Artigo Científico

RHEOLOGICAL AND THERMAL EVALUATION OF POLYACRYLAMIDE HYDROGEL PROPERTIES WITH ALUMINUM OR ZINC OXIDE

Avaliação reológica e térmica das propriedades do hidrogel à base de poliacrilamida com óxido de alumínio ou de zinco

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ABSTRACT

The increase in demand for oil-based energy and the difficulty in discovering new oil reserves mean that mature reservoirs need to be optimized. These reservoirs have already been widely explored and often have fractures or zones with high permeability contrasts. In these scenarios, the injected recovery fluids tend to flow preferentially, resulting in lower sweeping efficiency and lower oil production. To avoid these problems, conformance control techniques have been used to optimize reservoir sweep. This process works redirecting the injected fluids to the lower permeability segments, which increase the sweep efficiency. Polymeric hydrogels can work by blocking high permeability zones, and these systems consist of hydrophilic polymers, where polyacrylamide derivatives are the most common. To enhance the applicability in drastic reservoir conditions, gels nanocomposites can be produced with novel properties. This work approached the research for the best composition of the polyacrylamide derivative crosslinked with polyethyleneimine and evaluated the addition of zinc or aluminum oxide nanofillers. The study evaluated different oxides contents in terms of mechanical, thermal properties and morphology. The results showed that increasing the ZnO filler provided higher elastic modulus and thermal degradation resistance. These observations correlated with the microscopies, which showed better zinc oxide interaction with polymer matrix.

Keywords: Conformance Control; Polymer Hydrogel; Nanocomposite; Rheology; Thermogravimetry.

INTRODUCTION

Oil is obtained from oil reservoir rocks and the production process of oil can be carried out from onshore or offshore platforms, the operational processes being different, mainly in relation to the equipment used. Despite this fact, the extraction techniques are equivalent, with primary, secondary, and advanced oil extractions being performed (AGUIAR *et al.*, 2020; SHAMSIJAZEYI *et al.*, 2014). In the primary recovery, extraction occurs through the internal pressure of own reservoir, while in the secondary and advanced recovery, production proceeds by injecting fluids to accentuate the oil sweep and displacement (TONGWA & BAOJUN, 2015). In secondary recovery, water, carbon dioxide or both are used, whereas in enhanced oil recovery additives are added to the composition of these fluids (LAKATOS & LAKATOS-SZABO, 2008).

Nonetheless, even with the extraction techniques available, a significant oil volume that could be produced remains in the reservoir. This occurs due the recovery injected fluids flow through higher permeability zones, resulting in retained oil that could be produced in lower permeability zones (NAYAK & DAS, 2018; EL-KARSANI *et al.*, 2014; ABDULBAKI *et al.*, 2014). For this purpose, conformance control method can be used to modify the reservoir rock profile and optimize the oil production. This provides a better sweep efficiency after the injection fluids treatment (BAI *et al.*, 2015).

The operation of this device consists in the product insertion by the injection fluid, which follows the displacement to the areas of highest permeability and forms a blockage. As a result, the fluids injected after treatment will move to lower permeability spots and have greater sweeping efficiency (PEREIRA *et al.*, 2022; FRAGA *et al.*, 2020; LIU *et al.*, 2010; AL-MUNTASHERI, 2012).

A polymeric hydrogel is a chemical device that can potentially be used for this purpose. This material is formed by combining a hydrophilic polymer and a crosslinking agent, which can be inorganic or organic. Among the studied systems, there are in situ application hydrogels, when the crosslinking step occurs inside the reservoir, i.e., the gel components are injected and formed inside the wellbore (MENDES *et al.*, 2023; PEREIRA *et al.*, 2020; BAI *et al.*, 2013; GOUDARZI *et al.*, 2015).

Due to the drastic conditions of oil reservoirs, gels have some limitations regarding thermal and salinity tolerance (TANWAR *et al.*, 2021; ADEWUNMI *et al.*, 2018; SAGHAFI *et al.*, 2016). In view of this, nanoparticles are being used in the composition of hydrogels for the development of nanocomposites with greater resistance to exposed conditions (LASHARI *et al.*, 2018; AMARAL *et al.*, 2019).

