## *Short Communication*

# Improvement of Thermal Stability of Polyacryl amide Solution Used as a Nano-fluid in Enhanced Oil Recovery process by Nanoclay

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*Abstract*
*Research in nanotechnology in the petroleum industry is advancing rapidly and an enormous progress in the application of nanotechnology in this area is to be expected. In particular, adding nanoparticles to fluids may drastically benefit enhanced oil recovery and improve well drilling, by changing the properties of the fluid, rocks wettability alteration, advanced drag reduction, strengthening the sand consolidation, reducing the interfacial tension and increasing the mobility of the capillary trapped oil. In this study, we focus on roles of clay nano-particles on viscosity of polymer, temperature and salinity of polymer solutions different nanoparticles. The viscosity of these polymer solutions was measured using a rheometer and in each measurement, the shear rate was changed, and the effect of this change on the viscosity was measured. Results showed that increasing temperature on the viscosity of solution plays a positive role when the dispersed clay nanoparticles are present in the solution.*
*Keywords: Nanoclay, Polymer Viscosity, Reservoir temperature, Salinity.*

## 1. INRODUCTION

Reservoir engineering, however, has received the most attention for nanotechnology applications. Several experiments have been conducted to investigate flow behavior of nanoparticle suspensions through porous media. Polymer flooding is one of the most successfully methods in enhanced oil recovery. The polymers that are mainly used in oilfields are water soluble polyacrylamide, Xanthan gum and Associative Polymer. Polymer solutions, in contrast to water, exhibit non-Newtonian rheological behaviors, such as shear thinning and shear thickening effects, which lead to different viscosity properties in a reservoir, as compared with those in water flooding. When a polymer solution is injected into a reservoir from an injection well, the flow velocity, which is related to shear rate, will change from wellbore to in-depth of a reservoir; therefore, the viscosity of polymer solution will also change from near wellbore to in-depth of a reservoir correspondingly [1]. The volume of the

polymer solution injected may be 50% of injection pore volume, depending on the process design [2,3]. High molecular weight polyacrylamide and its derivatives are widely used in oilfield applications ranging from drilling fluids, enhanced oil recovery, and treatment of oil sand tailings. In these applications the adsorption characteristics of these polymers are essential since it would affect their applicability and efficiency [4]. Pancharoen [5] Studied on the physical properties of polymers used in enhanced oil recovery. The impact of increased salinity in the rheological behavior of polymer solution was examined. It was shown that with increasing the salinity of polymer solution, some properties such as polymer viscosity, inaccessible pore volume and permeability reduction factor are reduced. These studies were performed using associative polymers and it was shown that changes in viscosity versus shear rate of polymers which their behavior is similar to non- Newtonian fluids follow a power law function of the fluid viscosity, and also they show good resistance to adverse effect of salinity. Finally associative polymers were compared with conventional polymers. Magbagbeola [6] validated the Universal Viscosity Model for apparent viscosity of flowing polymer solution through the porous medium, and changes in the model parameters for the different polymers were studied and calculated. In that study, a partial hydrolyzed poly acrylamide and co-polymers were used. It concluded that UVM fits the core flooding data in wide range of condition for polymer used in EOR. In that case, by using the rheological data of polymer solutions, without the need for costly experiments the operating condition of the process can be analyzed. It was shown that some parameters such as permeability, polymer concentration, polymer molecular weight and salinity affect the rheological properties of polymers through the porous medium. Delshad et al. [7] developed and proposed a unified apparent viscosity model for the entire range of flow velocity. One major advantage of this model is that the dependence of polymer viscosity on the flow velocity through the porous medium can be estimated using only the bulk rheological properties of the polymer and petrophyisical features of the porous media. Parameters that impact on these polymers include: shear rate, polymer concentration, degree of sulfonate, molecular weight, NaCl concentration, divalent ion concentrations and temperature. Finally, the results showed that these polymers can be considered a substitute for hydrolyzed Polyacrylamide solution in high salinity and high temperature reservoirs [8]. Moradi et al. [9] performed the rheological measurements of two types of hydrolyzed polyacrylamide with different salinities. These polymer solutions showed both the Newtonian and shear thinning behavior. It was shown that salinity has a major impact on these polymers. The effect of polymer molecular weight and concentration of the polymer solution were analyzed, and the increase in viscosity due to these parameters was reported. Ghannam et al. [10] studied the flowing behavior of Alco flood polymer solution, and the changes in its viscosity and shear stress versus shear rate has been investigated. They showed that the apparent viscosity of the solution is a function of polymer concentration and shear rate. Their results also showed that the effect of polymer concentration at low shear rates is more sensible. With the passing of the era of easy oil and the increasing difficulty of finding new resources, attention of the traditional oil and gas industry has been directed to extract more resources from existing oil fields (enhanced oil recovery) and from the fields exposed to extremely harsh environments by using new technologies and solutions. Nanotechnology bears the promise and recently has received great attention from the petroleum industry and there is a general perception that more than a decade's nanotechnology hype may become nano reality in the oil field [11, 14]. The objective of this paper is to investigate the application of Nano particles in improved polyacrylamide performance to

