (mg·L⁻¹) | clay (mg·L⁻¹) | day 1 | day 7 | day 15 | day 30 |
|-------------------|---------------|--------------|---------------|-------|-------|--------|--------|
| HPAM/PEI-1        | 5000          | 1000         | 0             | A     | D     | D      | D      |
| HPAM/PEI-2        | 5000          | 1600         | 0             | A     | F     | G      | G      |
| HPAM/PEI-3        | 5000          | 2200         | 0             | A     | G     | G      | G      |
| HPAM/PEI/Bent-1   | 5000          | 1000         | 100           | A     | E     | E      | E      |
| HPAM/PEI/Bent-2   | 5000          | 1600         | 100           | A     | H     | H      | H      |
| HPAM/PEI/Bent-3   | 5000          | 2200         | 100           | A     | H     | H      | H      |
| HPAM/PEI/Orgbent-1| 5000          | 1000         | 100           | A     | B     | C      | D      |
| HPAM/PEI/Orgbent-2| 5000          | 1600         | 100           | A     | E     | E      | E      |
| HPAM/PEI/Orgbent-3| 5000          | 2200         | 100           | A     | G     | G      | G      |

Codes: A, no detectable gel formed; B, highly flowing gel; C, flowing gel; D, moderately flowing gel; E, barely flowing gel; F, highly deformable nonflowing gel; G, moderately deformable nonflowing gel and H, slightly deformable nonflowing gel.¹⁶
modifications. The main peak corresponds to the interplanar distances between clay layers, which were calculated by the Bragg equation:

\[ n \lambda = 2d \sin \theta \]

where \( \lambda \) is the wavelength used (0.179 nm), \( \theta \) is the half of diffraction angle in the main peak (obtained by \( 2\theta / 2 \)), and \( d \) is the calculated basal space between clay layers. Using the Bragg equation, the basal spacing \( d_{(001)} \) values of unmodified and organophilic clays were 1.51 and 2.06 nm, respectively. The \( d_{(001)} \) of sodium clay found is characteristic of a hydrated montmorillonite. The XRD patterns show that, after modification of the sodium clay with quaternary ammonium salt, the diffraction peaks shift to smaller angle values, proving the intercalation of the organic cations between the silicate layers.47,48

3.1.2. Fourier Transform Infrared Spectroscopy (FTIR).

The FTIR spectra of bentonite clay before and after modification with hexadecyltrimethylammonium bromide surfactant are shown in Figure 3. The spectra show the presence of peaks at 3635 and 3434 cm\(^{-1} \), which define the bands related to the free and/or combined OH group. The presence of H\(_2\)O is confirmed by the absorption at approximately 1650 cm\(^{-1} \), corresponding to the H–O–H angular deformation.49 These are present in both unmodified and modified clays. The spectra also have peaks at 1035 cm\(^{-1} \), characteristic of asymmetric Si–O stretching, Si–O, and O–Al vibration at 720 and 520 cm\(^{-1} \), respectively. The presence of the same peaks in all samples indicates that the structures of the modified clay samples were maintained after organophilic treatment. The FTIR spectra of the modified clays contain a pair of bands between 2851 and 2924 cm\(^{-1} \), which result from asymmetric and symmetric vibration C–H stretching of the CH\(_3\) and CH\(_2\) groups present in the amine chains and the angular deformation of CH\(_2\) group at 1470 cm\(^{-1} \).50 The appearance of these peaks confirms the organophilization of the clay.

3.2. Injectivity Evaluation of Gelling Solution.

The viscosity profiles of the gelling systems (before gel formation) were obtained in order to evaluate the injection capacity and propagation of these systems in the reservoirs. During the pumping of the fluid into the reservoir, higher shear rates can be found (above 300 s\(^{-1} \)), while for the fluid propagation inside of the reservoir, the shear rates are very low (less than 20 s\(^{-1} \)).51 Thus, the purpose of this test was to evaluate the applicability of the gelling solutions developed in relation to its injectivity considering 30 mPa\(\cdot\)s as an ideal viscosity for injection according to some studies.52,53 The viscosity values of the samples were obtained by flow curves, as shown in Figure 4.

The gelling systems showed a pseudoplastic behavior during all evaluated shear rates. For lower shear rates, it was observed that the fluids presented greater resistance to flow due to the hydrogen-bonding interactions, entanglements of the polymer and cross-linker chains, and intra- and intermolecular electrostatic repulsions promoted between components. For higher shear rates, the viscosity of the fluid is less dependent on shear and may be observed a moderate pseudoplastic behavior that is extremely desirable to ensure a good injectivity of the gel.51 The viscosity of the gelling solutions with and without clays was 18.0–19.1 mPa\(\cdot\)s considering a shear rate of 300 s\(^{-1} \). However, at a lower rate (10 s\(^{-1} \)), the viscosity values of the fluids were between 67.5 and 76.9 mPa\(\cdot\)s.