Therefore, this work proposes to find the preferable composition of polymer and crosslinker for those evaluated and to study the inclusion of ZnO and Al_2O_3 reinforcing fillers in the gel composition to improve these properties to optimize applicability. The polyacrylamide in the 30% hydrolyzed form, named partially hydrolyzed polyacrylamide (HPAM), and polyethyleneimine (PEI) were used. PEI is a good alternative of crosslinker due to water solubility, low toxicity and having its interaction mechanism well defined through the mechanism of transamidation (AGUIAR *et al.*, 2020; PEREIRA *et al.*, 2020).

MATERIAL AND METHODS

Materials

Partially hydrolyzed polyacrylamide (HPAM) with molar mass M_w 4.8x10^6 (FP 3130S) and degree of hydrolysis between 25-30%, was provided by SNF Floerger®Brazil (São Paulo, Brazil). Branched polyethyleneimine with M_w of 25.000 g.mol^{-1}, purchased from Sigma-Aldrich (São Paulo, Brazil), was used as an organic crosslinker. The salts used for brine composition were NaCl (27,870 ppm), KCl (717 ppm), $CaCl_2$ (429 ppm) and $MgCl_2.6H_2O$ (924 ppm), purchased from Neon (São Paulo, Brazil). The reinforced fillers ZnO (<100 nm particle size) and Al_2O_3 (<50 nm particle size) were purchased from Sigma-Aldrich (Brazil). All chemicals were used as received and solutions were set up with deionized water.

Production of neat hydrogels and hydrogel nanocomposites

Initially, a preliminary study was carried out to assess the influence of crosslinker composition. The contents can be seen in Table 1. To achieve this, the main polymer content was set at 1% w.v^{-1} and the crosslinker concentration was varied. The systems were homogenized due 20 minutes and stored in an oven at 70°C for 48h for the crosslinking reactions and formation of gels.

Table 1. Hydrogels composition for crosslinker content study.

HPAM content (% w.v^{-1})	PEI content (% w.v^{-1})
	0
	0.1
	0.5
1.0	1.0
	2.0
	3.0

For the methodology of nanocomposite gel formation, the ZnO or Al_2O_3 were dispersed in the solution of HPAM under magnetic stirring for 20 minutes, with subsequent addition of the crosslinker with another 20 minutes stirring step, and then the bottles were directed to gel the systems in an oven at 70 °C for 48h. Table 2 presents the composition of gel containing different fillers contents.

Table 2. Systems composition for filler content study.

Polymer content	ZnO content (% w.v^{-1})	Al$_2$O$_3$ content (% w.v^{-1})
HPAM (1% w.v^{-1}) PEI (3% w.v^{-1})	0	-
	0.1	
	0.5	
	1.0	
	2.0	
	-	0
		0.1
		0.5
		1.0
		2.0

Characterizations of neat hydrogels

The hydrogels were evaluated by dynamic oscillatory shear rheology test. The highest shear strength system was selected for nanofiller variation study. This was carried out by sweeping the oscillation frequency from 0.01 Hz to 10 Hz with 1% deformation (present in the linear viscoelastic region) to determine the storage modulus (G') and loss modulus (G") and obtain information about the microstructure of the hydrogels. Whereas the elastic modulus was used to provide the strength estimation, the viscous modulus was used to determine the material stiffness through the tandelta (tan δ), according to the equation 1.

$$Tan\ \delta = \frac{G''}{G'}$$

Equation 1

Characterizations of nanocomposite hydrogel

To evaluate the filler influence, ZnO or Al$_2$O$_3$ in the formulations, dynamic oscillatory shear rheology tests were performed as previously reported. In contrast to precursor ratios, the G' of nanocomposites were evaluated as the material strength indicator.

