Chapter 7

Synthesis and Characterization of Polymeric Material Consisting on Acrylamide Catalyzed by Maghnite (Algerian MMT) under Microwave Irradiation

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Additional information is available at the end of the chapter

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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 microwave 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. 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 ^{1}HNMR analysis.

Keywords: green catalysis, anionic polyacrylamide, hydrogel, maghnite-H^+, microwave irradiation, cationic polyacrylamide

1. Introduction

Green chemistry for chemical synthesis addresses our future challenges in working with chemical processes and products by inventing novel reactions that can maximize the desired products and minimize by products [1], designing new synthetic schemes and apparatus that

can simplify operations in chemical productions [2] and seeking greener solvents that are inherently environmentally and ecologically benign [3]. In addition, a desirable green solvent should be natural [4, 5], nontoxic [6, 7], cheap and readily available with additional benefits of aiding the reaction, separation or catalyst recycling. Most of the cationic initiators used in the synthesis of polymers and copolymers are expensive. They may be poisoned by products of the reaction or impurities present in the monomer feed, and contain heavy metals, such as chromium, mercury, antimony, etc., that presents environmental disposal problems for the user. As clay catalysts, montmorillonite a class of inexpensive and non-corrosive solid acids, have been used as efficient catalysts for organic reactions. Montmorillonite catalysts are easily recovered and reused [8]. In continuation of our studies on environmentally and green methods using solid supports, we report that acid-exchanged montmorillonite Mag-H+ is a novel and efficient solid catalyst for the synthesis of anionic polyacrylamide from acrylamide monomer. In contrast to the more usually used catalyst, maghnite-H^+ can be easily separated from the polymer and regenerated by heating to a temperature above 100–105°C [9]. 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 [10] and group transfer [11] 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 methodology 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 [12]. Moreover, the absence of solvent reduces the risk of explosions when reaction takes place in a microwave oven [13]. Reactions under "dry" conditions were originally developed in the late 1980s [14]. Synthesis without solvents under microwave irradiation offers several advantages [15]. The absence of solvent reduces the risk of explosions when the reaction takes place in a closed vessel in an oven [16]. Moreover, aprotic dipolar solvents with high boiling points are expensive and difficult to remove from the reaction mixtures [17]. During microwave induction of reactions under dry conditions, the reactants adsorbed on the surface of alumina, silica gel, clay [18]. Consequently, such supported reagents efficiently induce reactions under safe and simple conditions with domestic microwave ovens instead of specialized expensive commercial microwave systems [9]. Many researchers have studied cationic copolymerization of anionic polyacrylamide using "H_2O"/KPS initiator system and CH_2Cl_2 solvent [19, 20]. Frequently, these initiators require the use of very high or very low temperature and high pressures during the polymerization reaction. The separation of the initiators from the polymer is not always possible. Therefore, the presence of toxic initiators presents problems in the manufacture of polymers used especially in medical and veterinary procedures.

There is still a great demand for heterogeneous catalysis under mild conditions and in environmentally friendly processes. Montmorillonite, a class of inexpensive and noncorrosive solid acids, have been used as efficient catalysts for a variety of organic reactions. The reactions catalyzed by montmorillonite are usually carried out under mild conditions with high yields and high selectivity's, and the workup of these reactions is very simple; only filtration to remove the catalyst and evaporation of the solvent are required. Montmorillonite catalysts are easily recovered and reused [21, 22]. The purpose of this paper is to study the polymerization of anionic acrylamide catalyzed by maghnite-H^+ as proton exchanged montmorillonite clay. This new non-toxic cationic catalyst has exhibited higher efficiency via the polymerization of vinylic and hetero-cyclic monomers [18, 19]. This catalyst can be easily separated from the polymer product and regenerated by heating at a temperature above 100°C [23]. The effects of different synthesis parameters, such as the amount of maghnite-H^+, the molar ratio (acrylamide/maghnite), reaction time, on the yield of polymerization are discussed together with the mechanism of polymerization.

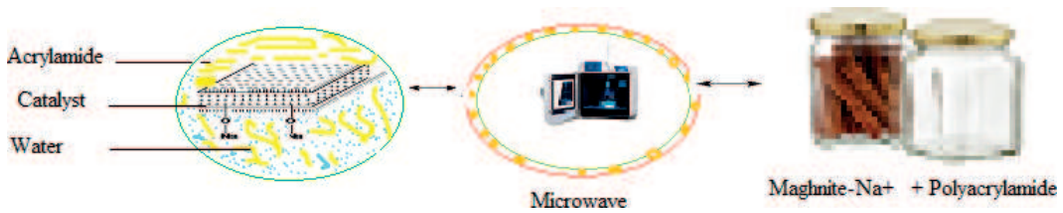
2. Experimental section

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 quarry 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 shown in (**Tables 1** and **2** and **Figure 1**). The cation exchange capacity (CEC) and



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

surface area of the clay was found to be 84 mEq (100 g^{-1}) of dried clay and 786 m^2 g^{-1} respectively, and its X-ray diffraction (XRD) analysis shows that the interlayer spacing of MMT-Na^+ is 1.29 nm [26].

2.3. Physical and chemical characterization of Maghnite

This clay has been characterized to determine the moisture content, pH, swelling, colloidality, loss on ignition and cation exchange capacity.

2.3.1. Humidity rate

The protocol consists in drying a sample of 20 g of maghnite (W_0) in the oven at 105°C for 24 h; the weight (W_1) is the weight of the dry sample. The moisture content (H% weight) is given by the following formula (i) [27].

$$H(\%) = (W_0 - W_1)/W_0 \times 100 \quad (1)$$

where W_0 = weight initial and W_1 = weight after drying.

When weight of catalyst is stoped 24 h at (9.50 and 9.72) for maghnite (100 μm) and maghnite (200 μm) respectively, we can calculate the humidity rate according to the formula (1).

Maghnite (100 μm): H (%) = $(W_0 - W_1)/W_0 \times 100$ = (20–19.5)/20 × 100 = 2.5%.

