



Research Article

Structural Investigation: Anionic Polymerization of Acrylamide under Microwave Irradiation using Maghnite-Na⁺ Clay (Algerien MMT) as Initiator

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Abstract

Intercalation of acrylamide into interlayer spaces of natural montmorillonite called maghnite (Algerian MMT) by the free solvent polymerization technique under micowave irradiation was studied. The transformation was carried out with using both the raw (Maghnite-Na fin) and treated clay (Maghnite-Na⁺ fin) in aqueous sodium hydroxide NaOH solution (1 M). It was shown that no initial modification of the layered mineral (by ion-exchange with Na⁺ cations or organophilization) is needed for the successful introduction of anionic hydrogels into the interlayer gallery. The goal of the present study was to synthesis anionic polyacrylamide/Maghnite composite with similar composition and structure to that synthesized of other catalyst. The Maghnite catalyst has a significant role in the industrial scale. In fact, the use of Maghnite is preferred for its many advantages: a very low purchase price compared to other catalysts, the easy removal of the reaction mixture. The anionic sodium-clay polyacrylamide material exhibited a tendency to the formation of exfoliated structure. The synthesized hydrogels, as monitored by the swelling behavior, were characterized by Fourier transform infrared and ¹HNMR analysis. Copyright © 2018 BCREC Group. All rights reserved

Keywords: green catalysis; Anionic polyacrylamide; hydrogel; Maghnite-H+; Microwave irradiation

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1. Introduction

Microwave irradiation has been widely used in the synthesis of organic-inorganic hybrid materials because of its well known advantages over conventional synthetic route towards well defined PAm (polyacrylamide) containing polymers include living anionic [1] and group trans-

* Corresponding Author. E-mail: ramaek23@yahoo.fr (A. Rahmouni) Telp: +213773157287 fer [2] polymerization techniques, both operating using protected analogues of the acrylamide monomers. However, traditional polymerization techniques show some practical disadvantages (e.g. requirement for extremely pure reagents, low functional group tolerance, limited combination with other monomers or polymer segments). It has long been known that molecules undergo excitation with electromagnetic radiation. This effect is utilized in household microwave ovens to heat up food. However, chemists have only been using microwaves as a reaction

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method for a few years. Some of the first examples gave amazing results, which led to a flood of interest in microwave accelerated synthesis. Microwave heating has been found to be particularly advantageous for reactions under "dry" media.

Enormous accelerations in reaction time can be obtained if overheating is carried out in closed containers under high pressure; a reaction which takes several hours under conventional conditions can be completed in a few minutes, in addition in the absence of solvent on a solid support with or without a catalyst, it offers a certain number of advantages: the solvents are often expensive, toxic, difficult to in the case of high-boiling aprotic solvents [3]. Moreover, the absence of solvent reduce the risk of explosions when reaction takes place in a microwave oven [4]. Reactions under "dry" conditions were originally developed in the late eighties [5]. Synthesis without solvents under microwave irradiation offers several advantages [6]. The absence of solvent reduces the risk of explosions when the reaction takes place in a closed vessel in an oven [7]. Moreover, aprotic dipolar solvents with high boiling points are expensive and difficult to remove from the reaction mixtures [8]. During microwave induction of reactions under dry conditions, the reactants adsorbed on the surface of alumina, silica gel, clay [9]. Consequently, such supported reagents efficiently induce reactions under safe and simple conditions with domestic microwave ovens instead of specialised expensive commercial microwave systems [10].

Anionic polyacrylamide is an important water-soluble polymer. It can be used as a flocculant for water disposal, strength additives for paper manufacture, oil displacement agents for enhanced oil recovery and application in water treatment [11]. This research provides, detail aspect of reactions of acrylamide on the montmorillonite (Maghnite-Na⁺) surfaces by different redox systems involving the intercalated metal ions and reports the preparation and characterization of newly developed anionic polyacrylamide/clay [12].

