Effect of Different Surface-charged Lamellar Materials on Swelling Properties of Nanocomposite Hydrogels

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Abstract

This study investigated the effect of different surface-charged lamellar materials on the swelling and diffusion properties of synthesized polyacrylamide-methylcellulose hydrogels (HG). Montmorillonite and hydrotalcite thermally activated at two different temperatures (300 and 550 °C) were incorporated in the preparation of nanocomposite (NC) hydrogels. A series of NC hydrogels were prepared by varying the lamellar material content (1:1, 2:1 and 4:1). The results showed that the HG with hydrotalcite (550 °C) was strongly dependent on the ionic intensity, and that the swelling degree increased by 50%, 65% and 78% with reducing the hydrotalcite content at (1:1), (2:1) and (4:1), respectively. The water absorption capacity of HG containing montmorillonite or hydrotalcite (300 °C) was slightly affected when the pH decreased from 7 to 3. However, the pH variation from 7 to 10 increased the water absorption capacity of most HG, except those containing hydrotalcite (550 °C) at (2:1) and (4:1). The presence of lamellar nanoparticles in hydrogels made the polymer matrix more rigid, and less likely to absorb water. In contrast, HG with hydrotalcite (550 °C) at (2:1) and (4:1) showed anomalous behavior with an increase in their water absorption capacity. The results support that the developed NC-HG can be suitable candidates for applications as controlled released materials.

1. Introduction

Superabsorbent materials, such as hydrogels, have attracted considerable attention due to their elevated water retention capacity as well as their vast potential for application in drug release, wastewater treatment and agriculture [1–4]. The intercalation of different hydrophilic monomers – such as in polyacrylamide/methylcellulose (PAAm-MC) or carboxymethylcellulose blends – is a promising approach to increase the swelling capacity of hydrogels, while replacing part of base polymer with renewable sources. Methylcellulose is an abundant, renewable, and biodegradable polysaccharide that has been added to acrylamide solutions to synthesize hydrogels with high hydrophilicity, due to the hydroxyl groups present in its structure. Polyacrylamide hydrogels are not biologically degraded and when replacing part of acrylamide with methylcellulose, there is a double gain: 1) insertion of glycosidic groups, which facilitates the hydrogel decomposition by bacteria and fungi; and 2) reduction of possible residues formed after the composite degradation process, contributing to minimize the toxicity potential of PAAm-MC systems for environmental applications [5–9].

Interpenetrating polymer network (IPNs) structures are generally used to control the hydrophilicity and release kinetics of hydrogels, since they are preferable in several biomedical and biotechnological applications due to their unique properties [10]. Semi-IPN polymers are prepared by dissolving a linear polymer in a hydrophilic monomer and a crosslinking agent. Thus, a synthetic hydrogel network is formed around a primary polymer chain that modifies the behavior of the hydrogel [11–12]. Moreover, the preparation of nanocomposite (NC) hydrogels compounding with lamellar materials results in systems with optimized mechanical, sorption, and nutrient desorption properties. It is possible to obtain responsive hydrogels, especially to environmental (or external) stimuli, such as temperature, pH, ionic strength and pressure [13–14]. As an example, Junior et al. (2020) prepared pH-responsive

poly(methacrylic acid)/laponite RDS hydrogels, and the influence of laponite on pKa, as well as the dependence between water absorption capacity and clay mineral content were evidenced [14].