enhance oil recovery. This study reviewed and assessed some of the recent advances. Specifically, it aims to discuss the implications of applying nanoparticles in chemical flooding.

| Abbreviations | |
|---|---|
| PAM | polyacrylamide |
| AP | Associative Polymer |
| Xc | Xanthan gum |
| EOR | Enhanced Oil Recovery |
| HPAM | Partially Hydrolyzed Polyacrylamide |
| PV | Injection pore volume |
| HMW | High molecular weight |
| UVM | Universal Viscosity Model |
| SEM | Scanning Electron Microscope |
| TEM | Transmission Electron Microscopy |
| DCN | Dispersed Clay Nanoparticles |

## 2. EXPERIMENTAL
### 2.1. Materials

A synthetic brine with the concentration, ranging from 20,000 to 200,000 ppm was prepared by dissolving NaCl = 1.71, $Na_2SO_3$ = 0.01, $CaCl_2$ = 0.32, $MgCl_2.6H_2O$ = 0.09 and $Na_2HCO_3$ = 0.02 percent of weight into distilled water (Table 1).

***Table1.*** *Preparation of Brine*

| Composition | Weight % |
|---|---|
| NaCl | 1.71 |
| $NA_2SO_3$ | 0.01 |
| $CaCl_2$ | 0.32 |
| $MgCl_2.6H_2O$ | 0.09 |
| $Na_2HCO_3$ | 0.02 |

All the polymers used were commercially available, completely water soluble and differed mainly in their concentration (Table 2). In particular we tested polyacrylamides that were similar in chemical structure from Beijing Hengju Company, having molecular weight of 14 million (Figure 1).

Local sodium bentonite with a mesh size of 200 and a particles size less than 50 nm (Figure 2) was used in this study. The bentonite was produced in Iran and amended with the chemicals shown in Table

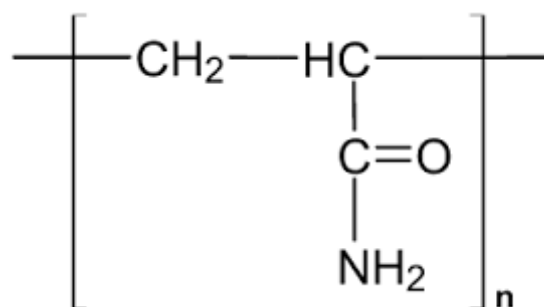3. XRF (Oxford-ED2000) was used for all chemical analyses.



***Figure1.*** *Molecular structure of HPAM.*

***Table2.*** *Properties of examined samples*

| Sample ID | Polymer Content (ppm) | Clay Content (wt%) | Saliniy (ppm) |
|---|---|---|---|
| **A** | 3150 | 0.9 | 200000 |
| **B** | 3150 | 0.9 | 20000 |

***Table3.*** *Chemical composition of bentonite.*

| Formula | **Wt. %** |
|---|---|
| L.O.l | 13.2 |
| $Na_2O$ | 2.04 |
| MgO | 2.22 |
| Al2O$_3$ | 14.59 |
| $SiO_2$ | 61.03 |
| $SO_2$ | 0.37 |
| Cl | 0.46 |
| $K_2O$ | 0.76 |
| CaO | 0.77 |
| $TiO_2$ | 0.22 |
| Fe2O$_3$ | 2.09 |
| BaO | 0.11 |

After the preparation and analysis of the raw materials, the clay was purified using a 2 inch hydrocyclon apparatus. To accomplish this, a suspension of 3 wt.% clay in distilled water was prepared and then passed through the cyclone at a pressure of 0.15 MPa. This resulted in the removal of impure and large particles. Montmorillonite particles with a diameter of less than 6 µm were then dried and used in the compatibility process [15]. To ensure compatibility following the dispersion of clay in distilled water, a clay suspension was prepared and amended with 10, 20, 30, 40 or 50 weight percent of the modifier materials silane. The mixtures were then heated at 80°C for 6 hours, after which the

products were washed with distilled water and dried.