Addition of maghnite clay to polymer caused an increase in the interplanar spacing, which shows polymer diffusion through the clay layers in material. The product achieved its yielded (85.05 %) and this composition is the most tensile resistant with a maximum stress of 57.55 MPa, the most flexible (E = 1.89 GPa) and the most ductile ($\varepsilon_r = 54.03$ %). The mixing rate has strong effect on the dispersion of silica layers in gel (anionic polyacrylamide) leads to the formation of exfoliation structure; besides the addition of maghnite clay to gel caused no reduction in the ratio (monomer/catalyst). Addition of maghnite to gel can lead to the improvement of its mechanics property, where this property is reduced by increasing of the clay addition. Aging increases the young's module of the material synthesized by maghnite and addition of the maghnite leads to delay in the thermal degradation of material. Finally, this study may be especially useful to the researchers in the field of polymer chemistry and even in the field of green chemistry in exploiting the tremendous catalytic potential of maghnite-Na⁺ (Algerian MMT) [13].

2. Materials and Methods

2.1 Microwave apparatus

Microwave irradiation was performed in a single mode focused CEM reactor (Model Discover, CEM Co., Matthew, NC) operating at 2.45 GHz with ability to control output power. Temperature in the system was measured by a fiber optic temperature sensor preventing interaction with MWs and influence on the temperature reading. The heat capacity Cp of the solution was approximated as the heat capacity of water. All experiments were done under the same conditions by keeping constant irradiation power, temperature, and initial reaction mixture volume (12 mL). With the experimental design that was used, the temperature was maintained at 160 °C in all experiments. The experimental equipment of microwave irradiation taking place is shown in Scheme 1.

2.2 Materials

All reagents in this work were of analytical grade and used as received without further purification. NaOH (98%) was used as the initiator, which was obtained from sigma Aldrich (french). The Maghnite-Na⁺ (MMT-Na⁺) used in this work came from a guarry located in Maghnia (North West of Algeria) and was supplied by the company "ENOF" (Algerian manufacture specialized in the production of nonferric products and useful substances). The chemical composition, structure of the MMT-Na⁺ and comparison with American and French MMT were shows in (Tables 1 and 2 as well as Figure 1). The cation exchange capacity (CEC) and surface area of the clay was found to be 84 mEq (100 g⁻¹) of dried clay and 786 m².g⁻¹, respectively, and its X-ray diffraction (XRD) analysis shows that the interlayer spacing of MMT-Na⁺ is 1.29 nm [14].

2.3 Measurement and characterization

The chemical structure of the products was determined by ¹H nuclear magnetic resonance (NMR), carried out on a 300 MHz Advance Bruker NMR Spectrometer; Fourier transform infrared spectroscopy (FTIR) analyses, obtained between 900 and 4000 cm-1 on FT-IR-Spectroscopy Alpha-P ATR Bruker No 9501165; and X-ray diffraction (XRD) for Mag-HC, obtained on D8 Advance Bruker AXS Xray diffractometer. Tensile tests were conducted using a LLoyd LR/10KN Universal Machine at room temperature and crosshead speed of 50 mm min⁻¹ for the determination of tensile modulus and yield strength, according to the standard ASTM D638. Differential scanning calorimetry (DSC) studies were conducted with a SETARAM-DSC92 in a nitrogen atmosphere at a heating rate of 10 °C/min.

2.4 Catalyst preparation method

The Montmorillonite used in this work came from a quarry located in Maghnia (North West

of Algeria) and was supplied by company "ENOF" (an Algerian manufacture specialized in the production of nonferric products and useful substances). The different chemical elements of the native Montmorillonite were transformed into oxides and analysed by FT-IR and X-ray fluorescence (experiment carried out at ENOF). These results confirm that the