Hydrogel nanocomposites have been developed for the controlled release of ionic compounds, such as fertilizers, mainly because the filler modifies the diffusion properties of the polymeric matrix [15–17]. Thus, NC hydrogels can be mixed with fertilizer sources, most of them ionizable compounds that provide the nutrients by dissolution (phosphates, nitrates, sulfates, etc.). However, these modifications often reduce the hydrogel swelling capacity due to the competition of modifiers with adsorption sites in the polymer network. For instance, Bortolin et al. (2016) analyzed the swelling performance of borate-loaded hydrogels, showing a remarkable reduction (more than 2 orders of magnitude) in their swelling due to interaction with the ionic solution [18–19]. Moreover, the development of NC hydrogels, incorporating lamellar nanomaterials in the chemically reticulated hydrogel network, allows the lamellae to act as a multifunctional cross linker in the formation of polymer-clay networks. Lamellar materials are highly hydrophilic and display high cationic (or anionic) exchange capacity and, therefore, they have affinity towards the hydrogel hydrophilic chains. In this context, the incorporation of layered double hydroxides (LDH) and smectites, such as hydrotalcite (HT) and montmorillonite (MMt), respectively, allow improvements not only in mechanical properties, but also in sorption and desorption of nutrients. HT and MMt stand out as candidate modifiers, given their characteristics and behavior of interaction with cations and/or anions into the polymeric network [20–25].

Herein, we investigated the role played by the surface charge of lamellar filler on the swelling and diffusion properties of montmorillonite- or hydrotalcite-loaded polyacrylamide/methylcellulose (PAAm-MC) hydrogels. The effect of the lamellar materials on the swelling degree was correlated with the structural and morphological properties of nanocomposite hydrogels. In this way, NC hydrogels were characterized, and their degree of swelling was evaluated in water and solutions with variable pH or salt concentration (NaCl).

2. Materials And Methods

2.1. Synthesis of hydrogels. The polyacrylamide-methylcellulose/hydrotalcite (PAAm–MC/HT) and polyacrylamide-methylcellulose/montmorillonite (PAAm-MC/MMt) hydrogels were obtained by *in situ* polymerization of acrylamide monomer (AAM, 3.73 w/v%, 98.53% purity, Neon), methylcellulose (MC, 0.25 w/v%, molar mass 40.000 g mol^{-1} , viscosity 400 cP, Sigma-Aldrich) and N'-N-methylene bisacrylamide (MBAAm, $5.40\text{ }\mu\text{mol mL}^{-1}$, 99% purity, Sigma-Aldrich). The reagents were placed in a bottle and homogenized by stirring. Different amounts of lamellar nanoparticles (calcium montmorillonite or commercial hydrotalcite, MMt and HT, respectively) were added to the solution, as shown in Table 1.

Table 1
Acrylamide monomer (AAm), methylcellulose (MC), montmorillonite (MMt) and hydrotalcite (HT) concentrations used in the synthesis of hydrogels. The concentrations of MBAAm, TEMED and Na₂S₂O₈ were kept constant at 5.40 $\mu\text{mol mL}^{-1}$, 3.33 $\mu\text{mol mL}^{-1}$ and 0.05 g, respectively.

Materials	(w/v%)			(w/w%)		
	AAm	MC	HT550	HT300	MMt	Lamellar material
HG	3.73	0.25	0	0	0	0
HG550 (1:1)	3.73	0.25	4.0	0	0	50.0
HG550 (2:1)	3.73	0.25	2.0	0	0	33.0
HG550 (4:1)	3.73	0.25	1.0	0	0	20.0
HG300 (1:1)	3.73	0.25	0	4.0	0	50.0
HG300 (2:1)	3.73	0.25	0	2.0	0	33.0
HG300 (4:1)	3.73	0.25	0	1.0	0	20.0
HGMMt (1:1)	3.73	0.25	0	0	4.0	50.0
HGMMt (2:1)	3.73	0.25	0	0	2.0	33.0
HGMMt (4:1)	3.73	0.25	0	0	1.0	20.0

