

NOVEL SUPERABSORBENT HYDROGEL COMPOSITE BASED ON POLY(ACRYLAMIDE-CO-ACRYLATE)/NONTRONITE: CHARACTERIZATION AND SWELLING PERFORMANCE

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A novel superabsorbent hydrogel (SH) composite based on a poly(acrylamide-co-acrylate) matrix filled with nontronite (NONT), a Fe(III)-rich member of the smectite group of clay minerals, is described in this manuscript. A variety of techniques, including FTIR, XRD, TGA, and SEM/EDX, were utilized to characterize this original composite. Experimental data confirmed the SH composite formation and suggested NONT was completely dispersed in the polymeric matrix. Additionally, NONT improved the water uptake capacity of the final material, which exhibited fast absorption, low sensitivity to the presence of salt, high water retention and a pH sensitive properties. These preliminary data showed that the original SH composite prepared here possesses highly attractive properties for applications in areas such as the agriculture field, particularly as a soil conditioner.

Keywords: composite; superabsorbent hydrogel composites; nontronite; swelling performance.

INTRODUCTION

Superabsorbents hydrogels (SH) are three-dimensional (3D) crosslinked networks built by hydrophilic polymers that can absorb, swell, and retain large contents of water or aqueous fluids. In general, SHs show excellent properties when compared to the traditional water-absorbing materials. As consequence, the interest about they have increased considerable and the result is the SHs utilization in the most varied fields, such as hygienic industries, agriculture, pharmaceutical, biomedical, biotechnology, and others.¹ Some SH matrices are able to swell up to 1,500 times relative to its dry weight² and maintaining their structure, which is formed by a porous structure. Such morphology as well the averaged porous-size, and porous-size distribution, are dependent on several factors some of them associated to the method used for hydrogel preparation (the polymer type, concentration of polymer and/or monomer solution, crosslinking agent, etc.) and others.³ Beyond the factors associated to the preparing conditions, the external stimuli (temperature, solvent, ionic strength, etc.) can affect the SH properties.³ In specific conditions, stimuli responsive SH in the swollen state can collapse in response to environmental stimuli changes releasing the absorbed water or fluid. During the deswelling process, the porous size of a 3D network change and any encapsulated solute can eventually diffuse outwards of 3D matrix.⁴ The swelling-deswelling-swelling cycle is often reversible.² This is a key-factor for application of stimuli responsive hydrogels in several fields.^{5,6}

Since the SHs appearing, the researches have been focused on their upgrading. Different materials have been tested to formulate and to tailor this kind of material for those applications. In recent years, clays have acquired important role in the formulation of a plenty organic/inorganic based superabsorbent composites, especially to improve their swelling properties. This statement can be proved by a brief search in the literature, where is possible to find out

several works discussing the preparation of superabsorbent hydrogel composites with different clays, such as kaolin, montmorillonite, attapulgite, mica, sericite, sepiolite, and vermiculite.³⁻⁹ On the other hand, nontronite (NONT), other clay with potential to act as filler in superabsorbent matrices, has been poorly explored. Nontronite is a Fe(III) rich smectite with a dioctahedral structure and low degree of aluminum hydroxide, with lamellar charge originated in tetrahedral layer, due to substitutions of cations of silicon (Si⁴⁺) for the cations of aluminum (Al³⁺), and with a concentration of Fe(III) higher than 3.0 mol-%.⁷ Almost all octahedral aluminum ions present in smectites are replaced for the Fe(III) ions in NONT. The chemical representation of NONT is ((M⁺)_xnH₂O(Fe⁺³))₄(Si_{4-x}Al_x)O₂₀(OH)₄, where M⁺ represents the cations of ionic compensation exchangeable.⁸ The negative charge excess can be attribute to the substitution of Si⁴⁺ by Al³⁺ cations into the tetrahedral sites in the silica layer. Additionally, in the octahedral sites of NONT, practically all the octahedral aluminum is replaced by Fe(III) ions.⁹

The development of a novel SH filled with NONT is described in this manuscript in order to evaluate the potential of this clay to act as filler and to study its effect on swelling properties. Additionally, the complete characterization concerning the structure of this original material is provided in this manuscript. The data and discussion presented here increase the range of applicability of this poorly explored clay and contribute to formulation or tailoring of superabsorbent hydrogel composites to be applied with better efficiency and benefits in different fields.

EXPERIMENTAL

Materials

Acrylamide (AAM), acrylic acid (AAc), *N,N,N',N'*-tetramethylethylenediamine (TEMED), as catalyst, and potassium persulfate (K₂S₂O₈), as initiator, were purchased from Sigma Aldrich (USA). *N,N*-methylenebisacrylamide (MBA), as crosslinker, was

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purchased from Pharmacia Biotech (USA). All these chemicals have analytical grade and were used as received. Potassium acrylate salt (KAc) was prepared by neutralization of acrylic acid with potassium hydroxide. NONT, kindly donated by Company Bentonite Northeast (Paraíba, Brazil), was previously ground and sieved through a 325 mesh (44 μm). The clay has cationic exchange capacity of 145 milliequivalent (meq) per 100 grams and chemical composition evaluated by X-ray fluorescence: silicon (5.32 meq/g), iron (0.82 meq/g), aluminium (0.60 meq/g), sodium (0.48 meq/g), magnesium, (0.12 meq/g) and calcium (0.08 meq/g). The commercial hydrogels (labeled as PAMACOM) produced for agriculture uses were purchased in a local agricultural products and supplies store (Ceará, Brazil). According to manufacturer's information, PAMACOM is based on acrylate monomers salts (sodium and potassium). The PAMACOM samples were sieved in order to obtain particles in the range of 9 to 35 mesh (2.00 - 0.71 mm).