3.3. Viscoelastic Behavior of the Hydrogels.

To examine the cross-linking properties at 70 °C, three types of hydrogels (HPAM/PEI, HPAM/PEI/Bent, and HPAM/PEI/Orbent) were employed in these experiments with a polymer concentration of 5000 mg L\(^{-1} \). PEI concentrations were from 1000 to 2200 mg L\(^{-1} \). Initially, the cross-linking process was monitored qualitatively through visual observation by using bottle testing. Sydansk’s gel strength code was used for assigning the gel strength. Table 4 shows the effect of cross-
linker concentration and the influence of the clay on the gelation rate and gel strength with time.

The gelation time is an important parameter for choosing the gelling system because it needs to be higher than the period required to inject the solution into the reservoir in order to guarantee the safety of the operation and also its ability to penetrate high region permeability. At the aging time of 1 day, the systems did not show a gel characteristic, suggesting that the cross-links and entanglements between the polymers molecules were insufficient to change the condition of the gelling solution. This fact is correlated with the type of interaction because, in the case of PEI, it is kinetically slow and occurs through the formation of covalent bonds by the transamidation mechanism, which involves direct interconversion of the amide group present in HPAM with the amine group present in PEI, resulting in cross-linking between macromolecules.

Thus, within the pre-established conditions of temperature, salinity, and component concentration, the samples showed only a significant change in viscosity after 24 h. From a practical point of view, this allows these materials to penetrate into deeper regions of the reservoirs, presenting a good safety time for the gelation process.

For the three systems, a higher gel strength can be achieved with increasing the PEI concentration above 1600 mg L\(^{-1}\). The high PEI concentration can increase the chance of PEI attacking the carbonyl carbon attached to the amide group. Therefore, increasing the PEI concentration is not recommended by using the targeted gel. On the contrary, the higher cross-linker concentration can greatly impact the gel stability for gel syneresis due to the excessive cross-linking characteristic.

At the period of 7–30 days, the hydrogels did not present significant visual variations, as shown in Figure 5. This indicates a stable plateau of the gelling process being related to the consumption kinetics of the cross-linking agent.

![Figure 5. Visual appearance of the hydrogels at the aging times of 7 and 15 days in the order previously presented.](https://dx.doi.org/10.1021/acsomega.9b02829)

3.3.1. Influence of Clay in Rheological Properties. Figure 6 shows the curves of elastic modulus (\(G'\)) and viscous modulus (\(G''\)) as a function of frequency for the conventional and nanocomposite hydrogel samples obtained with the highest cross-linker concentration (2200 mg L\(^{-1}\)) at days 1, 7, 15, and 30.

At the aging time of 1 day, the systems presented that the \(G''\) is higher than \(G'\) at low-frequency values. This indicates the presence of a viscous liquid material, where much of the fluid energy is dissipated. At high-frequency values, the component \(G'\) exceeds \(G''\), and the fluid begins to behave as an elastic solid material. This viscous–elastic transition is indicated by the cross-point of the curves \(G'\) and \(G''\) (around 2 Hz), which is a typical behavior of concentrated polymer solutions, where there is a large amount of entanglement between the macromolecules (Figure 6a).

This behavior is related to the ability to recover the equilibrium configuration by molecular Brownian motion, where, at low oscillatory frequencies, the polymer chains are capable of recovering the initial configuration, behaving like viscous liquids (\(G'' > G'\)). On the other hand, at higher frequency values, the oscillation becomes faster, and the macromolecules cannot be disentangled, behaving temporarily as if they were reticulated (entanglements). Therefore, the way to accommodate the energy stored in the system is through the deformation of the formed network, resulting in the elastic behavior above the cross-point.

At the aging time of 7 days, the samples exhibited the predominant elastic modulus, which confirms the formation of a characteristic three-dimensional gel network. At this time, supposed that \(G'\) represents the amounts of interactions PEI–HPAM and Clay–HPAM and entanglements between the macromolecules, consequently, it shows a higher elastic modulus, all on the same level. Also, the viscous modulus (\(G''\)) may represent the amount of chains in the free state; for this reason, the conventional material (HPAM/PEI-3) exhibited a slightly higher viscous modulus. By comparison, this is specifically related to the contribution of the amount of cross-linking points through clay–polymer interactions of the samples HPAM/PEI/Bent-3 and HPAM/PEI/Orgbent-3.

