

# Viscoelastic Properties of Polyacrylamide Nanocomposite Hydrogels Prepared in Electrolyte Media: Effect of Gelant Volume

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## ABSTRACT

In this work, nanocomposite (NC) hydrogels based on polyacrylamide/chromium triacetate were prepared at different reaction mixture (gelant) volumes and their crosslinking process and viscoelastic behaviors were studied. The X-ray diffraction (XRD) patterns taken from the NC hydrogels containing laponite nanoparticles did not show any distinct characteristic basal reflection for all of the NC hydrogels. Evaluating the crosslinking behavior of the gelants revealed that the torque value of the gelation increased with increasing the gelant volume. In addition, four successive steps in the gelation behavior were identified. According to the dynamic rheometry analysis of the prepared hydrogels, the storage modulus plateau range and its value decreased with increasing the gelant volume. Shear thinning behaviors were seen for all of the prepared gels. However, the gels prepared at larger gelant volumes showed a lower viscosity. The elastic properties of the NC gel were higher than that of the conventional gel. However, the addition of the laponite nanoparticles into the polyacrylamide gelling system slightly decreased the viscous energy dissipating and damping properties.

**Keywords:** Polyacrylamide, Gelation, Nanocomposite Hydrogel, Viscoelastic Properties, Water Shut-off

## INTRODUCTION

Partially hydrolyzed polyacrylamide (HPAM) is a well-known water-soluble and commercially available polymer, whose gels are employed in many commercial applications, especially in oil recovery treatments for the control of the excess water production through profile modification and blocking the paths with high permeability to water [1-7]. In recent years, the preparation of nanocomposite hydrogels has attracted more attention to overcome the weakness

and limitations of the conventional hydrogels [1,8-11]. Nanocomposite hydrogels have excellent properties such as mechanical toughness, large deformability, high swelling/deswelling rates, high transparency, dynamic restructuring, and unusual adhesive properties. These remarkable improvements in the properties of the nanocomposite hydrogels have been ascribed to their characteristic network structure [12-15].

The preparation and evaluation of the nanocomposite hydrogels synthesized by free-radical polymerization/gelation of the monomers in the presence of the nanoparticles with

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or without the additional use of organic crosslinkers, as well as the preparation of the NC hydrogels by metallic crosslinkers in the presence of the nanoparticles, has been studied extensively. In our already published works, we reported the gelation and swelling behavior of the nanocomposite hydrogels prepared in small volumes (200 ml) using montmorillonite type nanoparticles and partially sulfonated and hydrolyzed polyacrylamides [1, 2, 8, 16]. In this study, the effects of gelant volumes on the gelation behavior and viscoelastic properties of the NC hydrogels are investigated. To the best of our knowledge, there is no report about this issue, especially in electrolyte media. The study of the viscoelastic properties of hydrogels prepared at different gelant volumes is necessary for understanding of their gelation behavior during the scale-up of these hydrogels for water shut-off applications. For this purpose, at first, nanocomposite hydrogels were prepared at different gelant volumes (200, 2000 ml, and 4000 ml) by crosslinking the aqueous solutions of the partially hydrolyzed polyacrylamide/laponite nanoparticles with chromium triacetate using an overhead electronic stirrer. Then, the effects of gelant volume and the presence of laponite nanoparticles on the viscoelastic behavior of the previously prepared NC gels were studied via a dynamic rheometry analysis.

## MATERIALS AND METHODS

Partially hydrolyzed polyacrylamide (HPAM) with an average molecular weight of  $16 \times 10^6$  Dalton and a degree of hydrolysis of 25 mol. % was provided by SNF Co. (France). Chromium triacetate, as a metallic crosslinker, was purchased from Carlo Erba, (Italy). Organically modified laponite (92.32 wt.%  $Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$  and 7.68 wt.%  $Na_4P_2O_7$ ) was provided by Rockwood Co. (UK). Laponite is a synthetic layered silicate with a thin disc structure having a diameter of 30 nm and a thickness 1 nm. In tetra sodium pyrophosphate modified laponite, the edges of discs are negatively charged; thus the surfaces and edges of the discs

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exhibit the same charge, leading to electrostatic repulsion among discs and efficiently prohibiting the formation of "House of Cards" structures. Therefore, its dispersion and stability in water is better than the conventional laponite. It hydrates and swells in water to give clear and colorless colloidal dispersions of low viscosity.