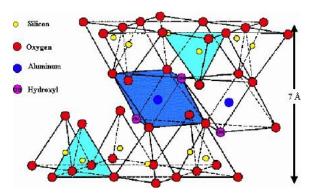


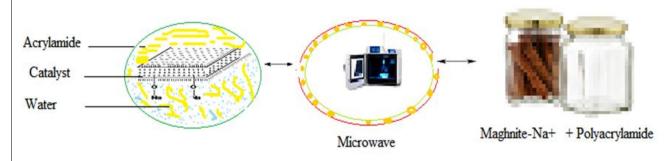
Figure 1. Crystallographic structure of Maghnite (Basic repeating unit is [Si₄O₁₀Al³⁺(2-x) Mg²⁺x(OH)₂]) [15]

Table 1. Elementary compositions of Protons exchanged samples "Maghnite" (wt%).PF* : Pert in Fire [16]

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na ₂ O	K_2O	${ m TiO}_2$	${ m SO}_3$	PF*
Raw-Mag	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	11
Mag-H ⁺	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	11

Table 2. Comparison in the composition (in %) of American, French, and Algerian MMT [17]

Sample	${ m SiO}_2$	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	Na ₂ O	K_2O	${ m TiO}_2$	SO_3
Wyoming (USA) (%)	50.04	20.16	0.68	00	1.46	0.23	\mathbf{Tr}	1.27	00	00
Vienne (France) (%)	57.49	20.27	2.92	0.19	0.23	3.13	1.32	0.28	0.12	00
Raw-Mag (Algeria) (%)	69.39	14.67	1.16	00	0.30	1.07	0.5	0.79	0.16	0.91
Mag-H ⁺ (Algeria) (%)	71.70	14.03	0.71	00	0.28	0.80	0.21	0.77	0.15	0.34



Scheme 1. Experimental equipment of microwave irradiation for synthesis of anionic polyacrylamide (APAm)

maghnite used consists essentially of Montmorillonite (MMT), have been prepared in laboratory chemistry of polymers in Oran University (LCPO), this clay is purified by separation of the argillaceous phase and the coarse phases. Rough clay is put in suspension in distilled water. In the suspension, the solid/liquid report/ratio is approximately 1/10. The suspension is then filtered on a sieve 0.02 mm in diameter of pores to eliminate the coarse matter and stones. It then versed in test-tubes and is left at rest during 2 hours. The separation of the argillaceous phase of the coarse fraction which remains at the bottom makes by siphonage. The recovered suspension is then centrifuged with 4500 tr/min during 20 min. Recovered clay is treated with a solution 1 M of sodium Hexametaphosphate (NaPO₃)₆ (clay 20 g in 100 mL), by maintaining agitation, during 3 h. The suspension is versed then in the testtubes of separation and Montmorillonite -Na is to separate while exploiting its falling speed, MMT crosses with 20 °C, a distance of 10 cm each 8 h. Therefore, Na-Montmorillonite is recovered by siphonage at a distance of 20 cm after 16 h of decantation. One adds water distilled to the test-tubes after each siphonage, one agitates during 15 min and one lets the suspension be elutriated before proceeding to new a siphonage. MMT is then recovered by centrifugation with 4500 tr/min during 1 h. With the end, it is washed with distilled water (on several occasions), filtered using one sintered of porosity 3 (maximum diameter of pores from 16 to 40 µm), dried in the drying oven with 105 °C, crushed using a mortar and kept in a desiccators [18,19].

2.5 Synthesis of product

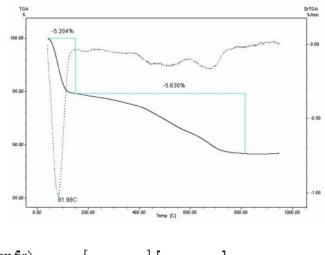
A solution of 2 g of acrylamide containing 0.5 M of sodium hydroxide (NaOH) was prepared and (2 wt%) of maghnite-Na⁺ (Algerian MMT) was then added. The mixture of (Am, Maghnite-Na⁺ and NaOH) was put into a flask with 100 mL and stirred to allow proper mixing. The mixture was subjected to several short burst of microwave irradiation using a microwave oven at frequency of 2.45 GHz at power output of 200 W. The reaction mixture was then submitted to microwave irradiation at 160 °C and for 4 minutes .The mixture was cooled (4 to 10 minutes at room temperature), filtered and washed extensively with distilled water and methanol to remove any unreacted acrylamide until the washing solution became neutral and air dried. The reaction taking place is shown in Scheme 2.