Scanning electron microscopy analyses were also performed to evaluate the surface morphology and filler dispersion in the gel. The samples were fixed with conductive adhesives on the sample holder and coated with gold in a BAL-TEC sputter coater, model SCD 005, making them conductive and suitable for this type of microscopy. The analyses were performed with a 10 keV electron acceleration voltage, primary and secondary electron detector, with magnification up to 5.000 times in the TESCAN electron microscope. Therefore, the dry gel samples were characterized in order to verify the filler content on the resistance to thermal degradation. For this, the samples were heated from 25 to 700°C, under a heating rate of 10 °C/min in an inert nitrogen atmosphere of 60 mL/min, in the TA Instruments Q500V.

For the microscopic tests and thermogravimetric analysis, the samples were lyophilized for 72h to obtain a dry three-dimensional structure.

RESULTS AND DISCUSSION

Determination of hydrogel crosslink content

The influence of crosslinker content on material strength and stiffness was first assessed. The G' curves are shown in Figure 1 and the tandelta are presented in Figure 2.

Figure 1 shows that higher concentrations of crosslinker provide increased G'. In order to allow clear visualization, a dotted line was sketched at 1 Hz. This occurs due to the crosslinker availability to react with the active sites of the main polymer chain to form the crosslinks. This process occurs through a transamidation reaction, and the mechanism has already been elucidated in the literature (PEREIRA *et al.*, 2020).
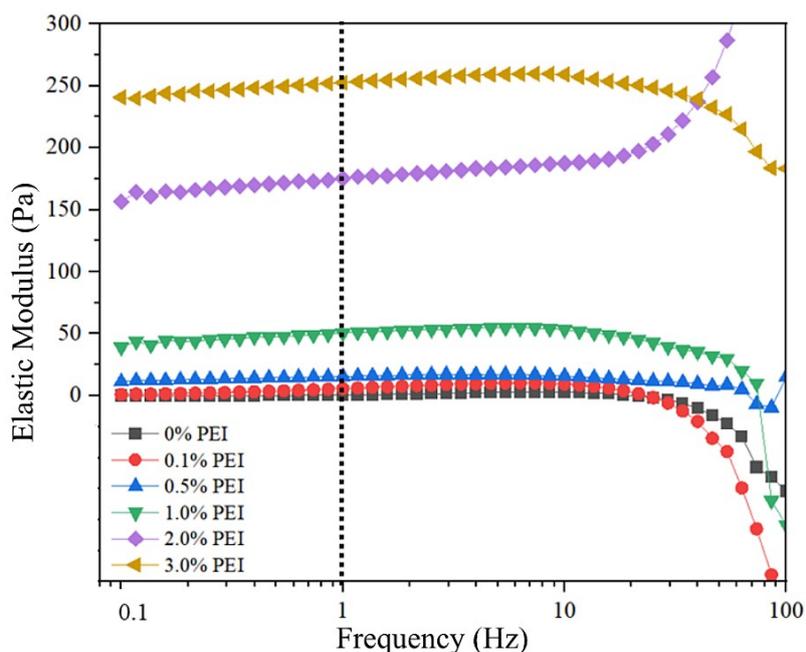
Figure 1. Elastic modulus profiles with crosslinker variation.

The structures form three-dimensional networks and, when sheared by the rheometer, more crosslinked systems also resist more to applied force. It was noted that crosslinking provides an increase in elastic modulus from 0.7 Pa to 252.7 Pa (at frequency of 1 Hz). Nevertheless, the tandelta results are shown in Figure 2.