Hydrotalcite was previously heat-treated using a muffle ($30\text{ }^{\circ}\text{C min}^{-1}$) at $300\text{ }^{\circ}\text{C}$ and $550\text{ }^{\circ}\text{C}$ for 120 min. These calcination temperatures were chosen based on previous reports [26–27], which indicate that at $300\text{ }^{\circ}\text{C}$ the hydration water is lost, but the HT structure remains unchanged. Yet at $550\text{ }^{\circ}\text{C}$, the structural water, as well as the hydrotalcite structure is lost. The use of both temperatures allowed two conditions of water interaction in the hydrotalcite structure to be compared. In addition, the miscibility of HT in water was observed after heating at temperatures above 300°C , which is why the hydrotalcite calcined at 300°C (HT300) was chosen to compose one of the synthesized hydrogels. For the other synthesis, the HT calcined at 550°C (HT550) was used, expecting to obtain a sample with new properties, since HT was totally unstructured, when compared to the HG synthesized with HT300. The prepared mixtures were deoxygenated by N₂ bubbling for 20 min. Then, the catalyst N,N,N',N'-tetramethyl-ethylenediamine (TEMED, $3.33\text{ }\mu\text{mol mL}^{-1}$, 99% purity, Sigma-Aldrich) and sodium persulfate (Na₂S₂O₈, 0.05 g, 99% purity, Sigma-Aldrich) was added to initiate the polymerization reaction via free radical [28–29].

The resulting solution was quickly placed between two glass plates (10 x 10 cm) separated by a rubber gasket (0.5 cm) and kept at room temperature for 24 h. The hydrogels were purified by dialysis with distilled water for five days and the water was changed every 24 h. The hydrogels were cut into a cylindrical shape (2.4 cm in diameter) and dried at 30°C . Hydrogels were named (1:1), (2:1), (4:1), and (1:0), which represent the samples prepared with 50% w/w, 33% w/w, 20% w/w, and 0% w/w (control) of

lamellar material. The acronyms HGMMt, HG300, and HG550 were used for hydrogels synthesized with montmorillonite or hydrotalcite calcined at 300 °C or 550 °C, respectively.

The hydrogels were characterized by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, solid-state Nuclear Magnetic Resonance (NMR) spectroscopy and Scanning Electron Microscopy (SEM). Full description is included in the Supplementary Material.

2.2. Swelling degree. The hydrophilicity of NC hydrogels was studied by swelling degree (Q) measurements in aqueous solution. The swelling degree was evaluated at different times to obtain the swelling kinetics. The samples were dried, weighed, and subsequently immersed in Milli-Q® water under different conditions (pH variation and ionic strength). The swelling degree was evaluated at three different pH values (4.0, 7.0 and 10.0) and three values of ionic intensity (0.025, 0.10 and 0.20 mol L⁻¹). Each dried sample was submerged into 50 mL of each solution/medium. The pH and ionic intensity of the medium were adjusted using HCl (aq) or NaOH (aq) and NaCl (aq), respectively. The measurements were done in triplicate ($n = 3$) under controlled temperature ($T = 25$ °C). The standard deviations were calculated and presented with the results. The swelling degree was calculated according to Eq. 1, in which M_t and M_0 correspond to the swollen hydrogel mass at time t and initial dried hydrogel mass, respectively [30–32].

$$Q = M_t / M_0 \text{ (Eq. 1)}$$

The samples were monitored until no significant mass variation was observed (≤ 0.05), indicating that the NC hydrogel reached a dynamic equilibrium. Moreover, the water absorption of samples was evaluated after 15 swelling cycles (re-swelling) to assess the loss of hydrophilic properties. Dried samples were immersed in 250 mL of Milli-Q® water at 25°C until equilibrium was reached. Then, the samples were removed from the medium and dried in an oven at 30 °C. This process was done in triplicate for each HG formulation.

2.3. Kinetic Parameters. The swelling kinetic parameters were determined to compare the diffusional water absorption process between the different hydrogels. The comparison was performed using the Ritger-Peppas model, as shown in Eq. 2 [33–34]. In Eq. 2, t is the time, k is the diffusion kinetic constant, n is the diffusional exponent, and M_t and M_{eq} are the sample mass at time t of swelling and steady state, respectively.

$$k t^n = M_t / M_{eq} \text{ (Eq. 2)}$$

The Ritger-Peppas model can be applied to fit the initial stages to approximately 60% of swelling degree, since the swelling behavior is an ascending straight line over time under these conditions. Above this point, the swelling degree tends to level off with no mass variation over time, thus the slope tends to zero [35–36]. Thus, to obtain the n and k values, graphs of $\ln M_t / M_{eq}$ vs. $\ln(t)$ were plotted for each treatment, and n and k were determined as the angular and linear coefficients, respectively.