Maghnite (200 μm): H (%) = $(W_0 - W_1)/W_0 \times 100$ = (20–19.72)/20 × 100 = 1.4%.

The results obtained allow us to draw two conclusions:

- The humidity rate depends on the diameter of the maghnite (MMT).
- The second conclusion allows us to say that the maghnite it's no hygroscopic as show in (**Table 3**).

Sample	SiO_2	Al_2O_3	$F_{e2}O_3$	CaO	MgO	Na_2O	K_2O	TiO_2	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

*PF: Pert in fire [24].

Table 1. Elementary compositions of protons exchanged samples "maghnite" (compositions wt%).

Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3
Wyoming (USA) (%)	50.04	20.16	0.68	00	1.46	0.23	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) (%)	71.7	14.03	0.71	00	0.28	0.80	0.21	0.77	0.15	0.34

Table 2. Comparison in the composition (in %) of American, French and Algerian MMT [19].

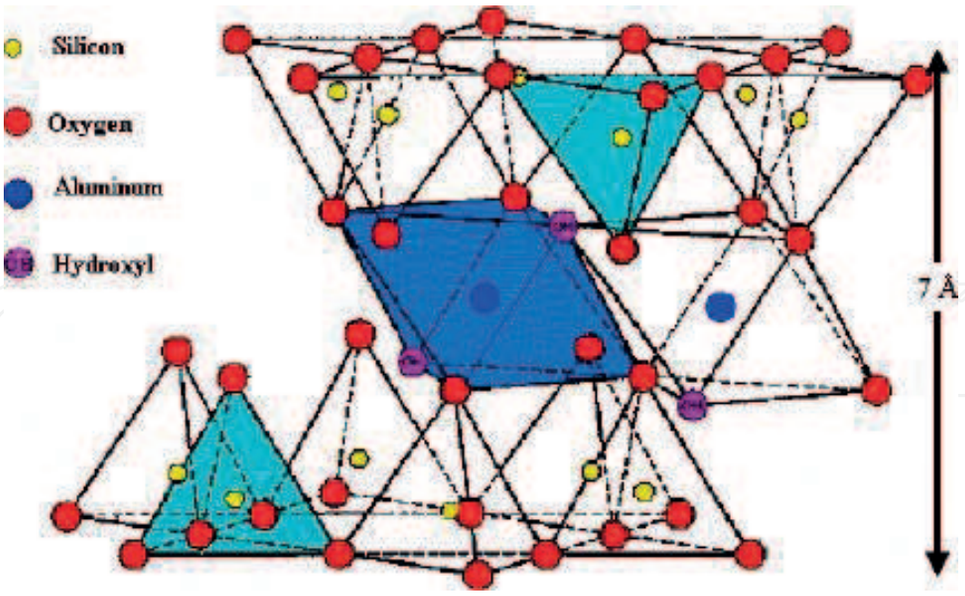


Figure 1. Crystallographic structure of maghnite (basic repeating unit is $[Si_4O_{10}Al^{3+}(2-x)Mg^{2+}x(OH)_2])$ [25] .

	S_1	S_2	S_3	S_4	S_5	S_6
Maghnite (100 μm)	19.56	19.53	19.49	19.51	19.50	19.50
Maghnite (200 μm)	19.82	19.79	19.70	19.72	19.72	19.72

Table 3. The weight obtained after 24 h of steaming stabilized.

Sample	pH
Distilled water	7.00
Maghnite (100 μm)	9.90
Maghnite (200 μm)	10.23

Table 4. The pH results obtained at room temperature.

2.3.2. pH measurement

Our method for pH measurement consists of stirring 10 g of maghnite (MMT) with 500 mL of distilled water for 20 min. After 24 h, the pH of the support is measured using a pH meter. The pH results obtained at room temperature show us a great basicity of the samples studied compared with distilled water. This may be due to carbonates, alkaline bicarbonates or silicates which usually go into the composition of the maghnite (MMT) as shown in **Table 4**.

3. Preparation of catalyst

The preparation of the "maghnite-H^+ 0.25 M" was carried out by using a method similar to that described by Belbachir and coworkers [28]. Indeed, the raw-maghnite (20 g) was crushed

for 20 min using a Prolabo ceramic balls grinder. It was then dried by baking at 105°C for 2 h. The maghnite was then weighed and placed in an Erlenmeyer flask together with 500 ml of distilled water. The maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M of sulfuric acid solution, until saturation was achieved over 2 days at room temperature, the mineral was washed with distilled water until it became sulfate free, and then dried at 105°C [29, 30].

4. Characterization spectroscopic and thermal of catalyst

The best value of copolymer yield was obtained with maghnite-H^+ 0.25 M, in which there is a complete saturation of montmorillonite with protons without destruction of catalyst structure [31]. Maghnite-H^+ was found to have a BET surface area (SSA) of 59.45 m^2/g, an average pore diameter of 62.46 Å and total pore volume of 0.00772 cm^3/g. The SSA of maghnite-H^+ is close to that (61 m^2/g) obtained by Belbachir et al. [32] for montmorillonite.

After the activation process and filtration, the samples were washed until pH close to 7 and dried at 105°C overnight. According to experimental data, chemical composition of clay varies with the H_2SO_4 concentration. Two regions can be revealed. In the region of 0.05–0.15 M H_2SO_4 the change of Si/Al molar ratio is a small-scale due to the leaching of interlayer Ca^{2+}, Mg^{2+} and Na^+ cations by H_2SO_4. At the same time when H_2SO_4 concentration is higher than 0.2 M the change of Si/Al molar ratio is pronounced that can be related to the dissolution of Al^{3+} cations from the octahedral sheet. Effect of the acid activation on the textural properties is also confirmed by XRD method. The X-ray of the samples are shown in **Figure 2a** and **b**. The position of the basal (001) reflection, i.e. interlayer distance, strongly depends on the H_2SO_4 concentration. The increasing H_2SO_4 concentration from 0.05 to 0.25 M leads to increase the basal spacing, from 12.5 to 15.0 Å. However the basal spacing decreases again for higher acid concentrations. Probably, this phenomenon can be attributed to the "cleaning" of the solid due to the elimination of possible soluble impurities and the substitution of interlayer ions (Na^+ and Ca^{2+}) by H^+.