The conventional and nanocomposite hydrogels were prepared according to the following procedure. Separately prepared nanoparticles/water dispersions were added to HPAM solutions, while stirring at room temperature for 1hr. Aqueous reaction mixtures (gelants) at different volumes were prepared by adding chromium triacetate/water solution to the solutions containing given amounts of HPAM and nanoparticles. Due to the large volumes of the gelants, the crosslinking process was monitored by stirring at 80 °C for 50-60 min, using an overhead electronic stirrer equipped with a torque meter and having a paddle type spindle (Heidolph PZR 2102). Then, the samples from these prepared hydrogels were used for XRD and rheological analyses. The detailed composition of the oil reservoir water, used for the preparation of the gelants, is given in Table 1.

**Table 1: Composition of the used water**

Ion type	Ion Concentration (mg/l)
Ca <sup>+2</sup>	6400
Mg <sup>+2</sup>	440
Na <sup>+1</sup>	30900
K <sup>+1</sup>	405
HCO <sub>3</sub> <sup>-1</sup>	32
SO <sub>4</sub> <sup>-2</sup>	71
Cl <sup>-1</sup>	79750
Total Dissolved Solid (TDS)	125000

The viscoelastic properties of the hydrogels (prepared in the previous step) were measured using a cone & plate MCR 501 rheometer (Anton Paar, Austria) equipped with a Peltier device for temperature control. To carry out the rheological tests, the system was first heated to the desired temperature, and then a small piece of the prepared gel was placed in the plate section. After

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doing the required adjustments, an oscillatory strain,  $\gamma(t)$ , was applied:

$$\gamma(t) = \gamma_0 \cos(\omega t) \quad (1)$$

The steady oscillatory shear stress,  $\sigma(t)$ , was measured from the resultant torque:

$$\sigma(t) = G^* \gamma_0 \cos(\omega t + \delta) \quad (2)$$

where,  $\gamma_0$ ,  $\omega$ ,  $t$ ,  $G^*$ , and  $\delta$  are strain amplitude, angular frequency, time, complex modulus, and phase angle respectively.

The following equations were then used to calculate the characteristic storage modulus ( $G'$ ), loss modulus ( $G''$ ), and complex viscosity ( $\eta^*$ ) from the complex modulus and phase angle:

$$G' = G^* \cos(\delta) \quad (3)$$

$$G'' = G^* \sin(\delta) \quad (4)$$

$$G^* = G' + iG'' \quad (5)$$

$$|G^*| = \omega |\eta^*| \quad (6)$$

During frequency sweep and strain sweep tests, deformation amplitude and frequency were 0.05 and 1 Hz respectively.

To evaluate the dispersion of the nanoparticles in the NC hydrogels, X-ray diffraction (XRD) was performed with a Philips Analytical X-ray using nickel-filtered Cu-K $\alpha$  radiation ( $\lambda = 0.154$  nm) at a voltage of 40 kV and a current of 25 mA. The XRD patterns were recorded with a step size of 0.05 $^\circ$ .

## RESULTS AND DISCUSSION

### XRD Analysis

Wide angle X-ray diffractometry was used for evaluating the microstructure and nature of the laponite nanoparticles dispersion in the NC hydrogels. The entrance of polymer into nanoparticles interlayers (intercalation) results in an increase in  $d$ -spacing and a shift of XRD peaks toward lower angles. A further shift to lower angles and a broadening or disappearing of the *Journal of Petroleum Science and Technology* **2016**, 6(1), 86-93  
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characteristic XRD peaks are the indications of the partial or complete exfoliation of the ordered nanoparticle structure [17].

The XRD patterns of the laponite nanoparticles and NC polyacrylamide hydrogels are shown in Figure 1. Laponite has two broad peaks at  $2\theta$  of 1.8 $^\circ$  and 5 $^\circ$ , which corresponds to  $d$ -spacings of 4.90 nm and 1.76 nm respectively (Figure 1a). The XRD patterns taken from the NC hydrogels containing laponite do not show any distinct characteristic basal reflection (Figure 1b) for all the NC hydrogels prepared at different gelant volumes; this might be interpreted to mean that the nanoparticles have a disordered/ intercalated microstructure.