3. Results And Discussion

3.1. Chemical and physical characterization

Figure 1 shows the XRD patterns of hydrotalcite (HT) calcined at different temperatures. The hydrotalcite structure remained stable until 200°C, keeping the symmetrical reflections at $2\theta = 11.6^\circ$ and 23.3° ascribed to (003) and (006) basal planes, respectively. The patterns also revealed the presence of asymmetric reflections at $2\theta = 60.7^\circ$ and 62.1° of (110) and (113) non-basal planes, respectively, similarly to hydrotalcite at 25 °C. However, significant structural changes occurred above 300°C, as the primary reflections were not observed. Specifically, the lamellar structure collapsed between 400°C and 550°C, leading to the formation of a mixed Mg/Al oxide – indicated by the reflections at $2\theta = 40-45^\circ$ and $2\theta = 60-65^\circ$. Moreover, the (003) basal reflection shifted to a higher diffraction angle, suggesting that a fraction of particles was their lamellar structure collapsed and/or unstructured.

Figure 2 shows the XRD patterns of the lamellar materials and their respective nanocomposite hydrogels. MMt showed a well-defined diffraction peak at $2\theta = 6.6^\circ$, corresponding to the characteristic montmorillonite phase with an interlayer distance $d_{001} = 1.35$ nm. On the other hand, the pattern revealed that the reflection at 6.6° was not perceptible in the nanocomposite hydrogels (HGMMt), suggesting that MMt was exfoliated and/or intercalated into the hydrogel matrix. Similar results were observed by Bortolin et al., 2013 [3]. Moreover, it was possible to note reflections at $2\theta = 25$ and 27° , which corresponded to common contaminants found in mineral-derived materials as impurity phases, such as quartz and feldspar.

Figures 2b and 2c show the XRD patterns of hydrogels containing hydrotalcite - HG550 and HG300. The HG550 sample matrixes showed a small displacement of the crystallographic plane (003) at $2\theta = 11.5^\circ$. Partial delamination of lamellar material is expected when the diffraction peak is broadened, suggesting formation of tactoids dispersed within the hydrogel matrix at a nanometric scale, although no significant shift was seen.

Figure 3 shows the FTIR spectra of pure (HG) and different modified hydrogels at the 1:1 proportion. All hydrogels (modified or not) exhibited characteristic bands of polyacrylamide, referring to the NH_2 stretching vibration modes ($3300-3450\text{ cm}^{-1}$), and stretching vibrations of C = O bond (1667 and 1466 cm^{-1}) and C–O group (1153 cm^{-1}). The stretching vibration bands between 2990 and 3600 cm^{-1} were attributed to hydroxyl groups. The characteristic bands of β -glycosidic bonds were observed at the $900-1230\text{ cm}^{-1}$ region, referring to the monosaccharide units of methylcellulose.

The bands referring to MMt in the spectrum of HGMMt were observed at $1010-1110\text{ cm}^{-1}$, $914-930\text{ cm}^{-1}$ and $400-800\text{ cm}^{-1}$, corresponding to axial deformations of Si–O, Al–OH–Al angular vibrations, and angular deformations of Si–O bonds, respectively. Also, the bands referring to HT in the HG550 and HG300 spectra were observed at $1360-1485\text{ cm}^{-1}$ and 850 cm^{-1} , corresponding to the symmetrical stretching of interlamellar carbonate and carbonate deformation, respectively. Moreover, the hydration

water and hydroxyl groups present in the HT structure were recorded close to 3440 cm^{-1} , which presents a broad and intense band [37–38].