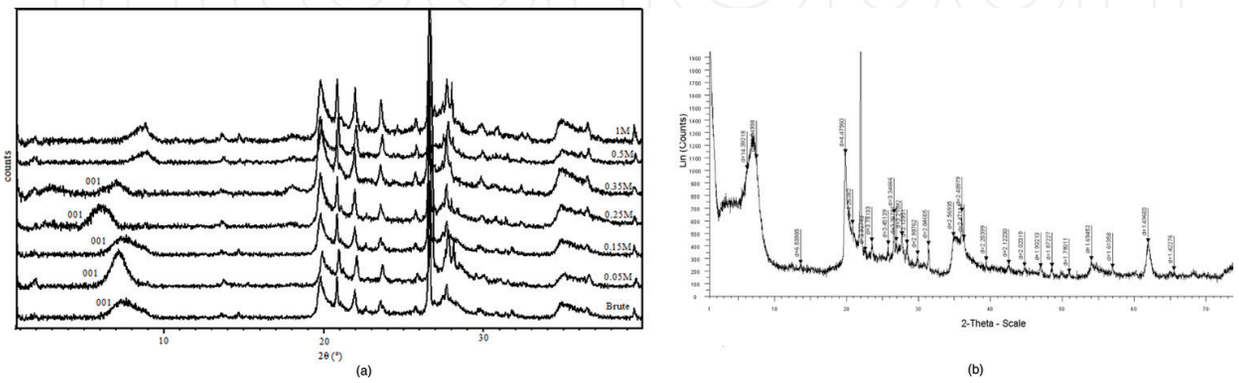


Figure 2. (a) XRD pattern of raw maghnite and activated maghnite (maghnite-H^+) [33] and (b) XRD profiles of maghnite-Na^+ [34].

The thermal characterizations of the catalyst include thermogravimetric analysis (TGA). **Figure 3** 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 Na^+-Mag 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 [35]. The total weight loss is only 13.94% up to 800°C. As can be expected, maghnite-Na^+ shows a high thermal stability.

Figure 4 shows the characteristic FT-IR spectra of Magh-Na^+ and Magh-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 the OH stretching vibration at 3425 cm^{-1} [36, 37].

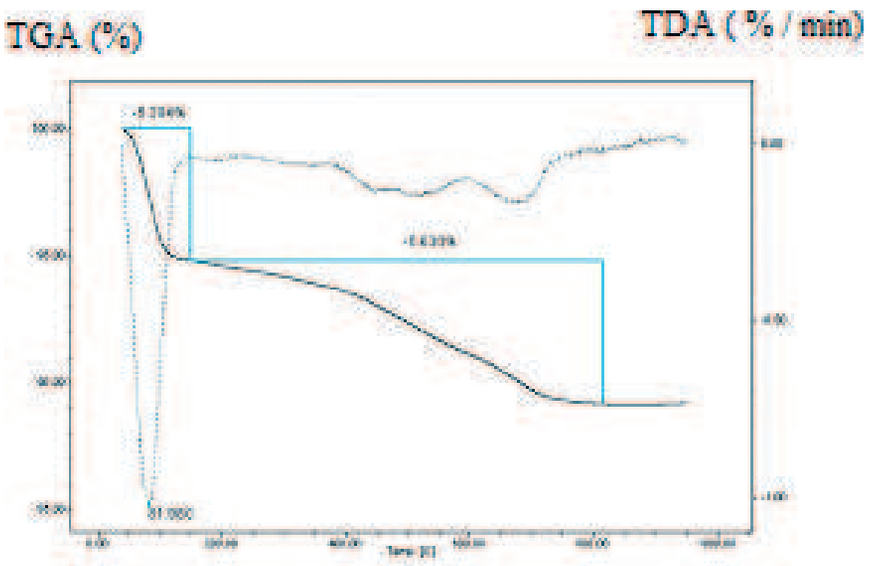


Figure 3. TGA curves of a maghnite-Na^+ obtained in nitrogen atmosphere at heating rate of 10°C/min.

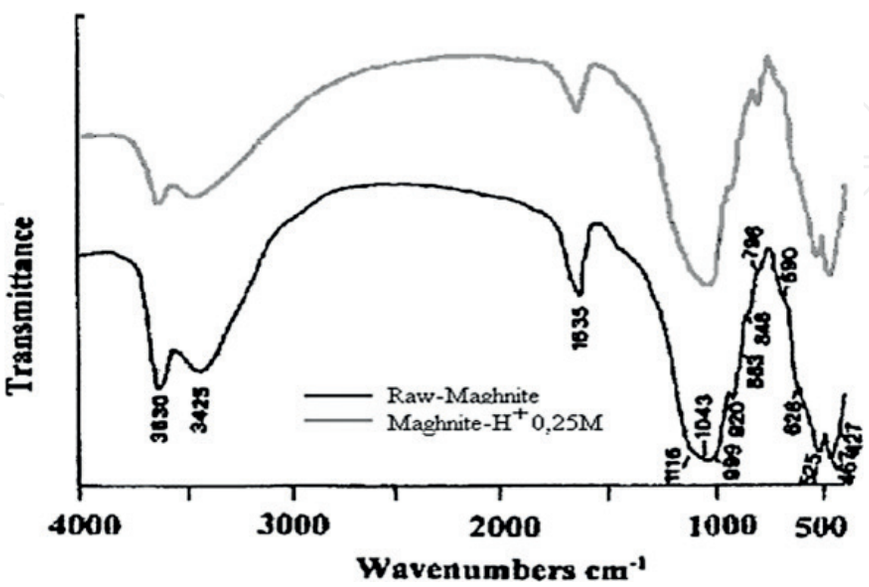
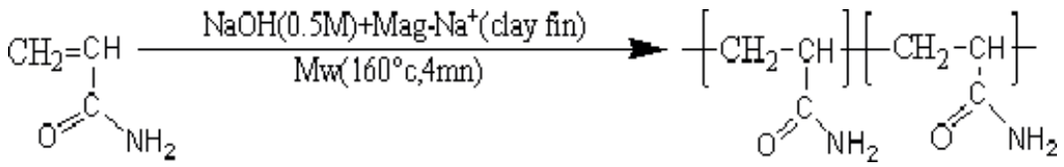


Figure 4. FTIR spectra of raw-maghnite and maghnite-H^+.