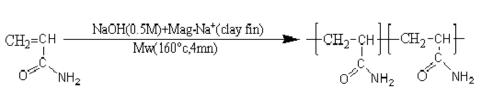
3. Results and Discussion

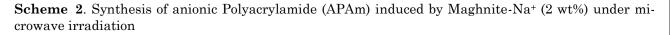
The thermal characterizations of the catalyst include thermogravimetric analysis (TGA). Figure 2 shows the weight losses (%) versus temperature (°C) curves for pure Maghnite-Na⁺, The TGA of pure Maghnite-Na⁺ show two stages of weight loss. The first weight loss in Mag-Na⁺ below 100 °C is a result of the release of free water. The second weight loss around 600 °C is associated with the dehydroxylation of silicate structure [20,21]. The total weight loss is only 13.94% up to 800 °C. As can be expected, Maghnite-Na⁺ shows a high thermal stability.

Figure 3 show the characteristic FT-IR spectra of Mag-Na⁺ and Mag-H⁺. The characteristic absorption peaks of MMT are assigned to the Si–O–Si skeleton vibration at 1043-1116 cm⁻¹, the strong absorption bands of Si–O and Al–O bending vibration at 525-628 cm⁻¹ and

Figure 2. TGA curves of a Maghnite-Na⁺ obtained in nitrogen atmosphere at heating rate of 10 °C/min







the OH stretching vibration at 3425 cm⁻¹ [22,23].

In the XRD spectra shown in Figure 4, the first broad peak of Mag-Na⁺ centered on a value of 1.29 nm is observed indicating that the layer distance in Mag-Na⁺ is 1.29 nm, the other weak peaks are related to the structure of aluminum-oxygen octahedron and silicon-oxygen tetrahedron in the MMT. The X-ray powder diffraction profiles exhibited the presence of other crystalline phases such as quartz, feldspath and calcite in (raw-Maghnite). Kwon *et al.* [24,25] reported that the decrease in the basal spacing indicates a loss of the interlayer water upon the replacement of Na⁺ for H⁺.

Under conventional conditions (CS), the polymer was produced with 75% yield after 5 h, if the reaction was continued the yield was 87.6% after 24 h at ambient temperature. By contrast, under microwave irradiation the ma-

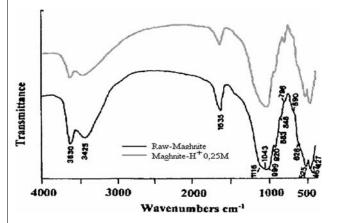


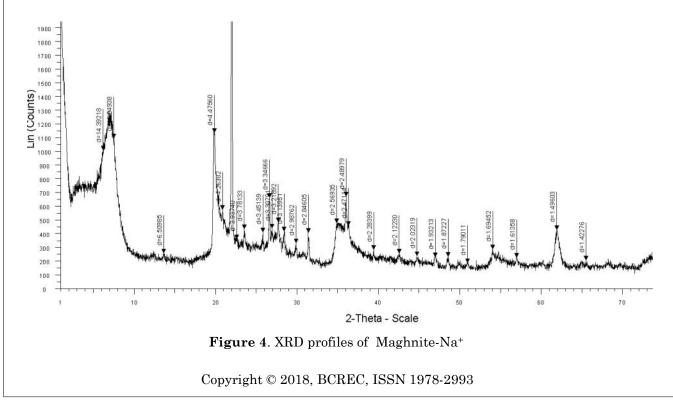
Figure 3. FTIR spectra of Raw-Maghnite and Maghnite-Na⁺

terial was produced with the remarkable yield 80.56 % after only 2 min after the beginning of the reaction, and 92.58 % after 20 min at ambient temperature.