Poly(acrylamide-co-acrylate) SH formation

The poly(acrylamide-co-acrylate) SHs (labeled as PAMACRYL) were prepared according to the follow procedures. In a round flask, distilled water (30 mL) was magnetically stirred and $\text{N}_{2(g)}$ degased for 15 min. Subsequently, AAM (2.1 g) and KAc (3.5 g) were added to the reaction system. After a while, $\text{K}_2\text{S}_2\text{O}_8$ (16.2 mg) was added, in order to promote the radical formation. MBA (0.05, 0.1, and 0.2 mol/wt-% relative to the monomers total mass) and TEMED solution (0.57 g L^{-1} - 100 μL) were also added. The reaction system was closed and kept under magnetic stirring and $\text{N}_{2(g)}$ atmosphere up to the gel formation (~30 min). To complete the gelling process the system was left to rest by 15h. At last, the as-obtained PAMACRYL hydrogel was collected and cut into small pieces, which were extensively washed with distilled water to remove some unreacted chemicals. Then, the PAMACRYL hydrogel was oven-dried at 70 °C up to constant weight and then smashed. The samples were sieved in order to obtain particles in the range of 9 to 35 mesh (2.00 – 0.71 mm).

Poly(acrylamide-co-acrylate)/nontronite SH composite formation

The poly(acrylamide-co-acrylate)/nontronite SH composite was labeled as PAMACRYL/NONT. The procedures to prepare the SHs composite were similar to those used to prepare the PAMACRYL gels. However, different NONT contents were added to reaction system. Three samples of PAMACRYL/NONT were prepared; herein the NONT contents were fixed at 5, 10, and 20 wt/wt-% relative to the monomers total mass. These samples were labeled as: PAMACRYL/NONT5, PAMACRYL/NONT10, and PAMACRYL/NONT20, respectively. For each composite sample, the acrylamide and acrylate monomers (AAM and KAc) were solubilized in an aqueous dispersion of nontronite. The resulting solution was stirred for 30 min and then $\text{K}_2\text{S}_2\text{O}_8$, MBA and TEMED solution were added to the reaction system. It is worthy to say that earlier the monomers addition, the aqueous dispersion of nontronite (~30 mL) was kept under magnetic stirring for 24 h.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of NONT, SH and SHs composites were recorded using a Shimadzu spectrometer (model FTIR-8300, Japan) operating in the region from 4000 to 500 cm^{-1} with resolution of 4 cm^{-1} and 64 scan acquisitions. Dry samples were mixed with KBr powder and pressed into pellets for spectrum acquisition.

X-ray diffraction (DRX)

X-ray diffraction (XRD) measurements were performed using a Shimadzu diffractometer (model XRD600, Japan) equipped with a Cu-K_α radiation source (30 kV – 20 mA) in a scattering angle (2θ) from 5° to 70°, with a resolution of 0.02°, at a scanning speed of 2 °/min.

Thermogravimetry (TGA)

Thermogravimetric analyses (TGA) were carried out in a Simultaneous Thermal Analyses System, Netzsch (model STA 409 PG/4/G Luxx, Germany) with a scanning rate of 10 °C/min under gas N_2 flowing at 20 mL/min in a range of temperature of 22 to 800 °C.

Scanning electron microscopy/energy dispersive X-ray analyzer (SEM/EDX)

Scanning electron microscopy (SEM) images were recorded using a Shimadzu (Model SS550 Superscan, Japan) microscope coupled with an energy dispersive X-ray (EDX) analyzer. Prior to the analyses, the SH and SHs composites were immersed in distilled water at room temperature up to the equilibrium swelling (~24 h). Then, the samples were frozen using liquid nitrogen. Thereafter, the frozen samples were lyophilized on a freeze dryer (Christ, Alpha 1-2 LD Plus, Germany) at -55 °C for 24 h. The dried samples were carefully fractured and then gold-coated by sputtering before SEM/EDX visualization.

Water uptake capacity

The ability of PAMACRYL and PAMACRYL/NONT(5-20) hydrogels to absorb water was evaluated by a gravimetric method. For this, dry gels samples (15 mg) were placed in crucibles filters (porosity $n^\circ 0$) pre-moistened and with a dried outer wall. This set was inserted in distilled water (at room temperature) in such a way the gel sample was completely submerged. After pre-determined time intervals, the set (filter with the sample) was removed; the filter outer wall was dried and then the set was weighed. This procedure was carried out three times to each gel sample ($n = 3$). The water uptake capacity of each sample was determined using Equation (1), where the parameter W estimates the mass of water absorbed per gram of gel, m is the mass of the swollen material and m_0 is the mass of the dry material.¹⁰ This method is conventional and versatile because it allows following the swelling kinetics of each gel sample.

$$W = [m/m_0] - 1 \quad (1)$$

Effect of salt solution on water uptake capacity

The effect of different salt solutions on the water uptake capacity of PAMACRYL and PAMACRYL/NONT(5-20) hydrogels was evaluated here. For this, hydrogels samples were immersed in different salt aqueous solutions with concentrations ranging from 0.001 to 0.10 mol L^{-1} at room temperature. NaCl and NaHCO_3 solutions were used for studying the anion effect while NaCl and CaCl_2 solutions were used for evaluating the cation effect on the swelling properties. The water uptake capacity of each hydrogel sample was determined according to the gravimetric method described in the section 2.4.1.¹⁰ Again, for each sample the procedures were carried out in triplicates ($n = 3$).