The distribution of clay particle sizes was measured before and after purification using a Laser Particle Size Analyzer. In addition, clay particles in the colloid state were analyzed by SEM. The SEM micrographs were prepared using a. LEO 440I scanning electron microscope. The intercalation of the samples was evaluated using an X-ray diffraction (Bruker D8-discover).

Most of the clay particles are in the agglomerated form prior to purification. In addition, all of the clay particles had diameters of less than 75 µm. Furthermore, 50 % of the particles in the clay were less than 7 µm and 80 % were less than 50 nm in diameter. Figure 3 shows the dispersed states of salts and nanoclay samples in polymer solutions after 10 days.

## 2.2. Methodology

The most important property of a polymer is its ability to increase the solution's viscosity. The polymer solution exhibits non-Newtonian behavior, and its viscosity is a function of the shear rate. The viscosity of these polymer solutions was measured using a DV-III Ultra+ Brookfield rheometer. The principle of operation of the DV-III Ultra is to drive a spindle (which is immersed in the test fluid) through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with a rotary transducer. The viscosity measurement range of the DV-III Ultra (in centipois) is determined by the rotational speed of the spindle, the size and shape of the spindle, the container that the spindle is rotating in, and the full scale torque of the calibrated spring. In each measurement, the shear rate was changed, and the effect of this change on the viscosity was measured. Because the viscosity is sensitive to temperature, some measurements were done for different temperatures.

## 3. RESULT AND DISCUSSION

Polymer solution is investigated for both high and low saline solutions. Moreover, the effect of Dispersed Clay Nanoparticles (DCN) on the rheological properties of the prepared solution is examined at high and low temperatures. In fact, the effect of salinity and temperature on the rheological properties of both polymer solutions with and without DCN was scrutinized simultaneously.
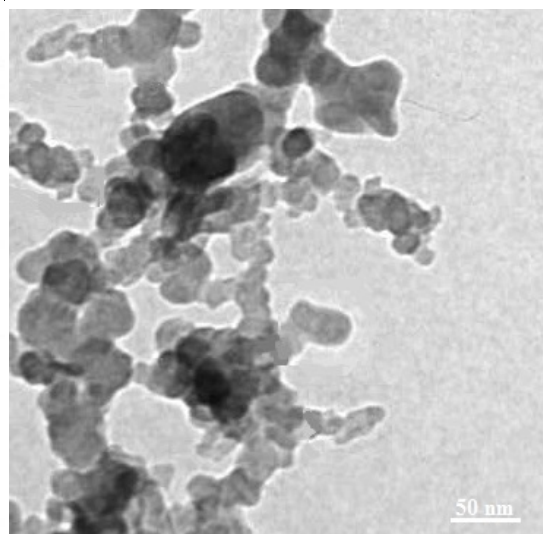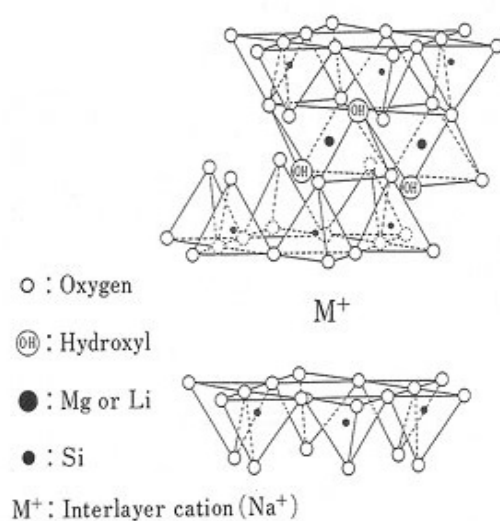