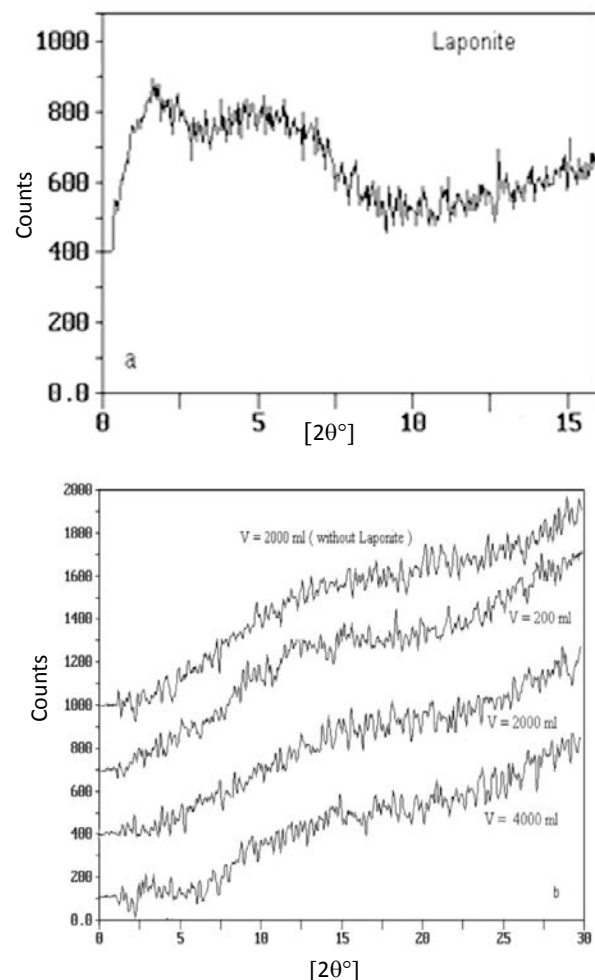


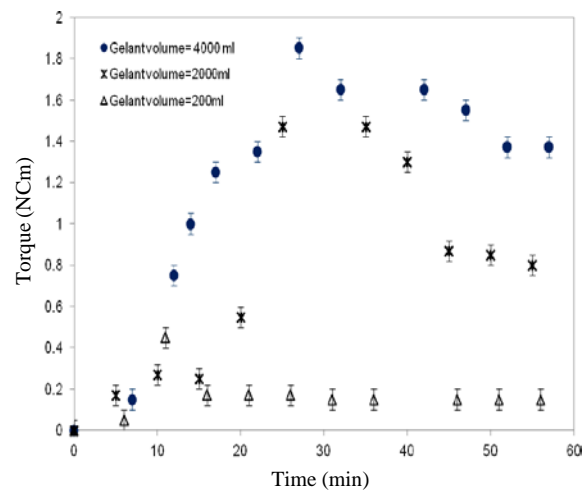
Figure 1: XRD patterns of (a) laponite nanoparticles and (b) NC hydrogels prepared at different gelant volumes containing 1000 ppm nanoparticle.

## Gelation and Viscoelastic Behavior

During crosslinking in a semi-dilute regime, i.e. when the polymer molecules overlap significantly, continuously recording the variations of shear viscosity as a function of time is an appropriate tool to monitor the steps of microgel formation under shear [18]. We believe that this is true for bulk gel formation under shear. However, in the case of our gelling systems, evaluating the gelation behavior by rheometry was not possible due to a large volume of gelant. Therefore, due to the relationship between mixing torque and viscosity, an overhead electronic stirrer equipped with a torque meter was used for having an indication of the gelation process of our aqueous reaction mixtures containing polyacrylamide, crosslinker, and nanoparticles. Figure 2 compares the gelation behavior of 200 ml, 2000 ml, and 4000 ml gelants. It can be observed that the torque value of gelation increases with increasing the gelant volume, which indicates that more energy is required for mixing a larger volume of gelant. However, their general trends are similar. One can find four successive steps in the gelation behavior: 1) the induction period, that is characterized by the formation of polymer doublets, which induce only a small increase in torque value (viscosity); 2) the pre-gelation period, in which the doublets and triplets begin to overlap; this overlapping causes a sharp increase in torque, which would reach an infinite value in the absence of shear; 3) the size limitation period characterized by the rupture of large gel aggregates by the torque; in this period, torque reaches its maximum and ceases to increase continuously; 4) post-crosslinking or the reformation period, during which the crosslinking continues by an increase in both intra and intermolecular crosslinks inside the gel networks. However, additional intra-crosslinks may reduce again the size of the gel aggregates, giving a slow decrease in torque value (viscosity).