Effect of pH on water uptake capacity

The effect of pH on water uptake capacity of SH and SHs composite was evaluated by immersion of the samples in different

buffers solutions (pH 2.4, 9.4, and 7.4) with constant ionic strength (0.1 mol L^{-1}) at room temperature. The water uptake capacity of each hydrogel sample was determined according to the gravimetric method described in the section 2.4.1.¹⁰ For each sample the procedures were carried out in triplicates ($n = 3$). At least, the effect of the swelling/deswelling cycles on the SH and SHs composites water uptake capacity was also evaluated. For each run, the hydrogel sample was immersed in distilled water (at room temperature) for 24 h and then the W parameter was determined as described above. Afterwards, the swollen sample was put in oven at $70 \text{ }^\circ\text{C}$ for 24 h. The dry sample was resubmitted to the swelling process again. This cycle was repeated 5 times for each hydrogel sample.

RESULTS AND DISCUSSION

Characterization

The FTIR spectrum of NONT (Figure 1a) showed bands ($2840 - 3000 \text{ cm}^{-1}$) assigned to C-H bonds stretching characteristic of alkanes, which evidences the presence of organic matter commonly aggregate to such material. As previously reported, these bands are found in the $2929 - 2858 \text{ cm}^{-1}$ wavenumber region.¹¹ The broad band between $3000 - 3750 \text{ cm}^{-1}$ is assigned to the O-H stretching of hydroxyl groups belonging to the octahedral layers and to the water molecules coordinated to cations for ionic compensation.¹² The bands assigned to Si-O bonds stretching are showed in 960 to 1150 cm^{-1} region. The bands are influenced by the composition of atoms on octahedral layer. Is worthy to say the band at 1039 cm^{-1} , also assigned to Si-O bond stretching, is due to the presence of octahedral coordinated iron atoms.¹² The bands found in the wavenumber region between $550 - 960 \text{ cm}^{-1}$ are assigned to octahedral deformations of R-O-H groups, in which R can be iron or magnesium ions. Finally, the strong band close to 550 cm^{-1} is assigned to the stretch vibrations of ions in octahedral plane and to its adjacent oxygen atoms.¹² The FTIR spectrum of PAMACRYL (Figure 1b) show bands at 1670 and 1564 cm^{-1} , which are assigned to the C=O and N-H stretching, confirming the copolymer formation. The FTIR spectrum of PAMACRYL/NONT10 (Figure 1c) showed all the characteristics bands observed for PAMACRYL. Additionally, the bands at 1035 and 470 cm^{-1} , which are assigned to the Si-O bonds proceeding from the NONT incorporation, are observed in Figure 1c.

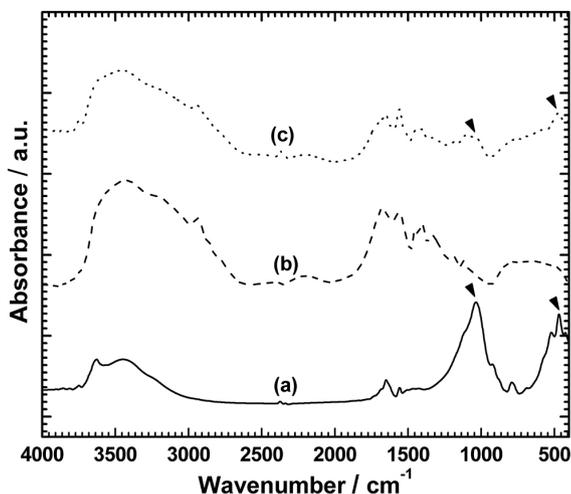


Figure 1. FTIR spectra of (a) NONT, (b) PAMACRYL, and (c) PAMACRYL/NONT10

The XRD pattern of NONT, showed in Figure 2a, provides important information about its main mineral constituents and structural

parameters. The XRD basal peaks at 7.14° (001) and 19.78° (061) are characteristic of clays like NONT, a dioctahedral smectite.¹³ Similarly, the peaks at 21.7° (101) and 26.6° (011) characterize the presence of silica minerals, any of the forms of silicon dioxide (SiO_2), including quartz, tridymite, cristobalite, coesite, stishovite, lechatelierite, and chalcedony, which are considered as clays impurities. These minerals show particle-size similar to those found for clay particles and as consequence they hardly ever can be separate of the clay. Mihaboub and Vreysen obtained similar XRD patterns of NONT in their works.^{13,14} The XRD patterns of PAMACRYL/NONT5, PAMACRYL/NONT10 and PAMACRYL/NONT20 (Figure 2a-c) did not show the characteristic basal peaks of NONT, regardless the concentration of clay in such gels. This suggests the copolymerization of AAm and KAc monomers to poly(acrylamide-*co*-acrylate) and subsequent crosslinking process has promoted a good dispersion of NONT platelets in the SHs composites. Such dispersion occurs due to formation of H-bonds between the amide and acid groups present on the SH matrix and water molecules surrounding the exchangeable cations on NONT. Further, ion-dipole interactions among the acrylate groups and the interlayer exchangeable cations can be formed. Both interactions might lead to a slight increasing in the basal spacing of NONT.

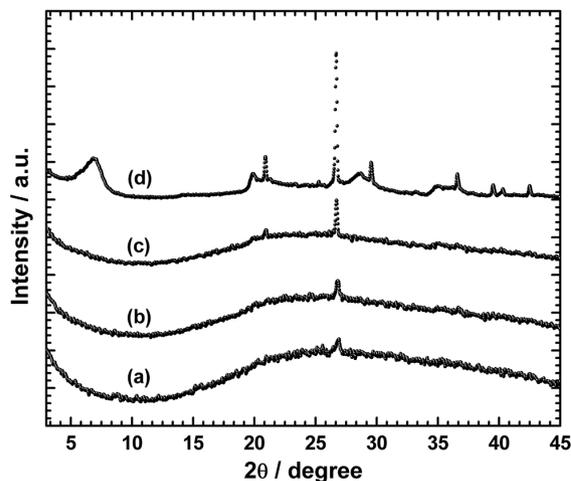


Figure 2. XRD diffractograms of (a) PAMACRYL/NONT5, (b) PAMACRYL/NONT10, (c) PAMACRYL/NONT20, and (d) NONT

The XRD patterns corroborate with the FTIR data and both confirm the formation of the superabsorbent hydrogel composite and evidence the presence of NONT in the poly(acrylamide-*co*-acrylate) SH matrix. The effect of the NONT incorporation on the thermal properties was evaluated by thermogravimetric analyses (TGA) (Figure 3).