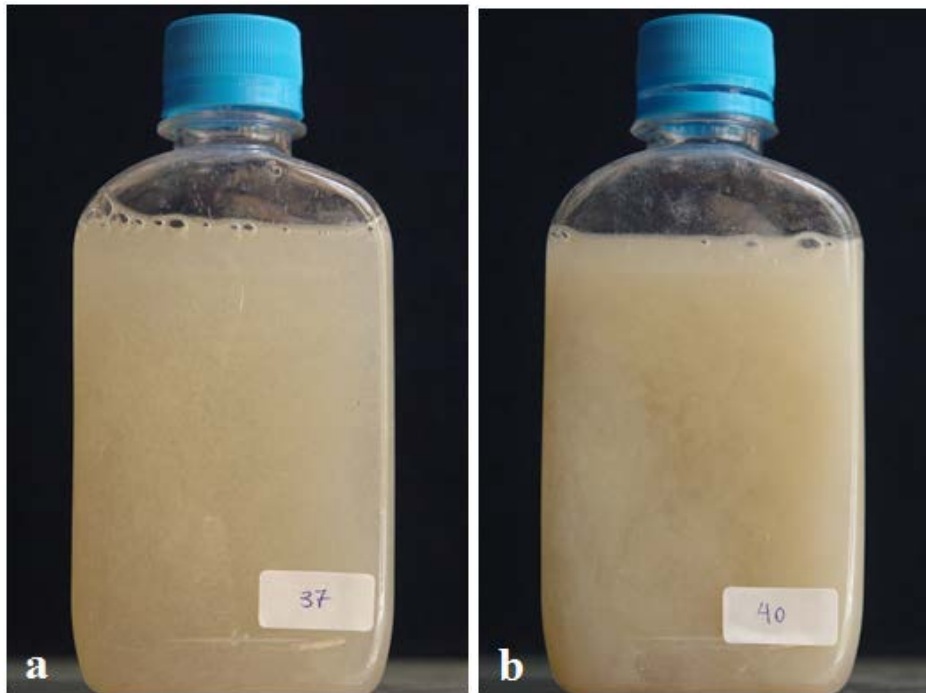*Figure2. Molecular structure of  Nanoclay and TEM image.*

**Figure3.** *Dispersion stability of 0.9 %wt nanoclay in polymer solution (a) after 1 day (b) after 10 days.*
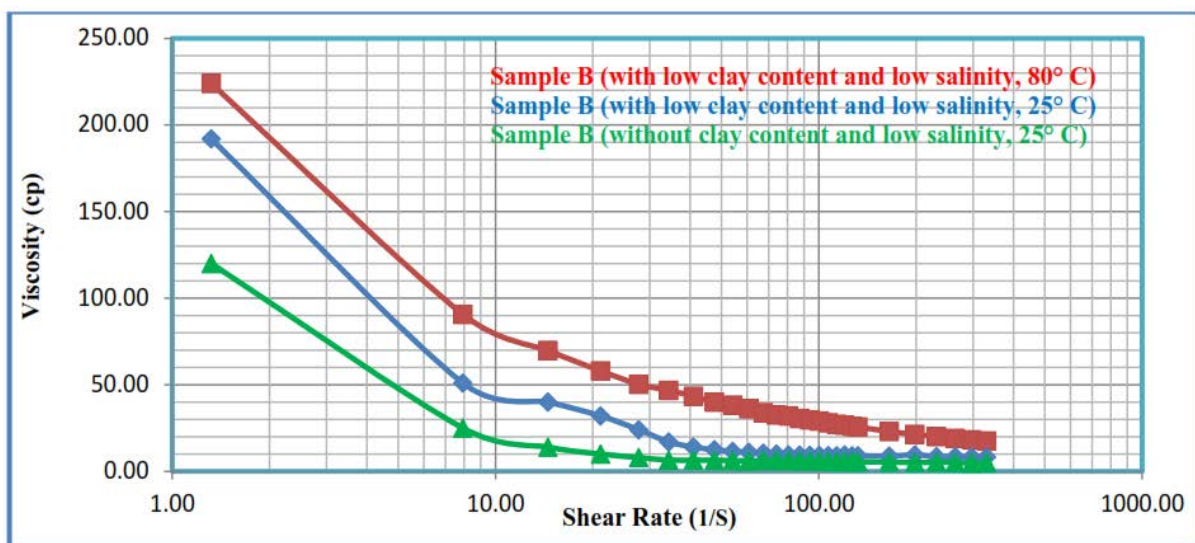


**Figure4.** *Solution viscosity vs. shear rate, to evaluate effect of increasing temperature for sample B.*

The two common types of polymer degradation are: chemical degradation and mechanical degradation. Shear degradation is an example of mechanical degradation. Degradation of polymer chains when polymer solution flows through pore throat is a good example of shear dependency of polymer solution. The other type of polymer degradation is a chemical degradation. Specially, chemical degradation is the result of salt presence in polymer solution. According to the experimental observations [16], the result for increasing the salinity of polymer solution is chemical degradation of polymer chains.