The results suggest that HG550 had more interlayer carbonates than HG300, given the higher number of bands attributed to symmetric stretching modes of carbonate ($1360\text{--}1485\text{ cm}^{-1}$). A third band (only in HG550 - Fig. 3b) at 1556 cm^{-1} can be associated with the presence of carboxylates (COO^-) in the hydrogel structure, since HT calcined at $550\text{ }^\circ\text{C}$ forms more Mg/Al oxides than hydrotalcite calcined at $300\text{ }^\circ\text{C}$ [39]. This phenomenon occurs during hydration, in which the oxides are converted to hydroxides, influencing the conversion of amide to carboxylic acid groups. Furthermore, no suppression or displacement of the hydrogel bands was observed, implying that the nanoclays-hydrogel interaction is weak.

The ^{13}C nuclear magnetic resonance (NMR) spectra of precursor materials (MC and AAm) used in the synthesis of hydrogels are shown in Figs. 4a and 4b. The MC presented intense peaks at $\delta = 61.30$ and 75.18 ppm , which refer to the C6, C7, C8 and C2, C3, C5 carbons, respectively. In addition, assignments of Am were observed at $\delta = 128.09$, 130.45 and 169.47 ppm , which refer to the C2, C1 and C3 carbons, respectively. Figure 4c shows the ^{13}C NMR spectra of the pure hydrogel, HG300 (1:1) and HG550 (1:1). The most intense peaks at $\delta = 41.92$ and 180.50 ppm were found in all spectra and refer to C1, C2 and C3, C5 carbons from polyacrylamide structure, respectively. The small-signal at $\delta = 59.63\text{ ppm}$ refers to the polyacrylamide C4 carbon. A new peak around $\delta = 170.70\text{ ppm}$ was found in the spectra of HG550 (1:1) and HG300 (1:1). This result indicates that a new chemical environment was formed by reactions involving the C3 and/or C5 carbons, suggesting a change in the network structure of nanocomposite hydrogels. This behavior was intensified when the calcination temperature was increased. FTIR confirms that the hydrolysis process was more efficient in the lamellar material calcined at $550\text{ }^\circ\text{C}$ (Fig. 3). Moreover, no peaks referring to AAm carbons (residual AAm) were found, indicating the complete polymerization of AAm after hydrogel formation. This suggests that relevant toxicity is not expected, since polyacrylamide is relatively stable and does not form significant acrylamide amounts in its degradation cycle, being considered non-toxic [40].

The ^{27}Al NMR spectra (Fig. 5) indicated that the HT calcination at $550\text{ }^\circ\text{C}$ only changed the Al chemical environment, as indicated by the peak widening, and shift from $\delta = 9.05$ to 13.11 ppm . However, the calcination process of HT at $300\text{ }^\circ\text{C}$ was insufficient to change its internal structure, given that the NMR spectrum of HT at this temperature was similar to that obtained at room temperature, e.g., no thermal treatment. Thus, this more pronounced change for HG550 indicates that hydrotalcite was unstructured at this temperature, intensely modifying the chemical environment of Al, as already discussed in the XRD patterns (Fig. 2).

The ^{27}Al NMR spectra of modified hydrogels (Fig. 5b) revealed that both systems regenerated the initial coordination of HT. However, an inversion was observed for HG550, which formed a hydrogel with aluminum in a less diversified chemical environment than in HT. In addition, this environment was similar to the original HT structure, indicating that the HT lamellas were restructured to a higher extent into the

hydrogel matrixes. On the other hand, a divergent profile compared to the original HT structure was obtained when using HT calcined at 300 °C (HG300), suggesting a less effective lamellar regeneration.

Figure 6 shows SEM micrographs of the fractured surfaces of HG, HG550, HG300 and HGMMt synthesized at the 1:1 proportion. In general, it was observed that the samples presented a porous structure with an irregularly leaf-shaped distribution or foliaceous characteristic. This morphology is typical of polysaccharide-based hydrogels, as described by Bortolin et al., 2013 [3]. However, a qualitative analysis of the micrographs at larger magnifications revealed that HG550 had a larger pore size than the other samples. Moreover, small piles or tactoids were well spread on the external walls of HG550, forming an organic-inorganic hybrid structure, thus confirming a better dispersion of HT calcined at 550 °C. A series of agglomerated particles or tactoids on the HG300 polymeric network walls was also observed, indicating the formation of an organic-inorganic hybrid structure. On the other hand, HGMMt had no traces of lamellar structures stacked on the polymeric network walls, indicating that this lamellar material was exfoliated and/or interspersed throughout the hydrogel matrix.