The functional groups of the synthesized product were investigated by Fourier transform infrared spectrophotometer. The spectrum of the product confirm the existence of the carbonyl and amide functionalities. Figures 5 and 6, shows the FTIR spectra for the final product and the monomer. The peaks at 3191-3331 cm⁻¹ were due to amine group, whereas, the absorption peak at 1651 cm⁻¹ is strong and sharp and is attributed to the carbonyl (C=O) of the carboxyl group [26]. The peaks at 2868.68 cm⁻¹ and 2909.55 cm⁻¹ and 2931.10 cm⁻¹ are assigned to *v*-CH₂ [27].

The ¹H NMR spectrum of (APAm) induced by Maghnite-Na⁺ (2 %wt) under microwave irradiation was recorded in deuterated deionized water (D₂O) solution using a Bruker Avance 300 MHz Spectrometer. Chemical shifts (δ) were given in ppm with tetramethylsilane (TMS) as a standard. Figure 7, represents ¹H NMR spectrum of APAm, which was obtained from purified polymer dispersion. The ¹H NMR spectrum was in accordance with the proposed structures of the product. The Methylene group of APAM was observed at 1.20-1.40 ppm and (CH) group from APAm appeared at 2.40-2.60 ppm. The strong peaks of 4.60-4.80 ppm were attributed to the solvent (D₂O) [28,29].

A thermal property of anionic polyacrylamide was characterized by TGA. According to Figure 8, crude dry particles were obtained by removing free water and solvent isothermally



at 110 °C. As the non polar solvent used to wash the products, chloroform would be expected to constitute the major part of volatile solvents since it could remain absorbed during synthesis but was not observed [30]. There are three main thermal degradations of the anionic polyacrylamide. The first degradation is at 186.53 to 252.51 °C with a weight loss of 0.721% due to absorbed and bonded water in polyacrylamide [31]. The second degradation temperature (T_d) is onset at 252.51 to 311.97 °C with a weight loss of 8.556 %. The degradation evolves ammonia from thermal imidization of polyacrylamide [32-33] removing of unreacted monomer or absorbed solvent. The main weight loss of 19.6 % onset at 390.15 to 487.93 °C results from degradation of the polymer chain backbone [34].

Table 3 show the effect of the amount of Magh-Na⁺ on the polymerization yield under effect of microwave irradiation. Indeed, using various amounts of Magh-Na⁺: 1.5, 2, 3, 4, and 5 % yield increased with the amount of Maghnite-Na⁺, thus clearly showing the effect of Mag-Na⁺ as a catalyst. This phenomenon is probably the result of an increase in the num-

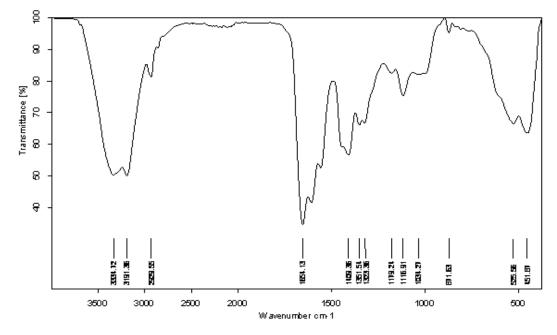
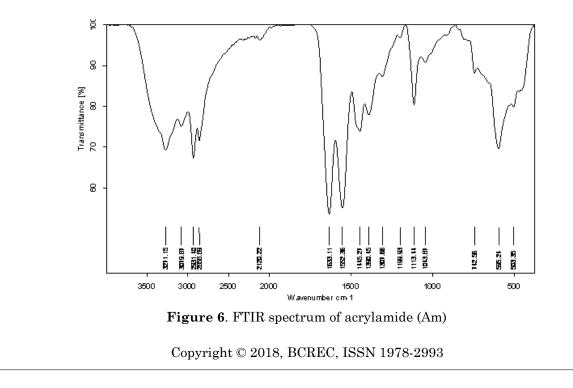


Figure 5. FTIR spectrum of anionic polyacrylamide (APAm) induced by Maghnite-Na $^+$ (5 % wt) under microwave irradiation



ber of "initiating active sites" responsible of inducing polymerization, a number that is prorating to the amount of catalyst used a reaction [35]. In the other hand the viscosimertic molecular weight are inversely proportional to the amount of Magh-Na⁺. This finding is in good agreement with the proposed finding that MMT-Na⁺ is present as the active initiator species since the number of those species by weight, the polymerization was carried under microwave irradiation in bulk at 160 °C. The polymerization should be related to their surface area. Ayat *et al.* obtained similar results [36].