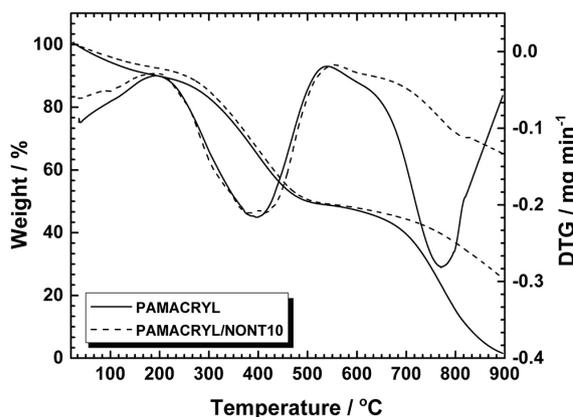


Figure 3. TGA and DTG curves of PAMACRYL and PAMACRYL/NONT10

The PAMACRYL and PAMACRYL/NONT10 TGA curves show clearly three stages for the weight losses. The first stage (50 - 200 °C) can be attributed to the moisture and volatile compounds losses by the samples. Following, in the temperature range of 300 - 450 °C the weight losses are attributed to the thermal decomposition of the acrylate and amide side groups of the copolymers and also MBA moieties spread in the SH matrix, leading to the evolution of ammonia and other gases for instance. During this period, the onsets in the PAMACRYL and PAMACRYL/NONT10 TGA curves are similar; however is possible to observe a slight increase in thermal stability of the SH composite due to NONT presence. For PAMACRYL, thermal decomposition temperature is 391°C (33.5%), while for PAMACRYL/NONT10 is 399 °C (33.3%). The last stage was attributed to the breakage of copolymer chains, in which was observed a displacement for higher temperatures when are NONT is incorporated in the SH matrix. Additionally, the total residue at 900 °C was c.a. 1.55% for PAMACRYL and c.a. 25.46% for PAMACRYL/NONT10. Figure 3 shows the NONT incorporation on the PAMACRYL matrix has positive effect on its thermal stability.

The fracture morphology of the SH and SH composite was examined by SEM as shown in Figure 4. As it is clear from Figure 4a, PAMACRYL shows microporous surface, with large and irregular pores heterogeneously distributed. Such morphology allows SH absorbing high amounts of liquid. On the other hand, it can be seen in Figure 4b the surface morphology of superabsorbent changes due to the NONT incorporation in its formulation. The morphology of the PAMACRYL/NONT10 superabsorbent exhibit rugged, coarsened, and correspondingly loose surfaces. Undulant and coarsened surfaces increase the surface contact area, which makes easy the diffusion of liquid inward the SH matrix. This ensures high water uptake capacity for the final superabsorbent composite. Additionally, such morphology demonstrates the filler (NONT in this case) is completely incorporated within the copolymer chains and well dispersed in the SH matrix (see Figure 4b). Such scenery is very desirable since the high dispersion of NONT particles in the SH network prevents flocculation of clay particles and enhances the water uptake capacity of the SH composite.

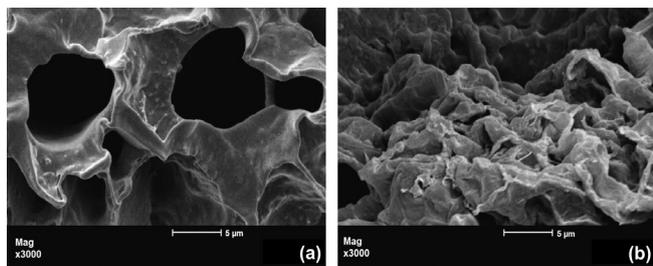


Figure 4. SEM images of (a) PAMACRYL and (b) PAMACRYL/NONT10 (fracture images; magnification x3000; scale bar 5 µm)

In addition from the SEM images, EDX spectra of the PAMACRYL and PAMACRYL/NONT10 were collected to evaluate their elemental composition. As can be seen in Figure 5, both PAMACRYL and PAMACRYL/NONT10 spectra showed three well-resolved peaks accounting to the elements C, O, and K. On the other hand, the EDX spectrum of PAMACRYL/NONT10 (Figure 5) also shows the characteristic peaks assigned to the elements Si and Al. The appearing of such peaks corroborates with the data obtained by other techniques utilized here. All of them confirm the successfully formation of the SH composite. Further, to confirm the NONT dispersion into the SH matrix, the Si elemental distribution map (EM) was recorded from PAMACRYL/NONT10 sample (Figure 5). As it is clear in the EM figure the characteristic Si element present

in the NONT structure can be easily observed through the entire mapped region. The EM confirms either the NONT presence as its high dispersion.