Figure 2 showed the TanDelta values at a frequency of 1 Hz. This is an important measure for hydrogel strength studies, this factor representing the ratio of energy dissipated to stored during a deformation cycle. Therefore, values of $\tan(\delta)$ above 1 are considered weak gels, whereas values less than (or equal to) 0.1 prove the formation of stronger gels, hence the gels with values in the range $0.1<\tan(\delta)\leq1$ were considered medium strength gels (OKAY & OPPERMANN, 2007).
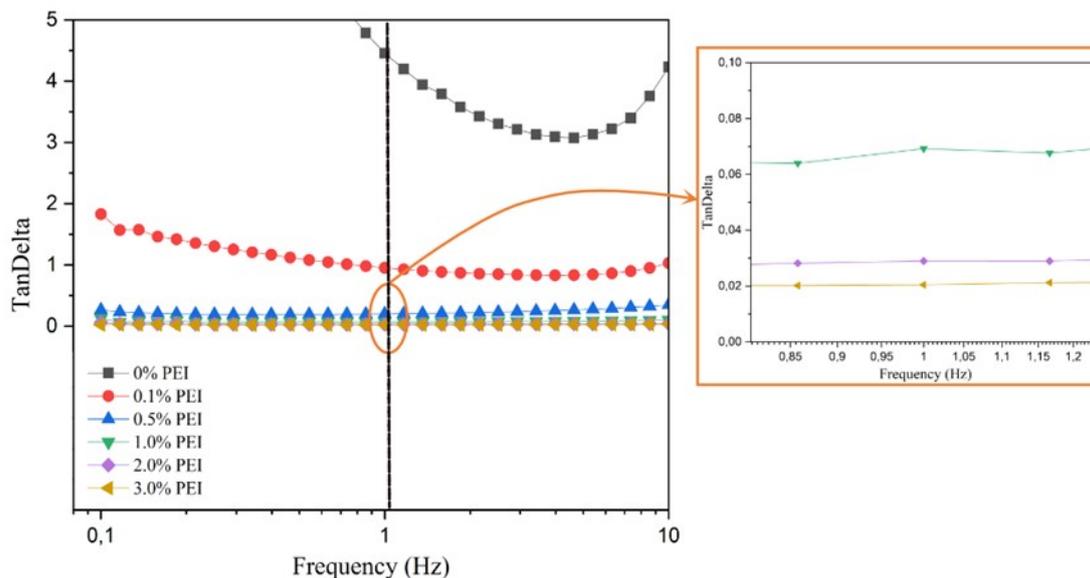
Figure 2. Tandelta profiles with crosslinker variation.

The samples exhibited that the compositions with higher than 1.0% crosslinker contents revealed predominantly solid behavior with tan δ values lower than 0.1. Another observation suggests that the values decreased with higher crosslinker species amount, increasing the hydrogels solid behavior. This can be attributed to amounts of crosslinking bonds formed, where the three-dimensional system became more rigid. The composition containing 3% w.v^{-1} of crosslinker was selected to nanocomposite evaluation as the study aims to achieve a stiffer material to resist high shear in oil reservoirs.

Evaluation of ZnO and Al$_2$O$_3$ content

The addition of zinc and aluminum oxides as reinforcing filler provided variations in G' as seen in Figure 3. The values were matched at 1Hz for study simplicity as presented in Table 3. The reductions in values when comparing with the neat nanocomposite are highlighted in red whereas the higher values are highlighted with blue. It is noted that generally the presence of filler increased the elastic modulus for both zinc and aluminum, but some points will be detailed below.
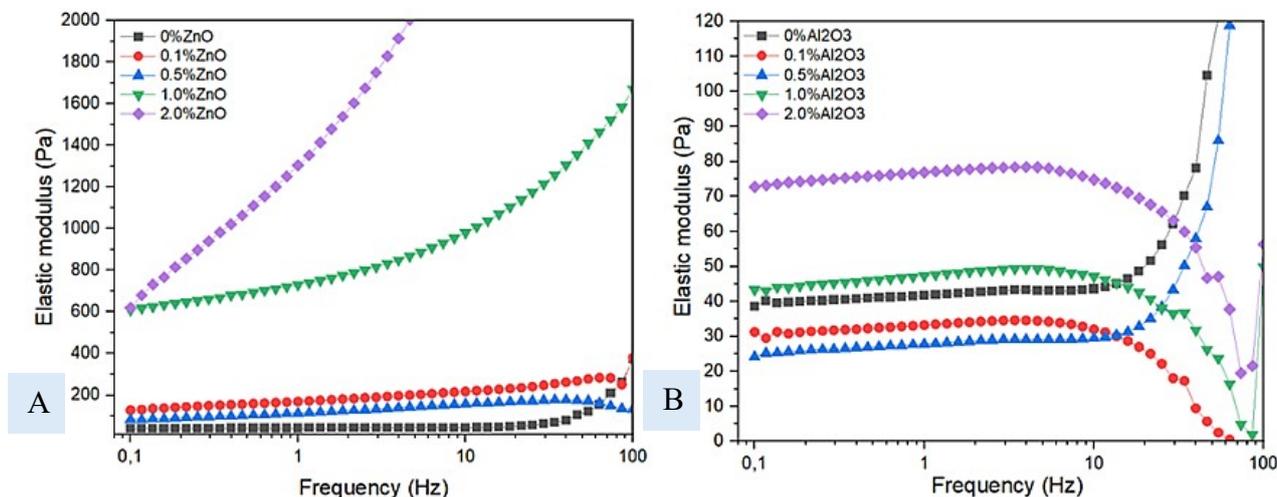
Figure 3. Elastic modulus profiles reinforced fillers ZnO (A) and Al_2O_3 (B).