Accordingly, the viscosifying property of polymers is reduced. Thermal degradation is another reason for reducing the effectiveness of polymers to increase the viscosity of solution. As the solution

temperature increases, the viscosity of solution decreases. The temperature effect is also greater than that found for shear degradation in extensional flows [17,20].

Table 1 shows the composition of prepared samples. Samples A and B have the same polymer content, but the amount of salinity of sample A is 10 times greater than sample B. So, the sample A is called low saline solution while sample B is called high saline solution. In addition, 0.9 wt% of clay nanoparticles was dispersed in both samples.

Figure 4 shows the rheological behavior of low saline solution at different shear rates. At the same temperature, the DCN increase the viscosity of polymer solution. The effect of nanoparticles is more dominant at low shear rates while increasing the shear rate of solution (when the shear rate is greater than 40 1/s) reduces the positive effect of dispersed nanoparticles on the rheological behavior of low saline solution.

Regarding the common rheological properties of polymer solution, increasing the temperature reduces the viscosity of solution because the thermal degradation of polymer chains causes a reduction in viscosity of solution. One of the most interesting features of clay nanoparticles is to prevent thermal degradation of polymer solution. Figure 4 clears that increasing the temperature of solution increases the viscosity of solution. In other words, increasing temperature on the solution viscosity plays a positive role when the DCN are present in the solution. As you can see in the following graphs increasing temperature means viscosity increment. The major likeness of these two systems is that the temperature increasing in the low salinity solution (sample B and A) has positive effect on the viscosity. This is very important for thermal stability of polyacrylamide solutions that applied as polymer front (in polymer flooding operation) for high temperature reservoirs. Since sample A is far more saline than sample B, so the positive effects of clay

nanoparticles are minimized at high temperatures in sample A.

Recalling that sample A was called high saline solution; the viscosity of this sample was measured at different shear rates. Figure 5 shows the rheological behavior of high saline sample. As the results depict, the DCN dramatically increases the viscosity of solution at both low and high shear rates compared to the effect of DCN on the viscosity of low saline sample. For instance, the difference between the viscosities of low saline with DCN and without them at low shear rates is relatively equal to 22 cP. In addition, the difference between the viscosities of low saline with DCN and without them at high shear rates is relatively equal to 12 cP. This trend indicates that the effect of DCN on the solution viscosity of high saline sample is more predominant at both high and low shear rates compared with the low saline sample. When compare two graphs for the sample B, one can see little difference between them; therefore regardless of having less clay content this sample has more positive effect than A.

Scanning Electron Microscope was used to determine the morphology (size and shape) of nanoparticles. Figure 4 shows the SEM images of HPAM nanoclay particles. In Figure 4a and 4b, it is obvious that 200000 and 20000 ppm salinity were coated with 9 %wt nanoclay, respectively. For conducting a more accurate study, polymer solutions and nanoclay particles were examined by SEM.

## 4. CONCLUSIONS

Based upon the conducted experiments, the following conclusions and observations are drawn:

• First, the test results indicated that an increase in polymer concentration caused viscosity to go up.

• To study the effects of salinity on the viscosity of polymer when the salinity of solution increased (200000 ppm salinity), we found that in lower shear rates there was a negative effect from high salinity which

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became less by decreasing shear rate. The effects of clay supplying on a low saline system was so that clay presence had positive effects on viscosity in an extensive range of intension rate.

- These results were investigated for a highly saline system which supported above mentioned results and even a range of shear tension in which clay had positive effects in low and high salinity, so nanoclay can protect polymer solution against temperature increase and salinity.