Effect of temperature on the polymerization of anionic polyacrylamide under effect of maghnite-Na⁺ (5 wt%) for 5 minutes in microwave irradiation is shown in Table 4. A polymerization yield reach maximum value around 160-164 °C. On the other hand, with the increase in the reaction temperature above 160 °C, viscosity of the obtained polymer increase and decrease the molecular weight of the polymer progressively, suggesting the possible occurrence of thermal

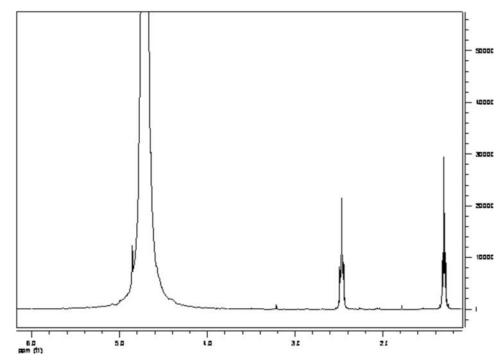


Figure 7. ¹H NMR spectrum of anionic polyacrylamide (APAM) induced by Maghnite-Na $^+$ (5%wt) under microwave irradiation

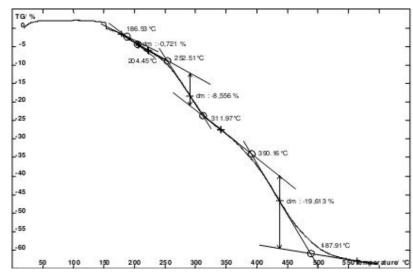


Figure 8. Thermogravimetric curve of the APAm, obtained after samples treated isothermally at 110 $^{\circ}$ C for 20 min

degradation [37-38]. On the basis these results, subsequent polymerization were carried out at 160 °C under effect of microwave irradiation.

The percentage moisture retains of Maghnite-Na⁺ and APAm/Maghnite-Na⁺ with increasing Am (acrylamide) and catalyst content are shown in Figures 9, 10, 11, and 12. It was observed that moisture retain gradually [39].

The decreases in moisture retain and water uptake can be attributed to the percentage of clay in the composite being limited, which reflects that the quantity of the polymer introduced in the layers reaches a limit and is enough to achieve maximum opening of the interlayers of clay and the formation of a crosslinked structure on a certain extent which prevents the insert on of water molecules [40-41]. Finally, water resistance of these composites which as defined the decreases in moisture re-

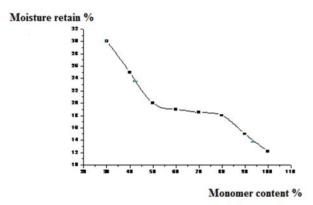


Figure 9. The percentage moisture retains values of acrylamide (Am) obtained including different percentages of (Am)

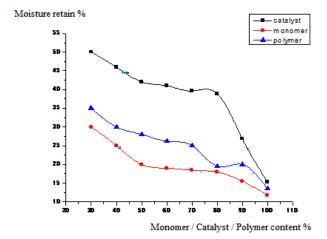


Figure 11. The percentage moisture retains values of Maghnite-Na⁺, Am, and APAm obtained including different percentages of Am, Maghnite-Na⁺, and APAm

tain and water uptake values can be greatly improved [42-43].