Table 3. Elastic modulus at 1 Hz frequency for nanocomposites with ZnO and Al_2O_3.

Filler content (% w.v^{-1})	ZnO nanocomposite	Al_2O_3 nanocomposite
	1 Hz Elastic Modulus (Pa)	
0	42	41
0.1	165	35
0.5	142	29
1.0	708	49
2.0	1280	78

The increase in G' was progressive with the inorganic filler content when considering the composites with ZnO. These results indicate efficient interactions between ZnO and the polymer matrix in all compositions evaluated. These values increased by 1685% for 1% w.v^{-1} and 3047% for 2% w.v^{-1} of ZnO on comparing the frequency at 1Hz.

On the other hand, when evaluating the systems with Al_2O_3, the modulus showed a decrease in the contents up to 0.5% w.v^{-1} of filler, and then increases in G' of 120% for compositions with 1% w.v^{-1} and 190% for compositions with 2% w.v^{-1} of Al_2O_3. The possible reason for this drop consists in the weak interaction between the polymeric matrix and the inorganic filler (Al_2O_3). The damage to the G' values due to the fracture points overcomes the possible positive effects provided by the interaction between the components, which results in the modulus reduction. However, increasing the content above 0.5% w.v^{-1}, the interactions exceed the disadvantages and reflect in higher modulus as the pure nanocomposite.

The gains in G' can be explained as interactions between ZnO and Al_2O_3 with the HPAM polymer matrix already reported by PEREIRA *et al.* (2020) and CANCELA *et al.* 2022 while using oxidizing as the reinforcing filler in their works. It is suggested that both Al_2O_3 and ZnO fillers may be interacting to HPAM by the hydrogen according to the scheme in Figure 4.
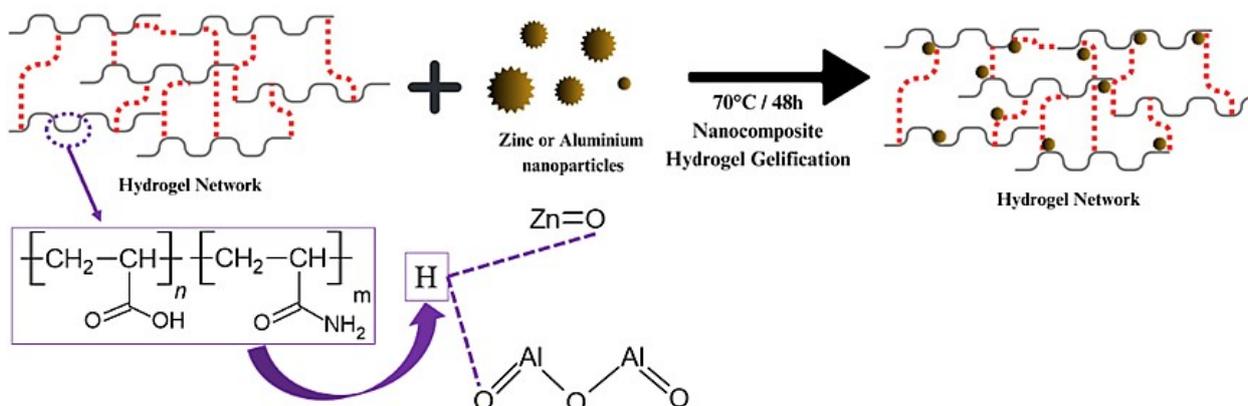
Figure 4. Elastic modulus profiles reinforced fillers ZnO and Al$_2$O$_3$.