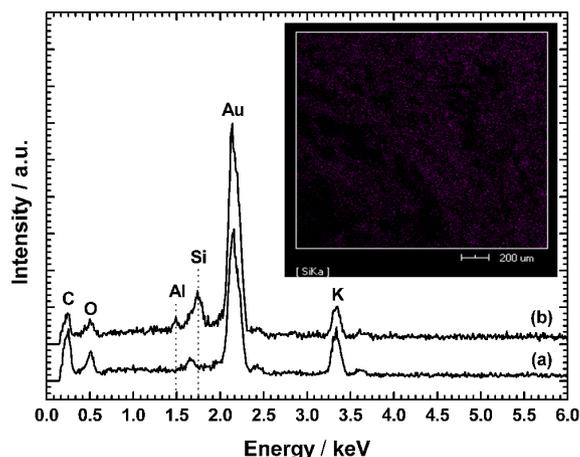


Figure 5. EDX spectra of (a) PAMACRYL and (b) PAMACRYL/NONT10

Swelling performance

Typically, hydrogels and superabsorbent hydrogels consist of physically or chemically crosslinked hydrophilic polymer chains forming a three-dimensional network. The process of swelling of a hydrogel is driven by chemical and physical forces and by the consequent elastic response of the constituent chains of the matrix. Swelling is primarily due to the penetration of aqueous liquid inward the hydrophilic polymer matrix by capillary and diffusion forces. Thus, liquid is absorbed by hydrophilic groups such as hydroxyl, carboxyl, and amino due to formation of H-bonds.¹⁵ The water uptake capacity and the rate of swelling of hydrogel has a direct relation to internal factors, such as the variation of osmotic pressure between the interior of the gel and the external media; the crosslinking density; the affinity between the hydrogel and the liquid; and by external factors (i.e. presence of salts, pH, and temperature, etc.) For hydrogel composites other factor has to be considered; the filler content. Before to compare the swelling performance of the SH composite in relation to the conventional SH some optimization conditions were tested. Besides, two variables for the SH formulations were tested: (i) the effect of NONT content; and (ii) the effect of MBA content (crosslinker agent) on the water uptake capacity.

As demonstrated in Figure 6a, the incorporation of 10 wt-% of NONT on the SH formulation leads to a maximum in the water uptake property when compared to the other formulations. According to Wang and Xie,¹⁶ cations present in the clay increase the hydrophilicity of the composite and the difference in osmotic pressure between the polymer and the outside solution. On the other hand, the incorporation of 20 wt-% of NONT resulted in a significant reduction in the *W* profile. This behavior can be attributed to extra crosslinking points in the SH network due to the NONT incorporation. High crosslinking density reduces the matrix elasticity and the water uptake capacity is negatively affected.^{10,17} Furthermore, the entrapment of NONT in the interconnected porous structure, caused by the excessive content of clay particles, decreases the empty space inside the SH matrix, which consequently decreases the content of absorbed water. The SH with 5 wt-% of NONT showed a intermediare water uptake behavior between those other two formulations. According to these data, the SH composite formulated with 10 wt-% of NONT (the sample PAMACRYL/NONT10) was utilized, as reference of SH composite, for all the subsequent swelling assays.

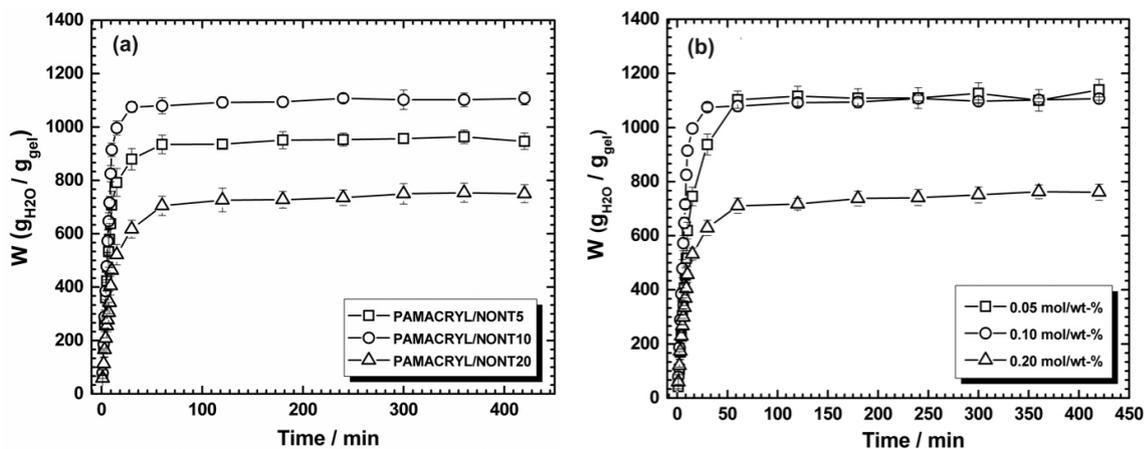


Figure 6. (a) Effect of NONT and (b) MBA contents on the water uptake capacity of the SH composite (*PAMACRYL/NONT10 was utilized to perform the assay showed in b)

PAMACRYL/NONT10 were prepared using different contents of MBA, a crosslinking agent that plays an important role in the swelling process.¹⁸ According to the Flory's theory,¹⁹ the crosslinking density is a key factor that influences the water uptake. In order, the water uptake is inversely proportional to the crosslink density. Herein, the content of MBA utilized in the PAMACRYL/NONT10 formulation was varied from 0.05 to 0.20 mol/wt-%. As it can be observed in Figure 6b the water uptake capacity of PAMACRYL/NONT10 decreases significantly as the content of MBA is increased from 0.10 to 0.20 mol/wt-%. On the other hand, such variation was not observed when the MBA content is 0.05 or 0.10 mol/wt-%. The PAMACRYL/NONT10 swelling profile is the same for both formulations. When high MBA contents (>0.10 mol/wt-% in this case) are used in the SH composite formulation a great number of crosslinking points among the copolymer chains are formed. Consequently, the crosslinking density increases and the SH matrix get rigidity. This reflects in a smaller network expansion and hinders the water diffusion avoiding its swelling.²⁰ According to these data, the MBA content used to prepare both PAMACRYL and PAMACRYL/NONT10 samples applied in the subsequent swelling assays was fixed in 0.05 mol/wt-%.