To evaluate the effect of Maghnite (Algerian MMT) catalyst in APAm, we prepared five samples with the same procedure. Tensile tests were conducted using a LLoyd LR/10KN Universal Machine at room temperature and crosshead speed of 50 mm.min⁻¹ for the determination of tensile modulus and yield strength, according to the standard ASTM D638. Compared with Pam, prepared by other catalyst, such as: Lewis acid and under conventional method, the young's modulus, and yield strength, are greatly enhanced as show in Table 5. It shows that the mechanicals properties depend on amount of catalyst.

The tensile test was carried out to evaluate the tensile properties of the various samples compositions in order to determine the influ-

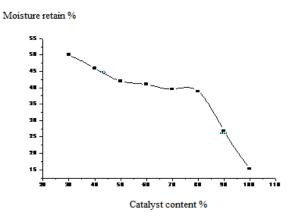


Figure 10. The percentage moisture retains values of Maghnite-Na⁺ obtained including different percentages of Maghnite

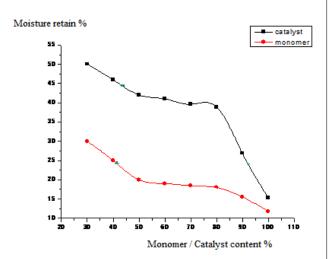


Figure 12. The percentage moisture retains values of Maghnite-Na⁺ and APAm/Maghnite-Na⁺ obtained including different percentages of Am

ence of the addition of the clay on the tensile properties of the virgin matrix. Young modulus, tensile strength and elongation at break were evaluated as a function of the mass fraction of clay in all series of samples. The test pieces are maintained during the test by pneumatic jaws preventing any sliding of the test piece during the traction. The initial strain rate was set at 5 mm min⁻¹. From these results, it can be deduced that the incorporation of the clay into the APAm matrix, with different percentages, has significantly improved all of its tensile properties. Thus, Young's modulus increased in compositions with the highest clay contents (1-12 wt%). The composition of clay (5 wt%) in APAm has the highest tensile values. This is attributed to the interactions between the polymer chains and the nanometric layers of the clay with a decrease in the value of the Young's modulus. This composition is the most tensile resistant with a maximum stress of 57.55 MPa, the most flexible (E = 1.89 GPa) and the most ductile ($\varepsilon_r = 54.03$ %). This result confirms the exfoliation of maghnite clay in polymer (APAm) which is in agreement with the literature [44].

In general, the anionic polymerization like in other vinyl polymerization methods consists of three main reactions: (a) initiation, (b) propagation, and (c) termination, as described in Figure 13. However, termination is brought about intentionally using a suitable electrophile, which can be useful for end group modification [45]. The initiation reaction is generally fast and is not reflected in the overall rate of

Table 3. Effect of amount of catalyst on polymerizationyield of anionic polyacrylamide(APAm) under microwave irradiation

the polymerization [46]. The kinetics of the polymerization is predominantly controlled by the propagation step [47].

The interaction of propagating ion pairs with functional groups of the vinyl monomer or the polymer chain can affect the propagation rate and in some cases induces side reactions that can cease the polymerization [48]. In a side reaction-free anionic vinyl polymerization; the termination is a simple rapid reaction wherein anions are quenched through acidic hydrogen or another suitable electrophile [49]. Hence, it is important to match the reactivity of the initiator with the propagating species in order to have fast and homogeneous initiation [50]. For example, the reaction of sodium metal generates a radical anion in polar solvent, which can be used as initiator for the anionic polymerization [51]. The anionic polymerization of acrylamide in free solvent and under microwave irradiation was first studied using the maghnite-Na⁺ as catalyst. The proposed anionic polymerization mechanism as shown in (Figure 13). The high reactivity of the methylene group of double bond in acrylamide, involves the formation of a strong proton donor by the reaction of the maghnite-Na⁺, followed by the protonation of the acrylamide molecule, whose ensuing carbenium ion rearranges to form a carbocation responsible for the propagation reaction [52]. This process is extremely rapid and exothermic. In order to obtain polymers with viable molecular weights of a few thousand, the polymerization temperature