3.2. Swelling degree and kinetic parameters

Figures 7 and 8 show the swelling degree values as a function of time and the swelling degree at equilibrium (Q_{eq}) for all nanocomposite systems. The swelling reduced for HT300 and all the MMT-containing samples. The addition of lamellar materials during the synthesis of hydrogels impacted the swelling capacity, probably because the nanostructures made the polymeric matrixes less flexible due to the hindered chain mobility. This was evidenced by the gradual reduction in the Q_{eq} values with calcination temperature, e.g. Q_{eq} for HGMMt was higher than HG300, which still had some bounded water in the HT structure. However, the HT calcinated at 550 °C significantly affected the water uptake of HG550 with an anomalous increase of Q_{eq} by 179% and 152% for the (4:1) and (2:1) treatments, respectively, when compared to HG. This behavior can be associated with the regeneration of hydrotalcite structure. In contrast, when compared to the same control matrix – HG, it was observed a reduction of 41% (similar to HG300) in the Q_{eq} values of HG550 (1:1). The fully unstructured hydrotalcite (550 °C) attained a better dispersion in the polymeric matrix, as observed in the SEM images (Fig. 6). This dispersion generated an adequate arrangement of the lamellar active centers, allowing the insertion of molecules in the HT galleries and increasing the hydrogel swelling degree. Probably, these lamellar materials acted as labile bridges in the hydrogel structure, leading to a synergistic effect in the swelling degree. Other effects are related to the increase of osmotic pressure gradient formed by the difference between the external and internal media caused by the cations coming from nanoclay, and the increase of electrostatic repulsion between O^- (hydrogel matrix) and $Si-O^-$ (nanoclay) anionic groups. Similar hydrophilic behavior was observed by Junior et al., 2020, for poly(methacrylic acid)/laponite RDS nanocomposite hydrogels.

The reduction observed in Q_{eq} for the (1:1) hydrogels probably occurred due to the excess of lamellar material, which affects the polymer chain rigidity, as evidenced by FTIR and NMR characterizations. Thus,

depending on the HT annealing, the lamellae regeneration during the hydrogel synthesis is favored, corroborating with the NMR results.

Table 2 shows the kinetic swelling parameters of the different hydrogels. The n values were between 0.5 and 1.0 for HGMMt (1:1), HG550 (2:1) and (4:1) (Table 2), indicating that the diffusion process occurred by anomalous transport. The highest value was obtained for the hydrogel with higher mobility of polymer chains (4:1). These results agree with the swelling degree values found for this sample. However, it is possible to notice n values close to 0.50 for HG (without lamellar material) and HG550 (1:1), which corresponds to Fickian diffusion, that is, water molecules are transported through the hydrogel structure by simple diffusion processes. Moreover, $n < 0.50$ were observed for all the other samples, suggesting that the nanoparticles made the polymer chains more rigid. This result was expected due to the possibility of the lamellar materials to act as physical barriers, influencing the diffusion and chain mobility.

Table 2
Kinetic swelling parameters of different hydrogels synthesized using water as swelling medium.