According to Haraguchi et al., the mechanism of interaction of polyacrylamide and clays occurs through hydrogen bonds between the oxygen atoms present in the clay structure and the protons of the amide group of the polymer. However, in addition to this interaction, since HPAM is an anionic polymer, ionic interactions may also occur with bentonite, which has positive charges on the surface. This justifies a lower viscous modulus of these materials at 7 days.

At 15 days of aging time, the nanocomposites exhibited that the \(G'\) is higher than the conventional hydrogel in the oscillatory frequency range of 1–10 Hz. So, HPAM/PEI/Orgbent-3 exhibited an elastic character slightly higher than the HPAM/PEI/Bent-3 sample probably due to the surfactant molecules present in the clay surface that interact with the polymer chains of HPAM. This difference was better observed at the 30 days of aging, where the \(G'\) of the HPAM/PEI/Orgbent-3 sample was noticeably larger than the \(G'\) of the HPAM/PEI/Bent-3 sample.

Therefore, it has been suggested that the mechanism of interaction of the HPAM/PEI/Orgbent nanocomposites also occurred by van der Waals interactions since the modified cation adsorbed in bentonite has alkyl chains in its structure. In addition, the organic clay promoted a better compatibility of bentonite as an additive to the polymer dispersion (visually compared), obtaining a better response in this property.

Other studies in the literature also showed that the addition of nanoparticles in gel systems increased the elastic property more significantly than the viscous property, indicating that the dynamic adsorption/desorption equilibrium with the polymer chains promotes a greater elasticity in the material.
The evaluation at day 30 showed in fact the superiority in the viscoelastic behavior of the nanocomposite hydrogels against the conventional hydrogel since this latter presented a drastic fall in the elastic modulus with the crossing of $G''$ and $G'$ curves, which indicates the flow state of the material and the possible breaking of its three-dimensional polymer network.

In contrast, the nanocomposite hydrogels exhibited the same plateau in the curve from the viscous modulus, while the $G'$ of HPAM/PEI/Orgbent-3 remained higher, like day 15. This shows the largest number of interactions in this system compared to HPAM/PEI/Bent-3. This observation can be attributed to the different types of interactions of conventional and nanocomposite hydrogels. In the first case, the mechanism is necessarily influenced by the cross-linking agent, while the nanocomposites have the synergistic effect of PEI and clay.

3.3.2. Stability of Conventional and Nanocomposite Hydrogels. Figure 7 shows the $G'$ values of HPAM/PEI, HPAM/PEI/Bent, and HPAM/PEI/Orgbent samples as a function of frequency at the aging times from 1 to 30 days.
allowing us to evaluate the elastic character in different times to the three samples studied.

As previously described, on the first day, the samples did not show a gel behavior. At 7 days, the rheological parameter $G'$ increased significantly due to the cross-linking process, becoming highly independent of the frequency, where, in all cases, the $G'$ was close to 10 Pa in the frequency range of 1–10 Hz. Some studies in the literature indicate that this behavior is found in most gels that presented a rigid structural state, with good organization and three-dimensional perfection.51,58

Commonly observed for frequency values above 10 Hz, the behavior of $G'$ showed variation with frequency. Some authors relate this effect to the breaking of a hydrogel 3D structure due to the increase in the amount of oscillations per unit of time, where the energy superimposed on the surface promotes the destruction of internal connections.51,59

At the aging time of 15 days, the $G'$ of the HPAM/PEI-3 sample remained in the same region of the evaluation of the aging time of 7 days, indicating that there was stabilization under the contribution of the amount of molecular interactions. Therefore, it is suggested that, in this period, all species of cross-linking agent (PEI) had already been consumed.

However, at the time of 15 days, the HPAM/PEI/Bent-3 and HPAM/PEI/Orgbent-3 samples still showed an increase in $G'$, which is related to the greater number of interaction sites promoted by the clay. In this way, PEI and clay would be contributing synergistically to the interactions between the macromolecules of HPAM. Some studies showed that this is related to the high interaction of polyacrylamide chains and clay so that they are fixed in the gel structure as additional interaction sites (polymer–clay).34,36

On day 30, the viscoelastic analysis of the conventional sample (HPAM/PEI-3) showed an abrupt drop of $G'$ modulus at low frequencies, and it was also observed that there is a great variation of $G'$ with the increase in oscillatory frequency, indicating destabilization of the hydrogel. On the other hand, both hydrogel nanocomposites presented the elastic modulus still independent of the frequency, showing the stability of these materials until the last evaluated time, although these hydrogels already show signs of destabilization since $G'$ of 30 days < $G'$ of 7 days.