5. Synthesis of polymeric material

A solution of 2 g of acrylamide containing 0.5 M of sodium hydroxide (NaOH) was prepared and (2 w%) 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 min. The mixture was cooled (4–10 min 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**.



Scheme 2. Synthesis of anionic polyacrylamide (APAm) induced by maghnite-Na^+ (2 wt%) under microwave irradiation.

6. Results and discussion

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 material 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.

6.1. Spectroscopic characterization

The functional groups of the synthesized product were investigated by Fourier transform infrared spectrophotometer. The spectrums of the product confirm the existence of the carbonyl and amide functionalities. **Figures 5** and **6** show 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 [38]. The peaks at 2868.68 and 2909.55 and 2931.10 cm^{-1} are assigned to υ-CH_2 [39].

The ^1H NMR spectrum of (APAm) induced by maghnite-Na^+ (2 wt%) under microwave irradiation was recorded in deuterated deionized water (D_2O) 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 (D_2O) [40, 41].

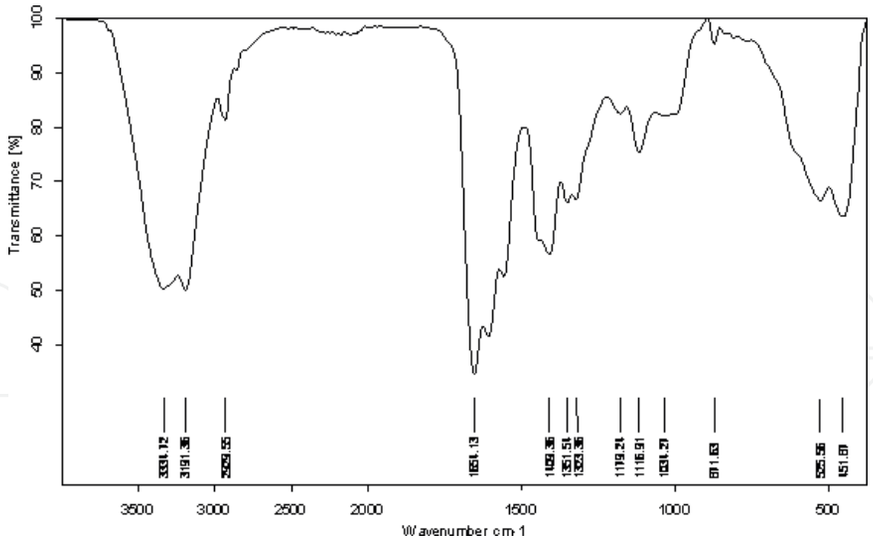


Figure 5. FTIR spectrum of anionic polyacrylamide (APAm) induced by maghnite-Na^+ (5 wt%) under microwave irradiation.

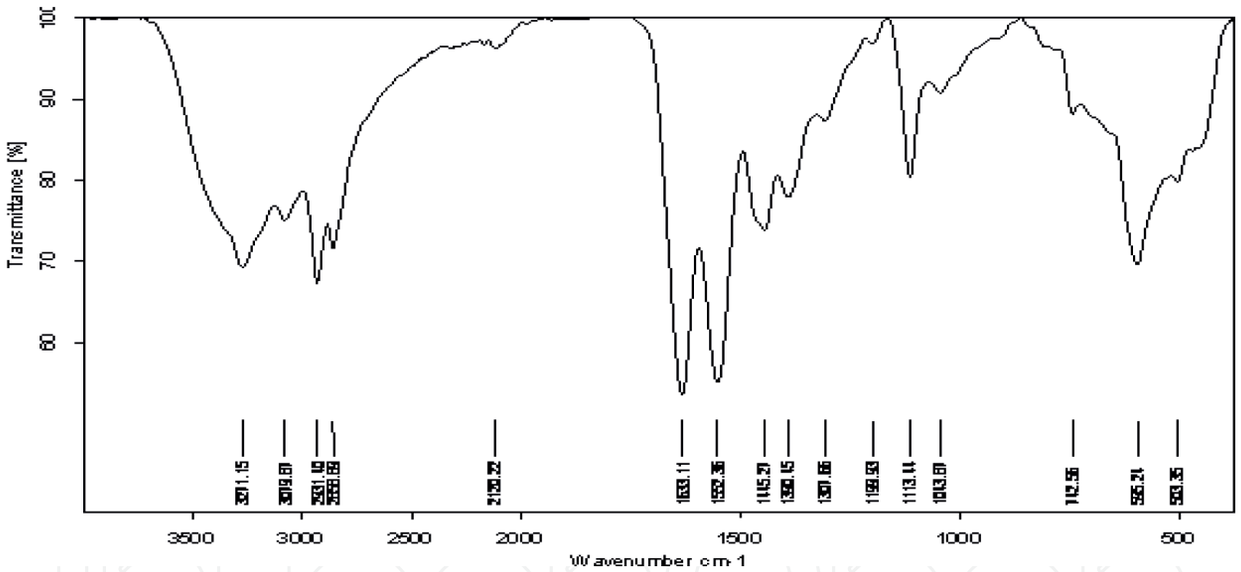


Figure 6. FTIR spectrum of acrylamide (Am).

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 nonpolar 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 [42]. There are three main thermal degradations of the anionic polyacrylamide. The first degradation is at 186.53–252.51°C with a weight loss of 0.721% due to absorbed and bonded water in polyacrylamide [43]. The second degradation temperature (T_d) is onset at 252.51–311.97°C with a weight loss of 8.556%. The degradation evolves ammonia from thermal imidization of polyacrylamide [44, 45] removing of unreacted monomer or absorbed solvent. The main weight loss of 19.6% onset at 390.15–487.93°C results from degradation of the polymer chain backbone [46].