Figure 7 shows the swelling kinetics curves of PAMACRYL, PAMACRYL/NONT10, and PAMACOM in distilled water media at room temperature. Here the label PAMACOM was used to denote a commercial SH based on poly(acrylamide).

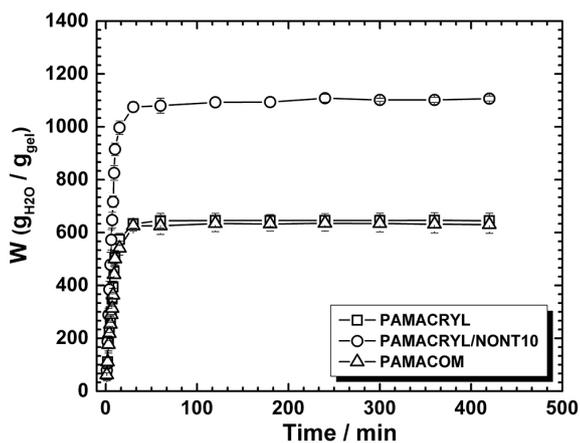


Figure 7. Swelling kinetics curves for PAMACRYL, PAMACRYL/NONT10, and PAMACOM

The swelling data displayed in Figure 7 highlight all the samples have high equilibrium swelling ratio, a common characteristic

found in superabsorbent hydrogels (SH). The main property of SHs is their capacity of absorbs hundred times its own weight of water. PAMACRYL and PAMACOM samples showed very similar swelling kinetics curves, where the equilibrium swelling is achieved fast in both cases and such equilibrium remains up to the assays end. The W values calculated for PAMACRYL and PAMACOM at the equilibrium were 645 and 634 g_{H₂O}/g_{gel}. From Figure 7 is possible to observe PAMACRYL/NONT10 sample presented the highest water uptake capacity. The W value calculated to the PAMACRYL/NONT10 sample at the equilibrium was 1,104 g_{H₂O}/g_{gel}, almost two times higher than those calculated for PAMACRYL and PAMACOM. The swelling kinetic curve of PAMACRYL/NONT10 showed a quick increasing during the first 15 min of immersion, reaching about 90% of the equilibrium value up to this immersion time, followed by a slower process until the equilibrium being reached at about 30 min. The mechanism that drives the swelling process of each sample as evaluated using a second-order swelling kinetics model,²¹ which can be expressed as follows:

$$t/W = A + Bt \quad (2)$$

where:

$$A = 1/k_s W_i^2 \quad (3)$$

and

$$B = 1/W_i \quad (4)$$

The A parameter corresponds to an initial swelling rate $[(dW/dt)_0]$ of the hydrogel sample, k_s is the constant rate for swelling and W_i is a theoretical swelling value at equilibrium. Wt and k_s were calculated by fitting experimental data shown in Figure 5 to equations (2), (3), (4) and the results are given in Table 1.

Swelling data presented in Table 1 corroborates with the data displayed in Figure 7 and both confirms the SH composite presents the highest water uptake capacity. This can be explained by two factors: the first one is the formation of intense interactions among -OH groups on the surface of the clay and the water molecules. The disposition of those -OH groups inside the SH matrix increases its hydrophilicity cause a higher water uptake. The second factor can be explained analyzing the XRD pattern of NONT (see Figure 2). When clays are dispersed in the SH matrix on a nanometric scale, as observed in this case, a higher interaction among the clay layers and the copolymer chains occurs and promotes the improvement of the water

Table 1. Kinetics parameters evaluated for the hydrogels samples swollen in distilled water at room temperature

Hydrogel	^a W	^b W _t	^c t _{eq} (min)	^d k _s (min ⁻¹)	^e r ²
PAMACRYL/NONT10	1,104 ± 28	1,125	26 ± 2	1.56 × 10 ⁻⁴	0,99976
PAMACRYL	645 ± 21	649	24 ± 3	6.54 × 10 ⁻⁴	0,99958
PAMCOM	634 ± 23	633	31 ± 1	9.78 × 10 ⁻⁴	0,99948

^aEquilibrium swelling (g_{H_2O}/g_{gel}); ^bTheoretical equilibrium swelling (g_{H_2O}/g_{gel}); ^cNecessary time (min) to reach the equilibrium swelling; ^dRate of swelling (g_{H_2O}/g_{gel}) / min; ^er squared correlation value.

uptake capacity. Similar results were reported by Santiago *et al.*²²

The high water uptake capacity presented by the SH after the incorporation of NONT is a desirable feature. Such outstanding capacity potentiates the application of our original SH composite in several fields, especially in those where high absorption rate and capacity are necessary (i.e. water reserving in soil and soil conditioning). The water uptake data presented here are very expressive when compared to others SH matrices filled with different clays. Taking into account, Table 2 shows some water uptake data for SHs composites filled with different clays.

In this work, the effect of some cations and anions on the water uptake capacity of PAMACRYL/NONT10 was evaluated in different concentration (0.001 - 0.1 mol L⁻¹) of NaCl, NaHCO₃, and CaCl₂ salt solutions. The W values calculated from the swelling assays are shown in Figure 8. As it can be seen, the W values were appreciably reduced as compared to those calculated in deionized water. Additionally, for all the salt solutions W gradually decreased as the salt concentration is increased. This well-known phenomenon is commonly observed when hydrogels swell in ionic environments, due to a decreased difference in the osmotic pressure (ionic pressure) between the polymer network and the external solution.³¹ With the increasing of salt concentrations in the solution where the gel is immersed, the difference in osmotic

pressure between the gel network and the external solution decreased and, as a result, the water absorbency of PAMACRYL/NONT10 is significantly decreased. Despite this behavior, the W values were very similar of both Cl⁻ and HCO₃⁻ ions, which suggest SH composite does not show sensibility to these anions neither to their sizes. An analogous observation was recently reported for a poly(acrylamide-co-acrylate) matrix filled with cellulose nanowhiskers.²⁰

To achieve a comparative measure of salt sensitivity of the hydrogels, a dimensionless salt sensitivity factor, *f*, defined as follow:³²

$$f = 1 - [(W_{saline} / W_{water})] \quad (5)$$

where *W*_{saline} and *W*_{water} are, respectively, the swelling capacity in saline solution and in deionized water. The *f* values calculated for PAMACRYL/NONT10 and PAMACRYL are displayed in Table 3.