Therefore, the nanomaterials presented a reinforcement capacity of the 3D network structure at the studied conditions, altering the stability of the hydrogel produced. From a practical point of view, it would guarantee a longer blocking time in fractured oil reservoirs compared to conventional hydrogels. However, in this study, no significant difference was observed between the systems composed of modified clay HPAM/PEI/Orgbent-3 and unmodified clay HPAM/PEI/Bent-3.

### 3.3.3. Influence of Cross-Linking Concentration in the Viscoelastic Behavior

**Figure 8** shows the elastic modulus and viscous modulus as a function of frequency for HPAM/PEI, HPAM/PEI/Bent, and HPAM/PEI/Orgbent samples at cross-linking concentrations of 1000, 1600, and 2200 mg·L$^{-1}$.

The cross-linking concentration is one of the responsible factors that change the gelling kinetics. This happens because, at high concentrations of PEI, a greater amount of chains is dispersed in the solution, which facilitates the encounter with the HPAM molecules, promoting the occurrence of cross-links.

A study by Jia and co-workers50 reported the influence of the cross-linking concentration, where the increase in its concentration contributed to a greater stiffness of the hydrogel due to a greater occurrence of intermolecular bonds.

On day 30, the viscoelastic analysis of the conventional sample (HPAM/PEI-3) showed an abrupt drop of $G'$ modulus at low frequencies, and it was also observed that there is a great variation of $G'$ with the increase in oscillatory frequency, indicating destabilization of the hydrogel. On the other hand, both hydrogel nanocomposites presented the elastic modulus still independent of the frequency, showing the stability of these materials until the last evaluated time, although these hydrogels already show signs of destabilization since $G'$ of 30 days < $G'$ of 7 days.

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**Figure 8.** Elastic modulus ($G'$) and viscous modulus ($G''$) for the samples (HPAM/PEI, HPAM/PEI/Bent, and HPAM/PEI/Orgbent) with different cross-linking concentrations at 15 days.

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happens because PEI is at low concentrations, which decreases the number of molecules that are available to form cross-links, contributing to fewer interactions.

Nanocomposite hydrogels with higher cross-linking concentrations (1600 and 2200 mg L\(^{-1}\)) had a higher \(G^\prime\) modulus because of the greater number of cross-links in this period. However, HPAM/PEI/Orgbent-3 showed a higher value of elastic modulus since the organically modified clay may have promoted van der Waals interactions of hydrogen bonds with clay-HPAM and clay-PEI, increasing significantly the behavior of the elastic nature of these samples.

3.4. Fourier Transform Infrared Spectroscopy (FTIR) of Hydrogel Nanocomposites. The chemical structures of the hydrogels were characterized by Fourier transform infrared spectroscopy, and FTIR spectra of the conventional HPAM/PEI hydrogel and nanocomposite hydrogels with unmodified bentonite (HPAM/PEI-Bent) and organophilic bentonite (HPAM/PEI-Orgbent) are shown in Figure 9. The conventional HPAM/PEI hydrogel presented a characteristic band of OH and NH\(_2\) groups at 3380 cm\(^{-1}\), small stretching vibrations of methyl groups at 2939 cm\(^{-1}\), and bands at the regions of 1659 and 1548 cm\(^{-1}\) corresponding to the C=O group and angular deformations of N–H, respectively.\(^{22,61}\) In addition, a low intensity band at 1456 cm\(^{-1}\) attributed to NH\(_2\) (amide) bending and C–N amide stretching vibrations at 1411 cm\(^{-1}\).\(^{1,22}\)

The nanocomposite hydrogels exhibited the same absorption bands demonstrated for the conventional hydrogel; however, they presented long peaks and with higher intensities. At values close to 3600–3400 cm\(^{-1}\), the enlargement was due to vibrations of stretching of O–H groups between the octahedral and tetrahedral sheets of the clay and the vibrations of water molecules hydroxyls (–OH) located between the layers of the clay, which were not removed in the drying of the hydrogels, and at 1649 cm\(^{-1}\), an increase in peak intensity occurred due to the band of the flexural vibration of the Si–O–Si characteristic of the bentonite.\(^{49,61}\) Comparing the nanocomposite systems, it was observed that the HPAM/PEI-Orgbent hydrogel presented CH\(_2\) asymmetric and symmetric stretching vibrations at 2924 and 2851 cm\(^{-1}\), which prove the presence of alkyl chains of the surfactant; axial deformation of the C–N group of aliphatic amines at 1174 cm\(^{-1}\) is also characteristic of the surfactant used for the modification of the clay according to the literature.\(^{48,50}\) Thus, it can be verified that the incorporation of the organophilic clay and unmodified bentonite occurred satisfactorily in hydrogels.