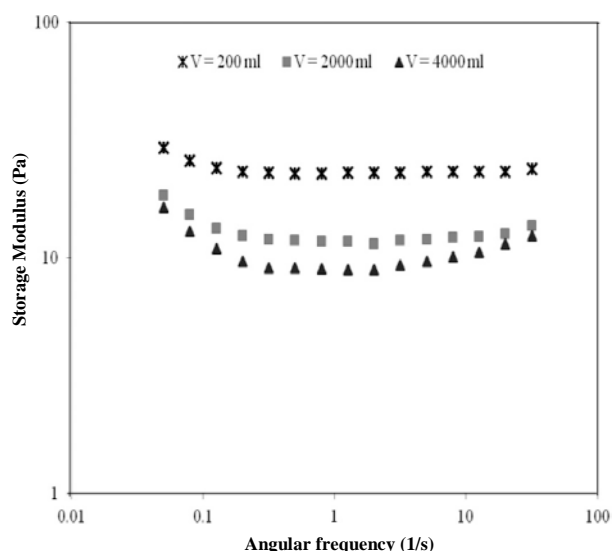
The effects of the gelant volume and the presence of laponite nanoparticles on the viscoelastic properties of

the prepared hydrogels were evaluated using dynamic rheometry. Figure 3 shows the effect of gelant volume on the frequency dependence of storage modulus for HPAM NC gels. The existence of a plateau value in the  $G'$  versus frequency curve indicates the gel formation. It can be seen that the storage modulus plateau range and its value decrease with increasing the gelant volume of the NC gels; this may be due to the better mixing and interactions of crosslinker-polymer-nanoparticles, and consequently better crosslinking at smaller gelant volumes. Due to the proportionality of storage modulus with the crosslink density [14], one may conclude that NC gels prepared at larger volumes have a lower crosslink density.

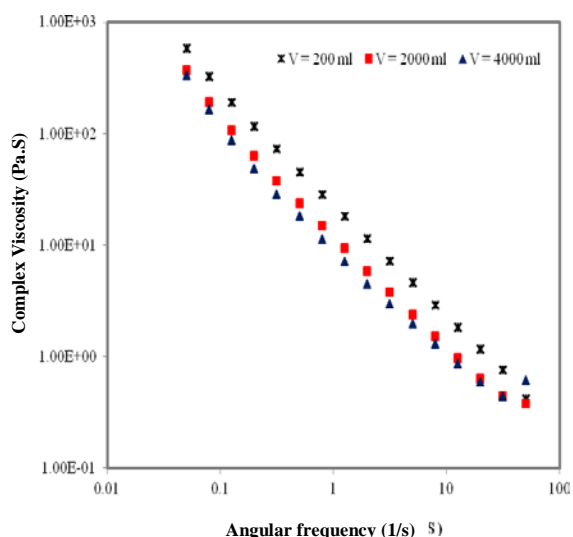


**Figure 2: Gelation behavior of the HPAM NC gels having different gelant volumes (polymer concentration: 5000 ppm, crosslinker concentration: 500 ppm, Nanoparticles concentration: 1000 ppm, T: 80 °C, Mixing speed: 14 rpm, and TDS: 125000 ppm).**

Figure 4 shows the effect of gelant volume on the complex viscosity of the NC gels. It can be seen that all of the prepared gels show a shear thinning behavior, which is common in polymeric systems. In addition, the gels prepared at larger gelant volumes show lower viscosity, which may result from their lower crosslinking density, as described earlier. Our further investigation showed that the yield stress of the gels slightly decreased by increasing the gelant volume.