The increase in the ionic strength reduces the difference in the concentration of movable ions between the bulk of polymer matrix and the external solution. Two main factors related to the cation presence can affect the water uptake capacity: (i) Shielding effect of the monovalent cations on the negatively charged groups present in the hydrogel matrix. This factor contributes to the compression or contraction of the three-dimensional structure driven by reduction on

Table 2. Comparative chart: Water uptake capacities presented by SHs composites filled with different clays

SH matrix	Clay	^a wt-%	^b W	Ref.
Poly(acrylamide-co-acrylamide) ^c	Nontronite	10	1,104	-
Poly(acrylamide-co-acrylamide)	Montmorillonite	2	750	23
Poly(acrylic acid-co-acrylamide)	Organo-attapulgit	10	1,282	24
Poly(acrylic acid-co-acrylamide)	Kaolinite	10	433	25
Poly(acrylic acid-co-acrylamide)	Organo-montmorillonite	12	510	26
Poly(acrylic acid)	Sodium humate	5.3	684	27
Poly(acrylic acid)	Attapulgit	50	675	28
Poly(acrylic acid)	Bentonite	20	1,562	29
Poly(sodium acrylamide)	Sepiolite	5	1,419	30

^aIn relation to the polymeric matrix total mass; ^bEquilibrium swelling (g_{H_2O}/g_{gel}); ^cSH composite prepared in this work.

Table 3. W (in g_{H_2O}/g_{gel}) and *f* values calculated for (a) PAMACRYL and (b) PAMACRYL/NONT10 hydrogels swollen in different salt solutions

Salt solution		Concentration of salt solution (mol L ⁻¹)							
		0.001		0.01		0.05		0.10	
		W	<i>f</i>	W	<i>f</i>	W	<i>f</i>	W	<i>f</i>
NaCl	(a)	361 ± 4	0.44	195 ± 2	0.70	85 ± 1	0.87	63 ± 1	0.91
	(b)	645 ± 8	0.41	347 ± 5	0.69	152 ± 3	0.86	121 ± 2	0.89
NaHCO ₃	(a)	353 ± 6	0.45	182 ± 3	0.72	76 ± 2	0.88	59 ± 1	0.91
	(b)	628 ± 7	0.43	318 ± 5	0.71	139 ± 3	0.87	113 ± 2	0.90
CaCl ₂	(a)	173 ± 3	0.73	90 ± 2	0.86	35 ± 1	0.95	17 ± 1	0.97
	(b)	363 ± 6	0.67	181 ± 3	0.84	64 ± 2	0.94	31 ± 1	0.97

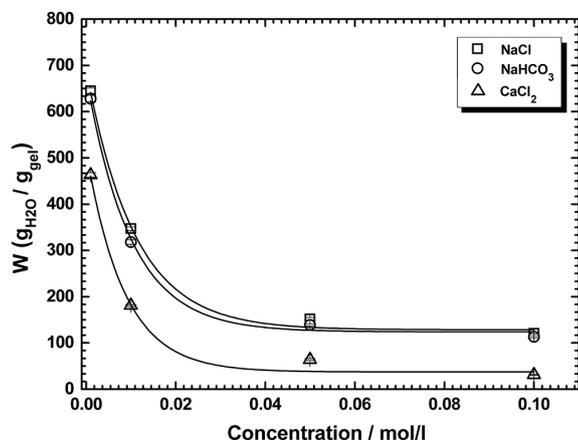


Figure 8. Water uptake variation of PAMACRYL/NONT10 in salt solutions with different concentrations

the repulsive forces proceeding from the negatively charged groups. Therefore, the osmotic pressure difference between the hydrogel matrix and the external solution decreases, which results in a lower uptake.³² (ii) Physical crosslinking promoted by the presence of multivalent cations (e.g. Ca^{2+} and Al^{3+}), which increases the matrix rigidity and avoids that considerable amounts of water had been absorbed. Mahdavinia *et al.* (2004) reports a decreasing in the water uptake of chitosan-graft-PAN hydrogels as function of the cation charge.³² This effect was attributed to the complexation ability of those multivalent cations with negatively charged groups of the copolymer based on chitosan, acrylic acid and acrylamide. Here, salts contained divalent and trivalent cations reduce the swell of PAMACRYL and PAMACRYL/NONT much more than salt contained only monovalent ions. This is due to the complexing ability of the carboxymide or acrylate groups and the formation of inter and intramolecular complexes.³³ Differently of the type of cation, the swell of PAMACRYL and PAMACRYL/NONT10 was not influenced by external type of anions, as can be seen in Table 3. The effect of pH on the swelling process of SH and SH composites has huge importance for targeting application of these kinds of materials. Normally, the variation of pH in the environments where the hydrogel is placed causes fluctuations in the free volume accessible for penetrating water molecules, which, then affects the characteristics of swelling of the hydrogel.³⁴ In light of this, a series of swelling assays were carried out, in order to determinate the water uptake capacity for the PAMACRYL, PAMACRYL/NONT10, and PAMACOM in different pH solutions ranged from 2.4 to 9.4. According to the data displayed in Figure 9, is possible to verify all the samples tested are pH sensitive. PAMACRYL, PAMACRYL/