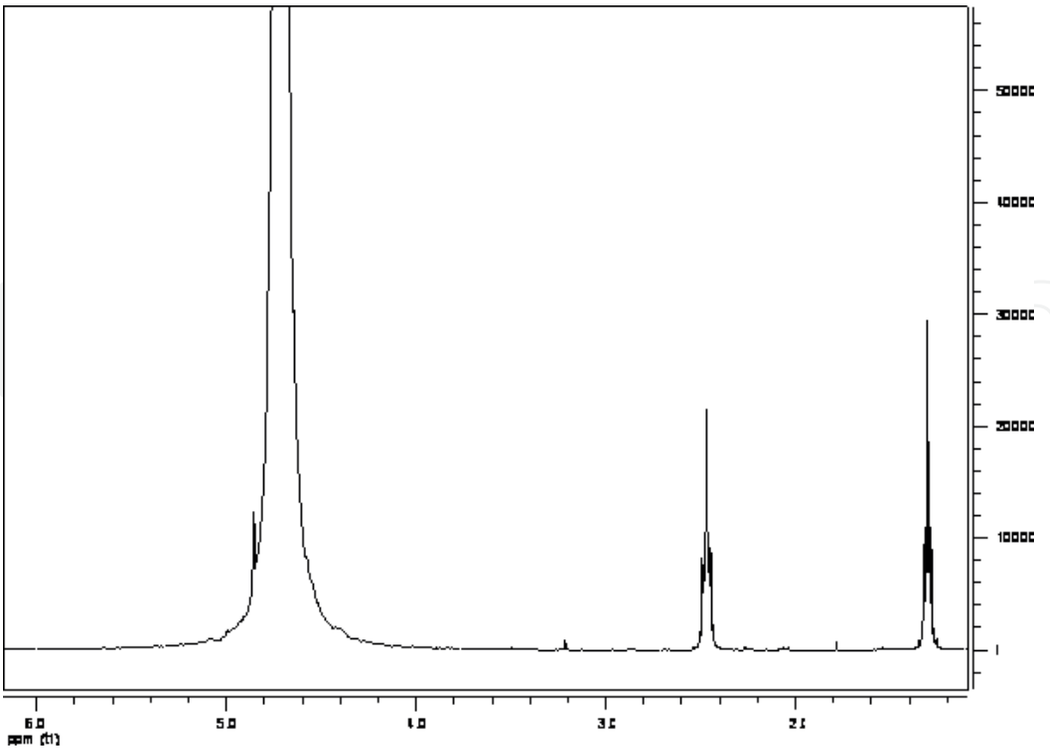


Figure 7. ^{1}H-NMR spectrum of anionic polyacrylamide (APAM) induced by maghnite-Na+ (5 wt%) under microwave irradiation.

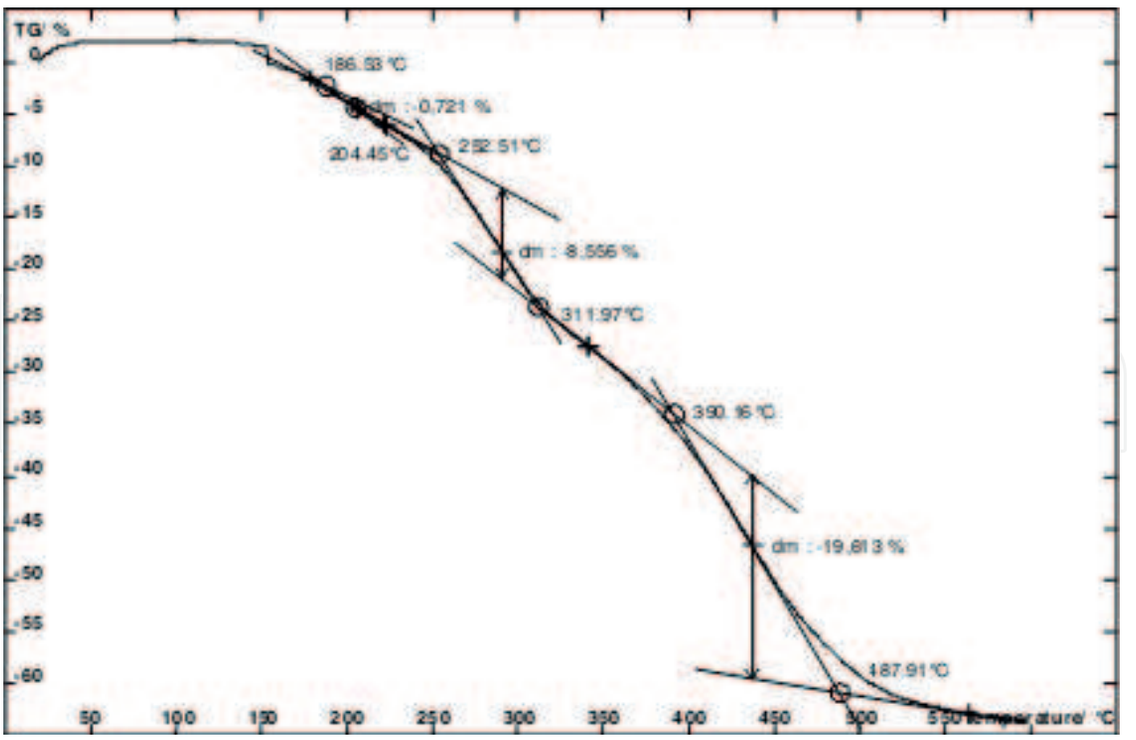


Figure 8. Thermogravimetric curve of the APAm, obtained after samples treated isothermally at 110°C for 20 min.

6.2. Kinetics studies

Table 5 shows 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 number of "initiating active sites" responsible of inducing polymerization, a number that is pro rata to the amount of catalyst used a reaction [47]. 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 proposal 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. obtain similar results [48].

Effect of temperature on the polymerization of anionic polyacrylamide under effect of maghnite-Na^+ (5% by weight) for 5 min in microwave irradiation is shown in **Table 6**. 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 degradation [49, 50]. 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 9–12**. It was observed that moisture retain gradually [51].