- Since sample A is far more saline than sample B, so the positive effects of clay nanoparticles like preventing degradation of polymer molecules are minimized at high temperatures in sample A.
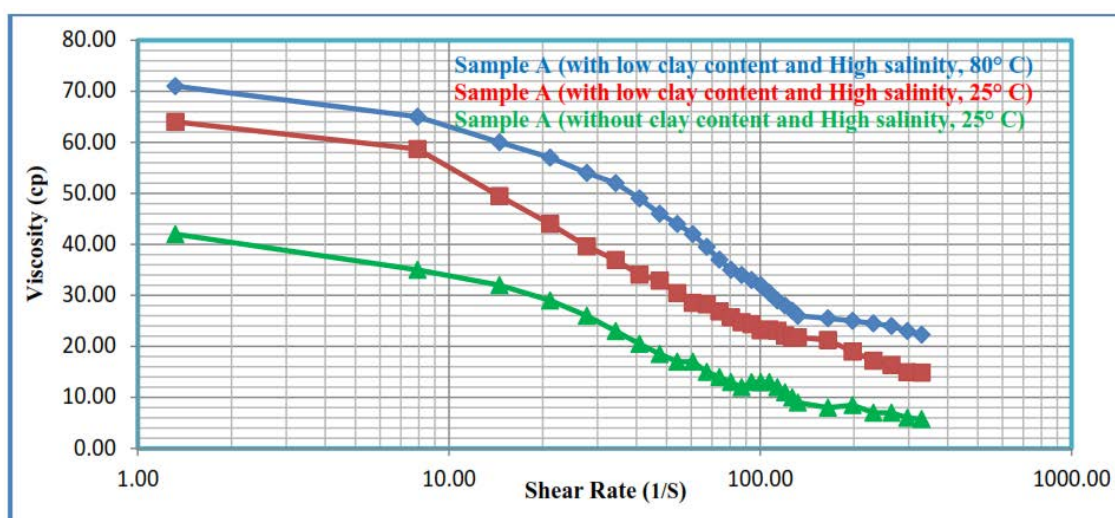
## ACKNOWLEDGMENT

**Figure5.** *Solution viscosity vs. shear rate, to evaluate effect of increasing temperature for sample A.*
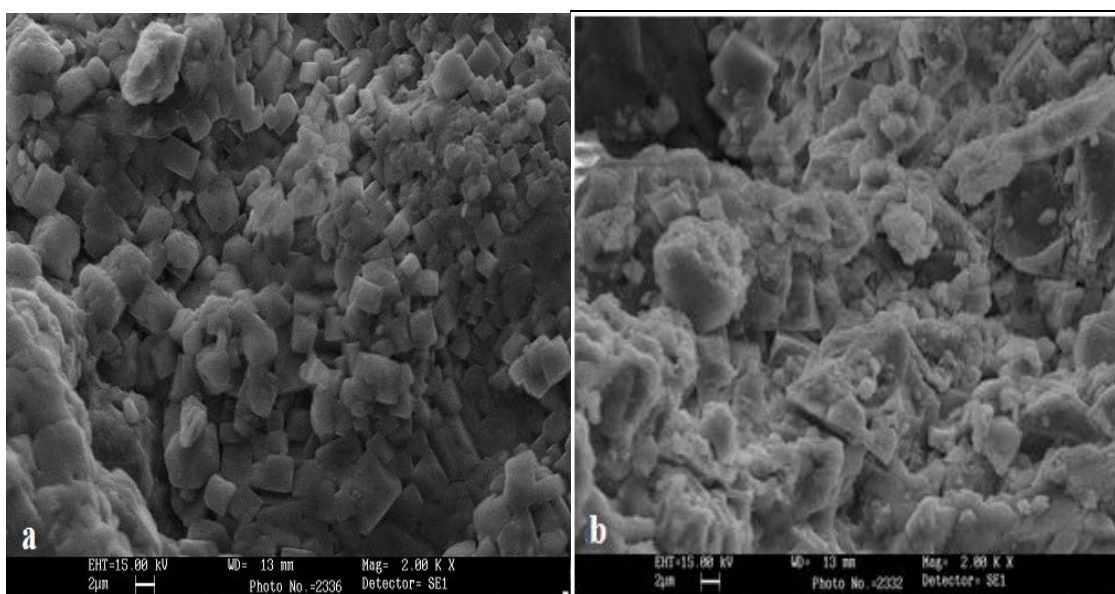


**Figure6.** *SEM micrograms of the clay nanoparticles absorbed by the polymer solutions; a) Sample B, b) Sample A.*

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