An additional point of interest is to evaluate the compositions with different inorganic fillers. In this case it is notable the higher efficiency of ZnO particles as reinforcing filler, which indicates more powerful interactions between the polymer matrix and zinc fillers than aluminum fillers.

Microscopic analyzes

Scanning electron microscopy analyses were performed to evaluate the possible differences between the interactions with ZnO and Al$_2$O$_3$ morphologically. For this step, micrographs are presented in Figure 5. The Figure shows the pure hydrogel (center micrograph) and the nanocomposites with the higher filler contents, with the left micrograph corresponding to the systems with zinc and the right to the systems with aluminum.

A harmonic and homogeneous surface with three-dimensional aspects typical of gels are observed in the neat hydrogel image. The nanocomposites demonstrated micrographs with random distributions of inorganic material for those compositions that had inorganic filler. In order to evaluate the difference between the nanocomposites, it was observed that the ZnO particles are significantly more bonded and impregnated than the Al$_2$O$_3$ particles. These results corroborate with the rheological analysis observations, which suggest a greater interaction between the polymer matrix with the zinc particles. Lastly, it is worth noting that the black cracks in the gel are from the gold coating to convert the sample into a conductive material and do not refer to fractures in the sample.
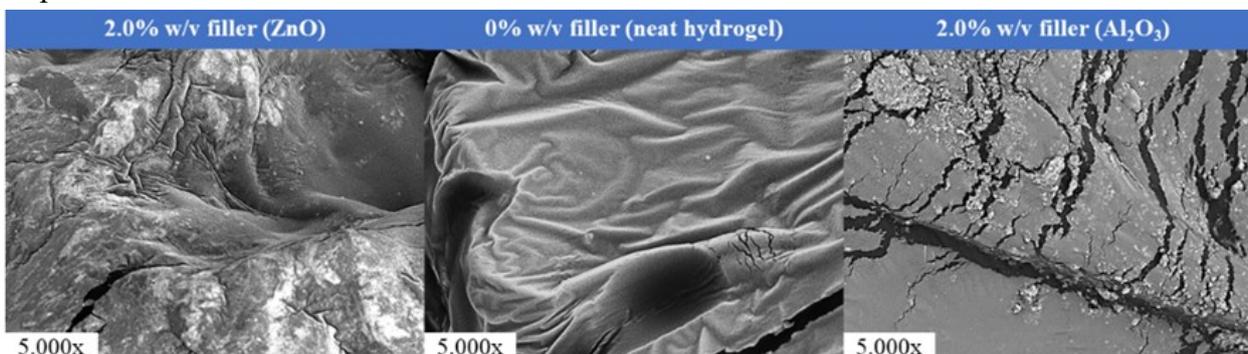
Figure 5. Hydrogels micrographs where the pure hydrogel (center), hydrogel with 2% w.v^{-1} ZnO (left) and hydrogel with 2% w.v^{-1} Al2O3 (right) are presented.