Table 4. Effect of temperature on polymerization yield of anionic polyacrylamide under microwave irradiation

Time (min)	1	2	3	4	5	Time (min)	5	5	5	5	5
Catalyst (%)	1.5	2	3	4	5	Temperature (°C)	100	130	145	160	164
Yield (%)	15.09	34.86	52.93	77.95	84.82	Yield (%)	19.34	39.06	59.81	79.91	84.94

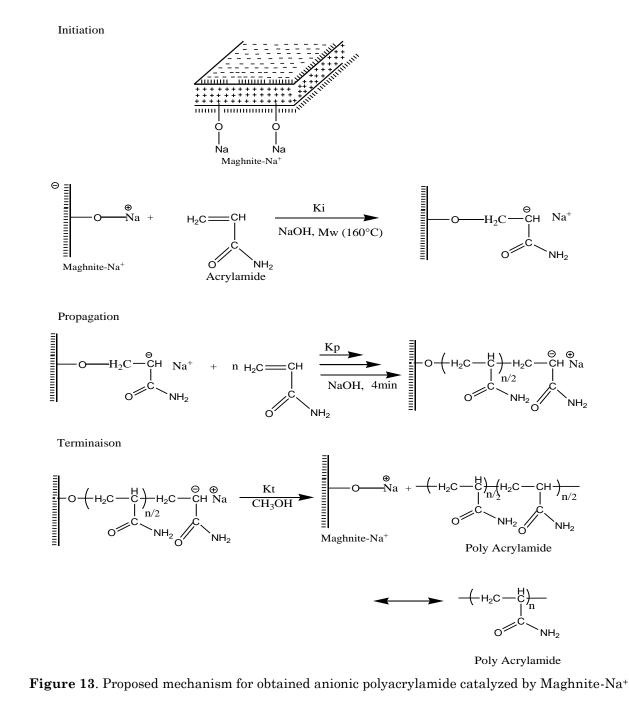
Table 5. Mechanical properties of APAm/Maghnite samples

Sample	Catalyst (wt%)	Young's modulus (GPa)	Deformation at break (%)	Maximum stress (MPa)	Yield strength (MPa)
Maghnite	-	1.23	54.36	43.26-	
APAm(pure	-	0.68	42.91	33.91	70.45
APAm-1/Magh	1	0.64	35.56	35.13	62.05
APAm-2/Magh	2	0.86	30.42	33.80	65.66
APAm-3/Magh	3	0.95	29.35	31.28	67.33
APAm-4/Magh	4	1.45	31.22	31.22	70.88
APAm-5/Magh	5	1.29	54.03	57.55	85.09
APAm-6/Magh	7	1.81	46.47	48.37	84.12
APAm-7/Magh	12	1.72	41.44	41.44	83.56

must be particularly low and around of -160 °C [53], to reduce the relative kinetic contribution of the transfer reaction with respect to chain propagation. The driving forces for the reaction are the high reactivity of the l double bond of monomer and the high reactivity of catalyst [54-55].

4. Conclusion

At the optimal conditions, anionic polyacrylamide material was successfully synthesized as an aqueous free solvant dispersion with acrylamide (Am) and maghnite-Na+ (MMT-Na⁺) in aqueous solution of sodium hydroxide NaOH under microwave irradiation. The influencing factors on the polymerization reaction were studied, and the optimal reaction conditions were obtained. The characterization of anionic polyacrylamide was measured by IR and H-NMR spectroscopy. The results indicated that, the polymerization was successful under microwave irradiation. In our previous papers, we already reported about polymerization catalyzed by Maghnite-Na⁺ (Algerian MMT) this new nontoxic cationic catalyst exhibited higher efficiency via the polymerization of vinylic and hetero-cyclic monomers. The objecti-



ves of this work are the synthesis of anionic polyacrylamide of by the use of MMT-Na⁺ as a catalyst. The interesting aspect of this new non-toxic catalyst is the environmentally friendly nature of the reaction because it does not imply the disposal of solvents or metal catalysts.

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