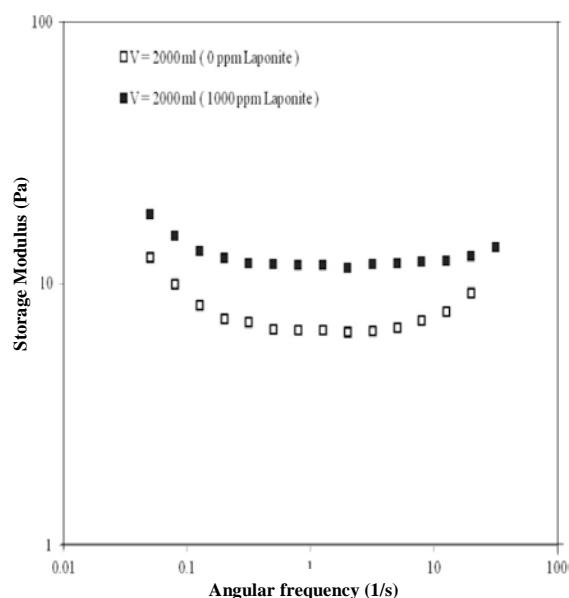
**Figure 3:** Frequency dependence of storage modulus for the HPAM NC gels prepared at different gelant volumes (polymer concentration: 5000 ppm, crosslinker concentration: 500 ppm, nanoparticles concentration: 1000 ppm, and  $T: 80^{\circ}\text{C}$ ).



**Figure 4:** Complex viscosity-angular frequency relationship of the HPAM NC gels prepared at different gelant volumes (polymer concentration: 5000 ppm, crosslinker concentration: 500 ppm, nanoparticles concentration: 1000 ppm, and  $T: 80^{\circ}\text{C}$ ).

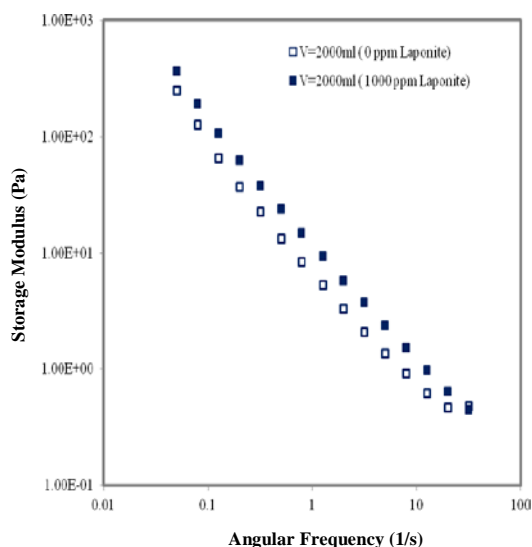
Figures 5 and 6 compare the storage modulus and complex viscosity of the conventional and NC HPAM hydrogels prepared at a constant gelant volume (2000 ml). It can be seen that both of the NC and conventional gels show a shear thinning behavior. In addition, it is obvious that the storage modulus and complex viscosity of the NC gel are *Journal of Petroleum Science and Technology* 2016, 6(1), 86-93  
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more than that of the conventional gel. These behaviors suggest the existence of interactions between polyacrylamide chains and laponite; thus the laponite nanoparticles are fixed in the gel network as additional effective junction points. According to the mechanism suggested by Haraguchi et al. [10-12], the polyacrylamide chains are bound to the surface of the laponite layers due to the hydrogen bonds between the oxygen atoms of laponite and the amide protons of the acrylamide, as well as due to complex formation between the metal ions on the laponite surface and the carbonyl oxygen of the acrylamide.



**Figure 5:** Storage modulus-frequency behavior of HPAM conventional and NC hydrogels prepared at a gelant volume of 2000 ml (polymer concentration: 5000 ppm, crosslinker concentration: 500 ppm,  $T: 80^{\circ}\text{C}$ ).

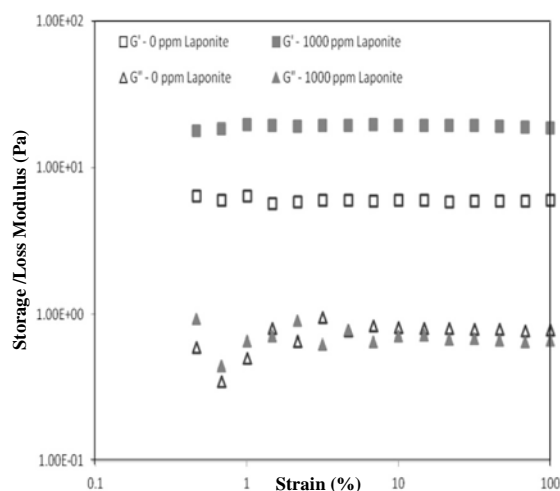
Figure 7 shows the strain sweep behaviors of storage and loss modulus for conventional and NC HPAM hydrogels prepared at a constant gelant volume of 2000 ml. One can see that the addition of laponite nanoparticles significantly increases the elastic properties of the polyacrylamide gelling system, but slightly decreases the viscous energy dissipating properties of the NC network.