3.5. Thermogravimetric Analysis of Hydrogels. The thermogravimetric analysis of the HPAM/PEI-3, HPAM/PEI/Bent-3, and HPAM/PEI/Orgbent-3 samples clearly demonstrates the thermal stability of nanocomposite materials. In Figure 10, a loss of moisture was observed from the beginning of heating to near 160 °C. After that, it was observed that there is the loss of ammonia released from the transamidation reaction between the amide groups of the HPAM chains and the amines of the PEI.\(^{62}\) The most significant mass loss occurred at 300 °C, which was attributed to the structural breakdown of the polymer chains and the intermolecular bonds between HPAM-PEI. From this temperature, it was observed that the nanocomposite hydrogels were less susceptible to degradation than the conventional ones (HPAM/PEI-3), which was attributed to the strong interactions between the clays with the polymer molecules. Hence, it appears that thermal stability of hydrogel increased by incorporation of bentonite and organic bentonite, perhaps due to the resistance to heat by clays present inside the hydrogel network.

3.6. SEM Analysis. The morphologies of the fully dry samples were analyzed by the scanning electron microscopy (SEM) instrument. The SEM micrographs of HPAM/PEI-3, HPAM/PEI/Bent-3, and HPAM/PEI/Orgbent-3 consolidate the results obtained in the rheological sections. In Figure 11a,b, HPAM/PEI-3 hydrogels, a continuous polymer network is not observed, indicating a possible fragile 3D structure, without junction points and low cross-link density. In Figure 11c,d, the HPAM/PEI/Bent-3 hydrogels, it is possible to observe the polymer structure with some interaction points but a little dense network. Further, a large porosity is observed, which may be related to the lower affinity of the unmodified clay. In Figure 11e,f, HPAM/PEI/Orgbent-3 shows a continuous network with few pores and a high polymer density. In both hydrogels with clays, no evidence of agglomerations from the clay mineral was seen. This analogy corroborated with the previous results, visually showing the greatest strength of hydrogels with modified clay. Previous studies on reinforced
nanocomposite hydrogels have reported similar SEM results.\textsuperscript{22,63,64}

4. CONCLUSIONS

In this work, partially hydrolyzed polyacrylamide (HPAM)-based hydrogels impregnated with bentonite clay (Bent) and bentonite clay modified (Orgbent) with the surfactant hexadecyltrimethylammonium bromide were developed and characterized as a sealing agent for high water producing zones in mature oil fields in petroleum industries. Polyethyleneimine (PEI) was used as the cross-linking agent. HPAM/PEI conventional hydrogels and HPAM/PEI/Bent and HPAM/PEI/Orgbent at 100 mg·L\textsuperscript{−1} clay were fabricated. The viscoelastic and thermal properties as well as the structural and morphological properties of these hydrogels were studied in detail. It was demonstrated that the use of bentonite and organic bentonite clays as reinforcement fillers in HPAM/PEI-based systems was a success. In terms of injectivity, these materials did not alter the viscosity of the solutions, which is considered an important factor for operational issues.

The gel strengths determined via rheological approach showed that (HPAM/PEI/Bent-3 and HPAM/PEI/Orgbent-3) hydrogels containing clay were practically more elastic than the HPAM/PEI conventional hydrogels, which can be attributed to the additional points of interaction of the clay with the HPAM chains. The nanocomposite formed with organic bentonite (HPAM/PEI/Orgbent-3) showed better stability (remaining stable at 30 days). FTIR analysis confirmed the chemical structures in all the hydrogels. TGA analysis revealed that the nanocomposite hydrogels were less susceptible to degradation than the conventional ones (HPAM/PEI-3). The SEM micrographs confirmed the results obtained in the thermogravimetric and rheological analyses, indicating that the addition of nanofillers provided an increase in the hydrogel strength and the system prepared with organophilic clay presented a denser structure with the absence of porosity and, consequently, more reinforcement, and this is due to the greater interaction of the modified bentonite with the polymer matrix.

Lastly, the variation in the content of the cross-linking agent also showed influence on gelation in the achieved state of the gels and, especially, on the elastic character acquired by these materials.

Figure 11. SEM micrographs of (a, b) HPAM/PEI-3, (c, d) HPAM/PEI/Bent-3, and (e, f) HPAM/PEI/Orgbent-3 hydrogels at 7 days of aging.
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Notes
The authors declare no competing financial interest.

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