Hydrogel	n	$k (\times 10^{-2}) (h^{-1})$
HG	0.47 ± 0.02	45.87
HG550 (1:1)	0.45 ± 0.01	51.98
HG550 (2:1)	0.57 ± 0.03	47.15
HG550 (4:1)	0.70 ± 0.04	37.14
HG300 (1:1)	0.21 ± 0.01	66.47
HG300 (2:1)	0.22 ± 0.01	68.58
HG300 (4:1)	0.12 ± 0.01	80.34
HGMMt (1:1)	0.69 ± 0.01	52.87
HGMMt (2:1)	0.32 ± 0.02	65.26
HGMMt (4:1)	0.31 ± 0.01	70.13

The increase in the lamellar material content matrixes decreased the k parameter for the HGMMt and HG300 series, suggesting a slower water absorption. However, an opposite effect was observed for the HG550 treatments, indicating that the water absorption occurred more quickly in these samples, with the highest absorption occurring for HG550 (1:1). Again, this is an evidence of the role played by the hydrotalcite regeneration process in the hydrogel structure, that is, the creation of more channels for water diffusion.

Figure 9 shows the swelling degree dependence at equilibrium (Q_{eq}) of the different hydrogels synthesized under three different ionic strength values. It is possible to see that the Q_{eq} values for all

HGMMt and HG300 compositions were little affected with increasing the ionic strength (Figs. 9a and 9b). The presence of salts in the solution increases the osmotic pressure of the swelling medium, which is related to absorption of water. Moreover, it can be noted that there were no significant changes in the water absorption for these treatments (HGMMt and HG300) after reaching a dynamic balance/equilibrium.

In Fig. 9c, the Q_{eq} values of the HG550 series substantially decreased by approximately 50%, 65% and 78% for the (1:1), (2:1) and (4:1) ratios, respectively, with increasing the ionic intensity, suggesting that these hydrogels (HG550) were salt-responsive. However, the samples with significant polymer mobility (observed by the swelling degree greater than that of HG) had higher sensitivity to ionic strength. The decrease in Q_{eq} is, in part, due to the localized interactions between positive ions (Na^+) and hydroxyl groups of MC, inducing the formation of $^-O-Na^+$ ionic complexes. Consequently, this complex formation could decrease the electrostatic repulsions between MC chain segments, which are entanglement with the crosslinked PAAm chains, making the polymer network expansion difficult [41]. Another effect related to the decreased Q_{eq} values is the stabilization of chloride anions by the anionic HT lamellas, which have positive charges on their surface, reducing the quantity of hydroxyl groups and water molecules inside the hydrogel as well as contributing to decrease the swelling degree.

It is worth mentioning that HG (composed exclusively of Am and MC) was also salt-responsive, which is in line with the results reported by our research group [42]. The swelling degree of HG decreased by approximately 20% with the increase in ionic strength, although this reduction occurred to a lesser extent, when compared to the HG550 series. Probably, the main reason for this decrease is also related to the interactions between the Na^+ ions and hydroxyl groups of MC, as previously explained. In this way, these results prove that the hydrotalcite played an essential role in the water uptake of the hydrogels in matrixes in saline medium.

The influence of pH on the swelling degree and Q_{eq} values for the different synthesized hydrogels is shown in Fig. 10. It was observed that the water absorption capacity of HGMMt and HG300 was slightly affected when the pH decreased from 7.0 to 3.0 (Figs. 10a and 10b). This indicates that only a small fraction of amide groups in the polymer chains was ionized, which slightly contributed to the expansion-contraction of the hydrogel polymer chains. On the other hand, the pH variation from 7.0 to 10.0 increased the water absorption for most samples, suggesting that the synthesized hydrogels were pH-responsive. These results agree with findings reported by other authors [43]. The control of the water uptake by pH and salt variation improves the applicability of the synthesized hydrogels, mainly in the agriculture field, such as for water remediation and controlled release of substances.

The HG550 (2:1) and (4:1) samples exhibited different behaviors (Fig. 10c), since their structures encompassed polymer chains with higher mobility, thus showing higher sensibility to changes in the external swelling solution, as discussed in the previous section. The decrease in Q_{eq} observed at high or low pH values relates to the increase in the ionic intensity of medium, which occurred by increasing the

number of sodium (pH 10) or chloride (pH 3.0) ions, since NaOH or HCl solutions were used to adjust the pH of the swelling solution.