Thermogravimetric analyzes

The thermogravimetric analyses provide neat hydrogel and nanocomposites reinforcement details as shown in Figure 6. The curves revealed the occurrence of two degradation stages for both systems. The first stage until 150°C can be assigned to weight loss resulting from water molecules evaporation, extending up to 150°C due to possible physical adsorption or chemical hydrogen bonding interaction with the three-dimensional polymeric network. A second degradation stage is observed towards 300°C to 450°C and is attributed to the loss of mass caused by decarboxylation or decomposition of the amide groups.
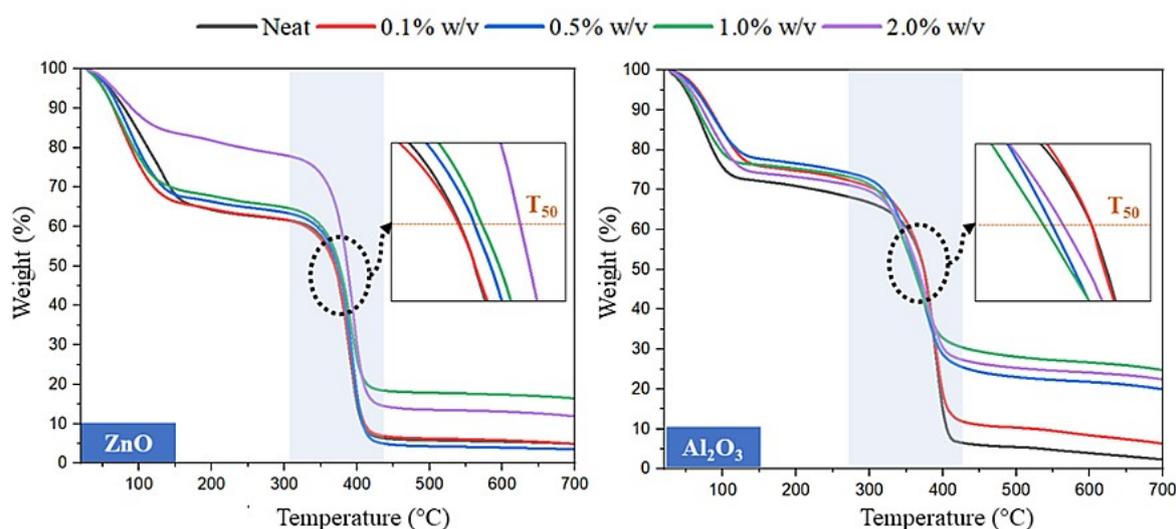
Figure 6. Neat hydrogel and nanocomposites thermal gravimetric results.

The measurements from the first stage were not used to evaluate the degradation resistance as water molecules are not included in the chemical structure of the hydrogel. On the other hand, the T_{50} output data were used as a metric to analyze the thermal degradation performance as the mass loss corresponds to the hydrogel structure. These values as well as the residual mass at 700°C are shown in Table 4.

Table 4. T_{50} values and residual mass at 700°C for neat hydrogels and nanocomposites with ZnO and Al_2O_3.

Filler content (% w.v^{-1})	T_{50} (°C)		Residue at 700°C (%)	
	ZnO	Al_2O_3	ZnO	Al_2O_3
0	369	372	4.7	3.3
0.1	369	372	4.7	6.3
0.5	374	363	3.5	19.9
1.0	376	361	16.1	24.1
2.0	387	366	11.6	22.8

The divergence between the inorganic fillers and the polymeric structure was also observed in the thermal analysis. The Zinc particles provided higher 50% weight degradation temperatures as the content increased. The progressive increase reflected from 369°C of neat hydrogel to 387°C with 2.0% w.v^{-1} filler. However, the weaker aluminium filler interaction resulted in reductions in T50, which acted as a catalytic effect. In short, the inorganic particles probably were not degraded until 700°C and the residual analysis showed an evident trend towards an increase with the filler concentration.

CONCLUSIONS

The high demand to maximize the efficiency of oil reservoirs requires conformity control devices to be increasingly useful. In this work, hydrogels were developed with formulation based on the maximum shear strength evaluated by rheology, being 1% w.v^{-1} of main polymer (HPAM) with 3% w.v^{-1} of crosslinker (PEI).

To optimize the properties in the face of drastic shear and temperature conditions, formulations with different ZnO and Al_2O_3 contents were prepared. Rheological analyses showed remarkable increases of 3047% for the highest G' condition with zinc, while the aluminum was 190% (both at 2% w.v^{-1} of filler). Morphological studies confirms that zinc oxide interactions visually appeared to be more effective than aluminium. Thermal degradation tests indicated that zinc nanocomposites promoted degradation displacement to higher temperatures, while aluminium systems operated as a catalytic effect. This investigation allowed the identification of the condition between the evaluated options, even regarding the inorganic oxides, which was 3% of crosslinker with 2% w.v^{-1} of ZnO.

DECLARATIONS

Conflict of interest. The authors have no competing interests to declare that are relevant to the content of this article.

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