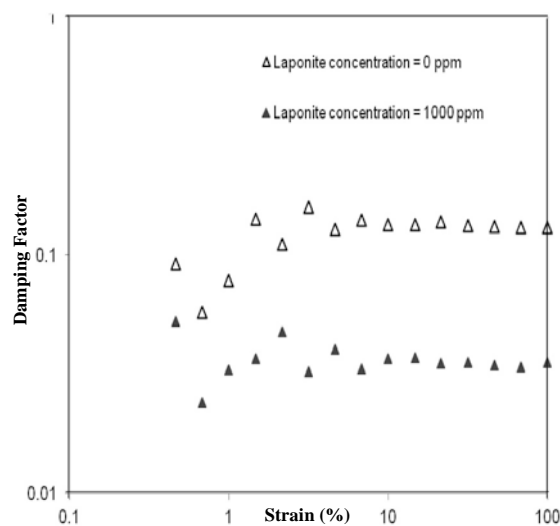
**Figure 6:** Complex viscosity-frequency behavior of HPAM conventional and NC hydrogels prepared at a gelant volume of 2000 ml (polymer concentration: 5000 ppm, crosslinker concentration: 500 ppm,  $T$ : 80 °C).

As mentioned earlier, the elastic behavior of the NC gel is more than that of the conventional one due to the existence of interactions between polyacrylamide chains and laponite. In addition, the decreased friction at the nanoparticles-polymer interface led to a slight decrease in the loss modulus. It can be noted that the  $G''$  values never decrease to 0, which suggests the viscoelastic nature of these hydrogels under the applied physical conditions.

The damping factor ( $\tan(\delta) = G''/G'$ ) of HPAM conventional and NC hydrogels prepared at a gelant volume of 2000 ml is shown in Figure 8. The quantity of  $\tan(\delta)$  represents the ratio of the dissipated energy to the stored energy during one deformation cycle. Figure 8 shows that the damping property of the prepared NC gel is lower than that of the conventional gel. According to Figure 7, the presence of nanoparticles in the network structure increases the storage properties of the network more than that of the viscous properties; therefore, the damping property of the NC gel is lower than that of the conventional gel.



**Figure 7:** Strain sweep behaviors of storage/loss modulus for HPAM conventional and NC hydrogels prepared at a constant gelant volume of 2000 ml (polymer concentration: 5000 ppm, crosslinker concentration: 500 ppm, and  $T$ : 80 °C).



**Figure 8:** Strain sweep behavior of damping factor for HPAM conventional and NC hydrogels prepared at a constant gelant volume of 2000 ml (polymer concentration: 5000 ppm, crosslinker concentration: 500 ppm, and  $T$ : 80 °C).

## CONCLUSIONS

The effects of gelant volume and the presence of laponite nanoparticles on the gelation behavior and viscoelastic properties of the polyacrylamide/chromium triacetate gelling system were studied. The main conclusions which can be drawn from the results reported in this work are:

- Evaluating mixing torque variations with time during gelation revealed that there are four successive steps in the gelation behavior of this gelling system.
- The XRD patterns of the NC hydrogels containing laponite did not show any distinct characteristic basal reflection for all of the NC hydrogels prepared at different gelant volumes.
- The storage modulus plateau range and its value decreased with increasing the gelant volume.
- The presence of laponite nanoparticles in the network structure increased the elastic properties of the network more than the viscous properties; therefore the damping of the NC gel was lower than that of the conventional gel.

The results of this research showed new insights into the gel formation during the scale-up of hydrogels for water shut-off applications.

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## NOMENCLATURE

NC: Nanocomposite

HPAM: Partially hydrolyzed polyacrylamide

XRD: X-ray diffraction

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