Figure 11 shows the Q_{eq} values of each sample as a function of number of swelling cycles. When the hydrogel is subjected to the swelling process from its dry state to the maximum swelling, significant structural changes occur in the polymer chains. When the swelling/drying sequence is repeated consecutively, reorganization in the polymer chains can occur, causing small changes in the swelling degree between each cycle [44].

There was a tendency to decrease the hydrophilic property of HG with increasing the number of swelling cycles, while a slight variation was found for the hydrogels reinforced with lamellar materials (Figs. 11a and 11b). For the hydrogel with anomalous behavior (HG550 4:1), which have polymer chains with higher mobility, the variation in the swelling degree was more significant, but its hydrophilic property was not dependent on the swelling cycle number (Fig. 11c).

The tendency to maintain the swelling degree of nanocomposite hydrogels after several swelling/drying cycles can be explained by the dispersion of lamellar materials in hydrogel matrixes, protecting and reinforcing the polymeric network structure against damage during the drying process. These results indicate that the nanocomposites (HG550, HG300 and HGMMt) have improved behaviors with respect to the control (HG), and that these materials can be reused favorably for up to fifteen cycles without losing their water retention effectiveness.

4. Conclusion

Nanocomposite hydrogels containing hydrotalcite or montmorillonite were successfully synthesized by in situ polymerization with different lamellar material proportions. The water absorption capacity of hydrogels containing montmorillonite and hydrotalcite (calcined at 300 °C) were slightly affected by pH, since the presence of these lamellar nanoparticles increased the hydrogel polymer matrix rigidity. The hydrogels with hydrotalcite (calcined at 550 °C – 2:1 and 4:1) were strong dependent on the ionic strength of medium, and displayed anomalous behavior regarding the water absorption, increasing the swelling degree at equilibrium (Q_{eq}) with decreasing the lamellar material content. Moreover, there were no significant changes in the water absorption properties of nanocomposite hydrogels when they were subjected to swelling/drying cycles.

Declarations

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DECLARATION ON CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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Figures

Figure 1

X-ray Diffraction (XRD) patterns of hydrotalcite treated at different temperatures.

Figure 2

X-ray Diffraction (XRD) patterns of hydrogels synthesized with different proportions (by mass) of montmorillonite (a) and hydrotalcite calcined at (b) 550 °C and (c) 300 °C.

Figure 3

(a) FTIR spectra and (b) detailed view in the region between 1800 and 1500 cm^{-1} of pure hydrogel (HG) and its respective nanocomposites with calcined hydrotalcite (550 and 300 $^{\circ}\text{C}$) and MMt.

Figure 4

High-resolution solid-state ¹³C-NMR spectra of (a) methylcellulose (MC), (b) acrylamide (Am) and (c) synthesized NC hydrogels. The structures of MC, Am and PAAm are included as inserts.

Figure 5

^{27}Al -NMR spectra of (a) hydrotalcite and (b) modified hydrogels with hydrotalcite.

Figure 6

Scanning Electron Microscopy (SEM) images with two different magnifications of: (a-b) HG (1:0), (c-d) HG550 (1:1), (e-f) HG300 (1:1) and (g-h) HGMMt (1:1). The hydrogel and lamellar material are highlighted in blue and green, respectively. Original images are available in the Supplementary Material – Figure S1.

Figure 7

Swelling degree as a function of time for synthesized hydrogels with different contents and types of lamellar materials: (a) HG550, (b) HG300 and (c) HGMMt.

Figure 8

Comparison of swelling degree at equilibrium (Q_{eq}) for different hydrogels synthesized using water as a swelling medium.

Figure 9

Swelling degree at equilibrium (Q_{eq}) at different concentrations of NaCl for HG compared to (a) HGMMt, (b) HG300 and (c) HG550.

Figure 10

Swelling degree of equilibrium (Q_{eq}) at different pH values for HG compared to (a) HGMMt, (b) HG300 and (c) HG550.

Figure 11

Comparison of swelling degree at equilibrium (Q_{eq}) evolution with swelling/drying cycle number for (a) HGMMt, (b) HG300 and (c) HG550.

Supplementary Files

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