NONT10, and PAMACOM, showed an increase in the water uptake with the pH increasing from 2.4 to 9.4. At low pH, the acrylate anions are protonated and the anion-anion repulsive forces no longer exist. This leads to a minimum in the water uptake of the SHs and SH composite. On the other hand, at high pHs those acrylate groups get charge and such charges promote electrostatic repulsion among COO^- groups. The repulsive forces weaken the polymeric matrix stability and allow its expansion. As result, a high water amount diffuses inward the SH as can be seen in Figure 9a.³⁴ At pH 9.4 all the SH samples swelled about 10 folds or more than at buffer of pH 2.4 due to the repulsion of the ionized groups. PAMACRYL/NONT10 showed the highest W values for all the pH range as can be seen. At pH low pH conditions the carboxylate groups present in hydrogel matrix are in their protonated form, which reduces the repulsive forces among the negative charges and the water uptake. However, at high pH conditions, those carboxylate groups are in their ionized form. Therefore, the negative charge density within the hydrogel matrix increases as well the repulsive forces that destabilizes and expand the SH and SH composites matrices that absorb considerable water amounts.

The data presented in Figure 9a, as said above, show PAMACRYL/NONT10 is a pH sensitive SH composite. Such feature allows applying this original SH composite with great efficacy in agriculture, for instance. Besides the ability of to absorb and to retain considerable water amount, which contributes to conserve the soil moisture, PAMACRYL/NONT10 can be act as a soil additive. Several active substances utilized in agriculture as soil conditioners (i.e. fertilizers, minerals, pesticides, etc.) can be incorporated in the SH composite formulation and then be released in a controlled way. The pH sensibility showed by the SH composite presented in this work encourages its application as a soil conditioner. The variation in the soil pH can stimulate the release or the retention of those active substances. Taking into account this possible application, if a SH is undergoing an application as soil conditioner, it will be subjected to water swelling/deswelling cycles and it must maintain as long as possible its water absorption characteristics. The repetition of the swelling/deswelling cycle significantly affects the water absorption capacity. For this reason, in this work the water uptake behavior of PAMACRYL, PAMACRYL/NONT10, and PAMACOM was studied after several swelling/deswelling cycles (Figure 9b). According to the experimental data, the trend for decreasing the water uptake up to 4th or 5th cycle is observed for all the hydrogels and the swelling seem to be stabilized after the 6th cycle. In comparison to the other two SHs, PAMACRYL/NONT10 showed the smallest reduction in the water uptake capacity when the swelling/deswelling process is done 6 times. Such reduction was about 38% in the value calculated for W . This demonstrates clearly the incorporation of NONT contributes

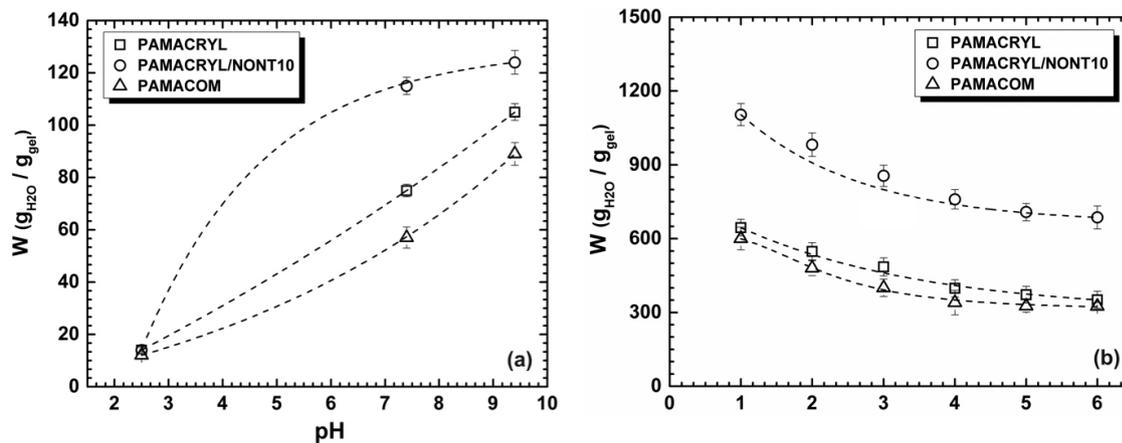


Figure 9. (a) Water uptake variation at different pH condition and (b) swelling/deswelling cycles for PAMACRYL, PAMACRYL/NONT10, and PAMACOM

to increase the number of times that PAMACRYL/NONT10 can be utilized. From the economic point of view this is a very attractive aspect. On the other hand, PAMACRYL hydrogel showed moderate reduction in the water uptake capacity (ca. 46%), while PAMACOM showed the greatest trend in reduction (ca. 49%).

CONCLUSIONS

An original SH composite based on poly(acrylamide-co-acrylate) matrix filled with nontronite (NONT) based were successfully prepared and characterized here. The SH composites showed to be more efficient in water uptake than the conventional SH without NONT. The incorporation of NONT in the poly(acrylamide-co-acrylate) matrix improved the water uptake capacity of final material, providing an increase of 71% in the W when compared to conventional SH. The water uptake capacity presented by the SH composites depends on the clay and MBA contents, and the maximum values of W were recorded for the sample prepared with 10 wt-% of NONT and 0.05 wt/mol-%, of MBA. The sample PAMACRYL/NONT10 showed faster and more efficient water absorption, lower sensibility to presence of salt and higher water retention than the PAMACOM, a commercial SH. Furthermore, this novel SH composite has a pH sensitive property, which can improve its applicability, especially as soil conditioner. These preliminary data suggest PAMACRYL/NONT10 possesses very attractive properties and encourage future studies about its application in agriculture field, as potential soil-conditioner.

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