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 interlayer of clay and the formation of a cross-linked structure of a certain extent which prevents the insert on of water molecules [52, 53]. Finally, water resistance of these composites which as defined the decreases in moisture retain and water uptake values can be greatly improved [54, 55].

Time (min)	**1**	**2**	**3**	**4**	**5**
Catalyst (%)	1.5	2	3	4	5
Yield (%)	15.09	34.86	52.93	77.95	84.82

Table 5. Effect of amount of catalyst on polymerization yield of anionic polyacrylamide (APAm) under microwave irradiation.

Time (min)	**5**	**5**	**5**	**5**	**5**
Temperature (°C)	100	130	145	160	164
Yield (%)	19.34	39.06	59.81	79.91	84.94

Table 6. Effect of temperature on polymerization yield of anionic polyacrylamide under microwave irradiation.

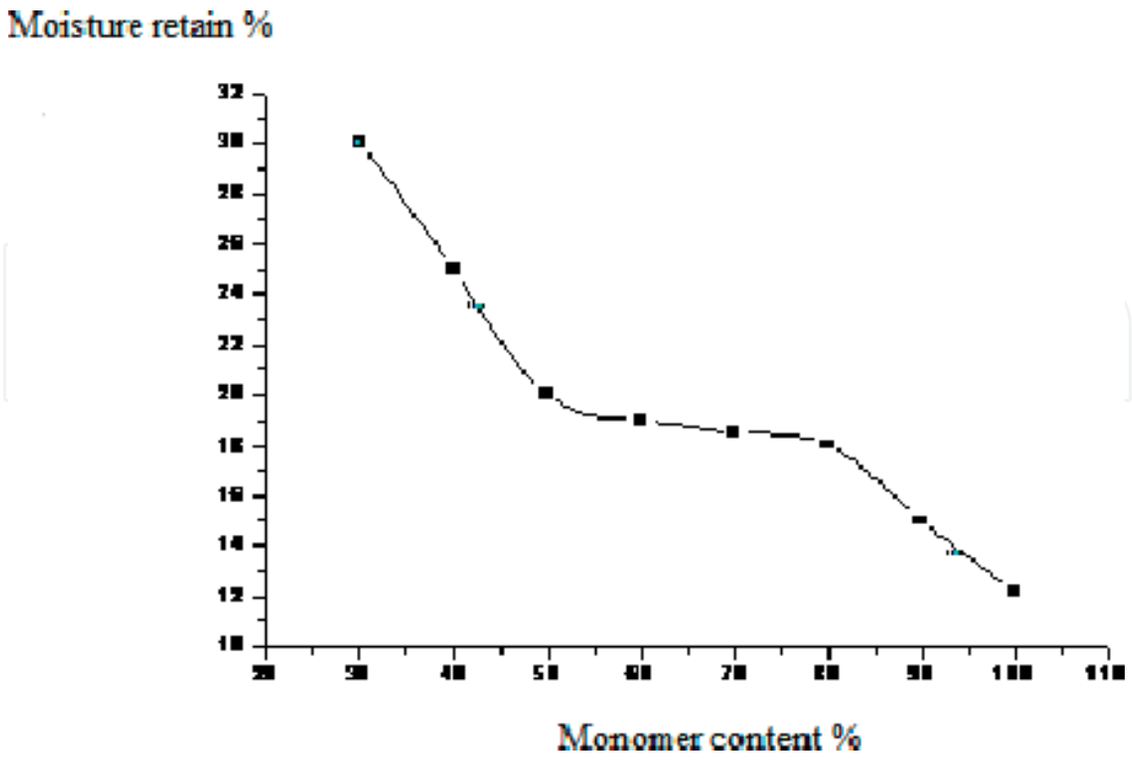


Figure 9. The percentage moisture retains values of acrylamide (Am) obtained including different percentages of (Am).

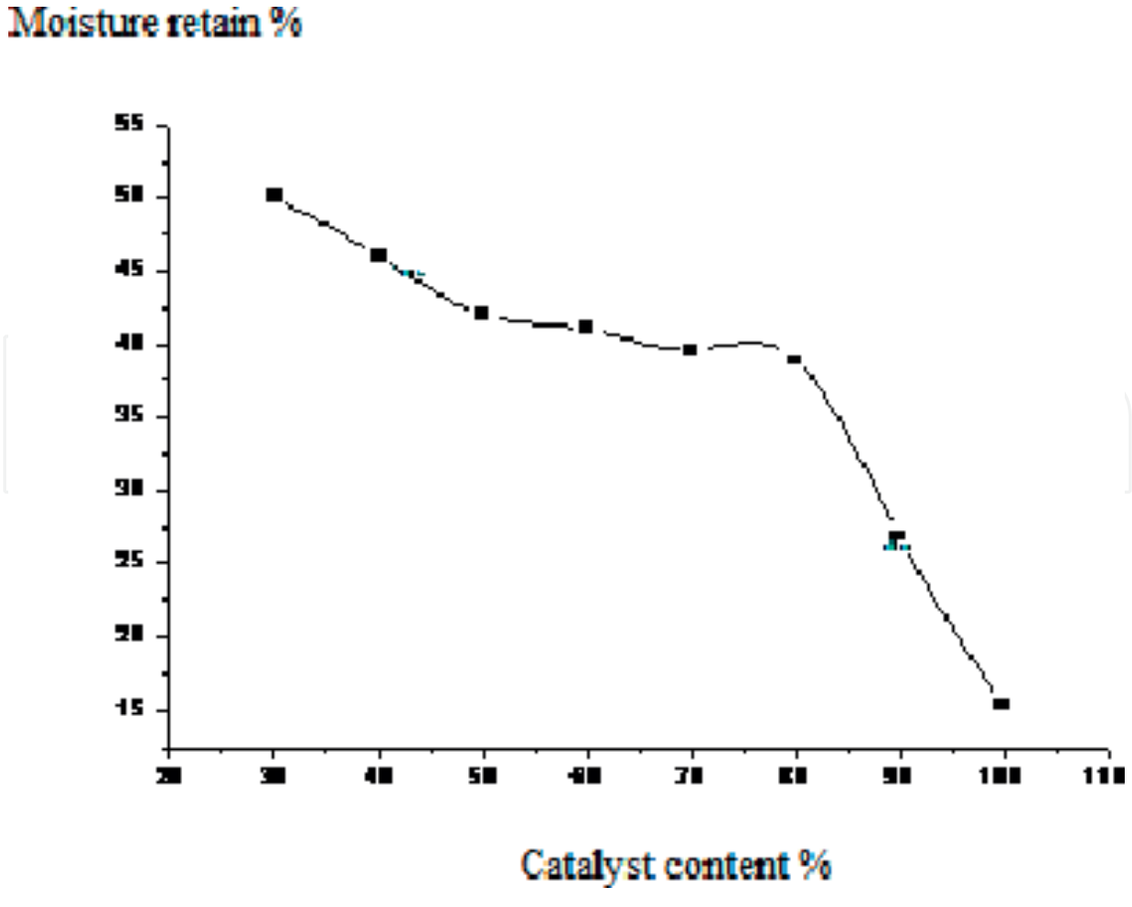


Figure 10. The percentage moisture retains values of maghnite-Na^+ obtained including different percentages of maghnite.

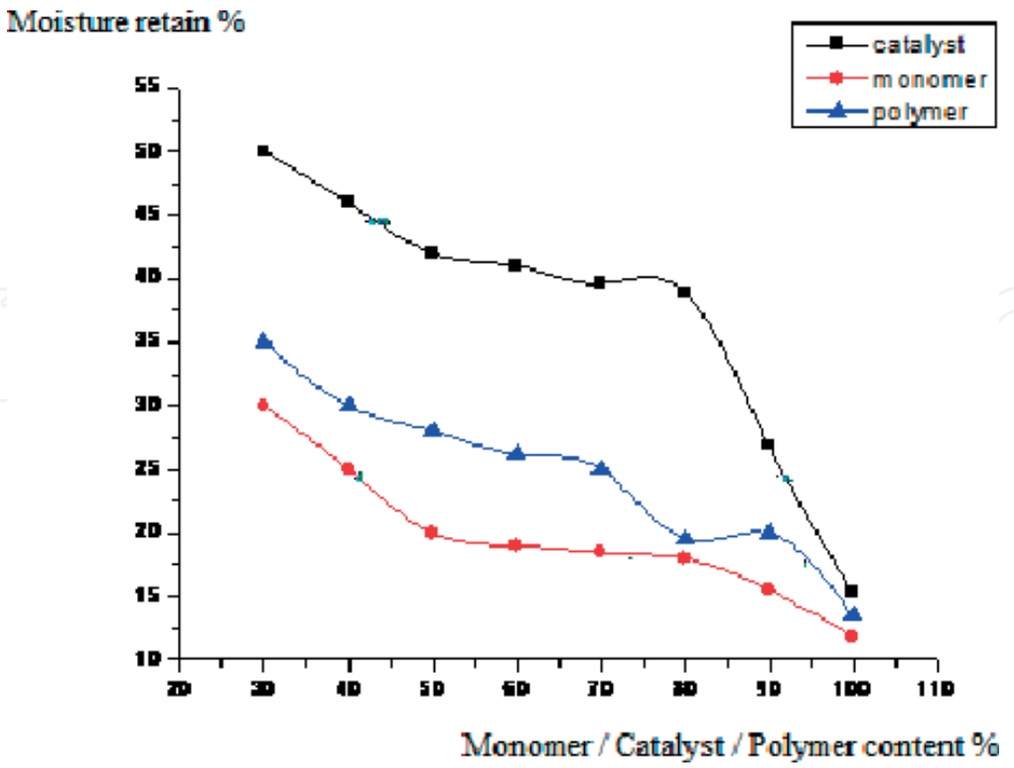


Figure 11. The percentage moisture retains values of maghnite-Na+, Am and APAm obtained including different percentages of Am, maghnite-Na+ and APAm.

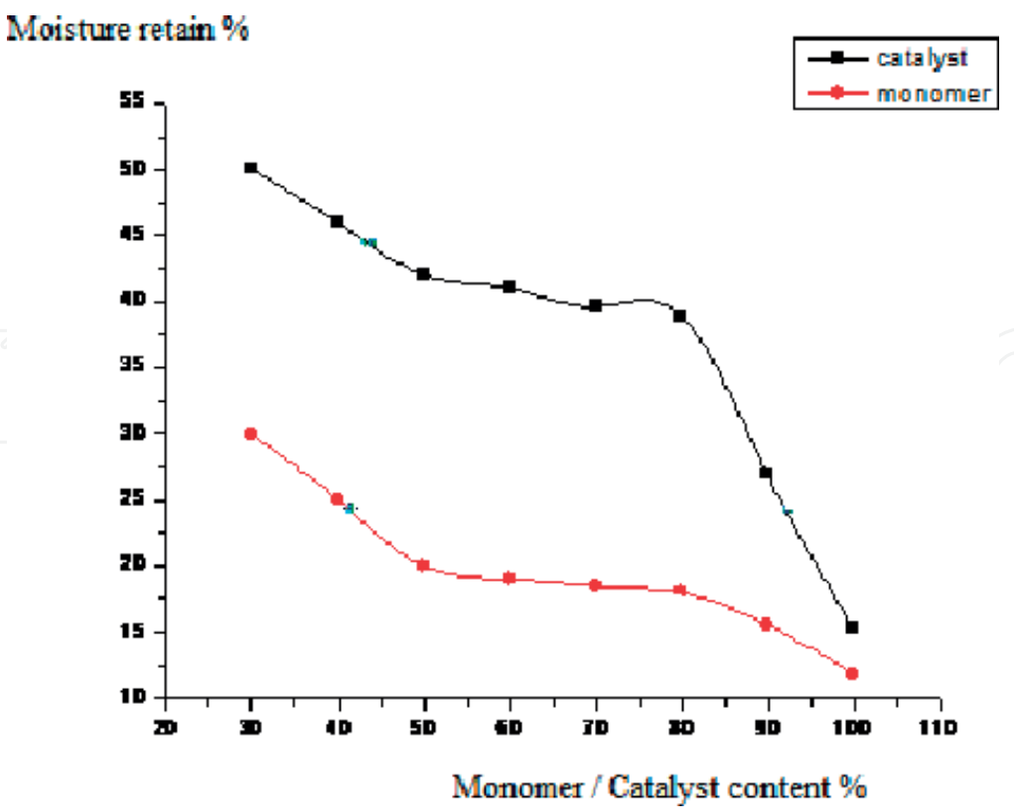


Figure 12. The percentage moisture retains values of maghnite-Na^+ and APAm/maghnite-Na^+ obtained including different percentages of Am.

6.3. Mechanical properties

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 shown in (**Table 7**). It shows that the mechanical 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 influence 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 w%). The composition of clay (5 w%) 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 (ε_r = 54.03%). This result confirms the exfoliation of maghnite clay in polymer (APAm) which is in agreement with the literature [56].

6.4. Proposed mechanism

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 [49]. The initiation reaction is generally fast and is not reflected in the overall rate of the polymerization [57]. The kinetics of the polymerization is predominantly controlled by the propagation step [58].

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 [49]. 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 [45]. Hence, it is important to match the reactivity of the initiator with the propagating species in order to have fast and homogeneous initiation [44]. For example, the reaction of sodium metal generates a radical anion in polar solvent, which can be used as initiator for the anionic polymerization [59]. 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

Sample	Catalyst (w%)	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

Table 7. Mechanical properties of APAm/maghnite samples.

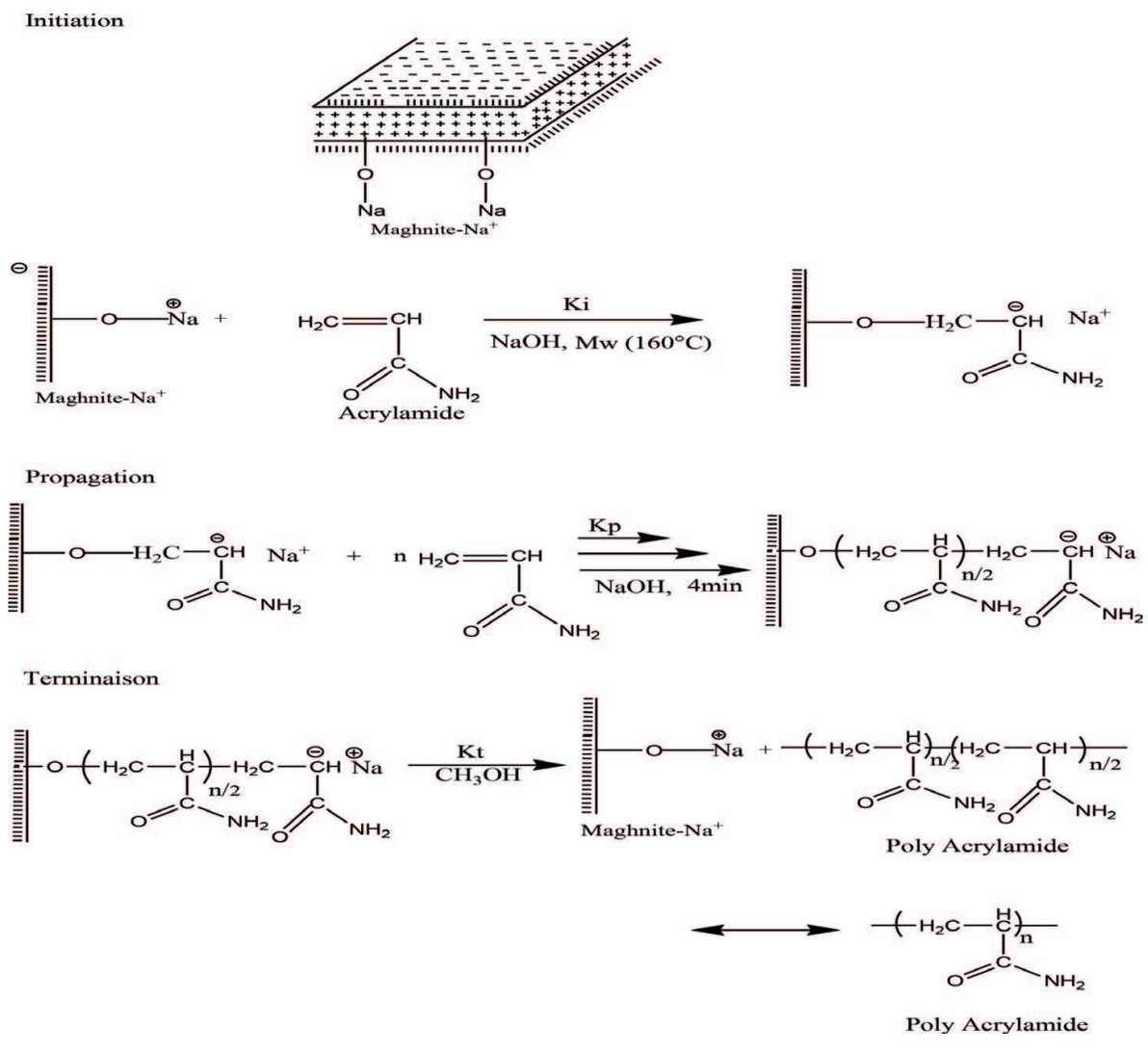


Figure 13. Proposed mechanism for obtained anionic polyacrylamide catalyzed by maghnite-Na^+.

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 [60] . This process is extremely rapid and exothermic. In order to obtain polymers with viable molecular weights of a few thousand, the polymerization temperature must be particularly low and around of −160°C [61], 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 [62, 63, 64, 65].

7. Conclusion

At the optimal conditions, anionic polyacrylamide material was successfully synthesized as an aqueous free solvent 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 HNMR 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 objectives of this work are the synthesis of anionic polyacrylamide of by the use of MMT-Na^+ as 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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