Hydrogels Composite of Poly(acrylamide-*co*-acrylate) and Rice Husk Ash. I. Synthesis and Characterization

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ABSTRACT: Composite hydrogels of poly(acrylamide-*co*-acrylate) with rice husk ash (RHA) were synthesized and studies of the swelling variables were accomplished comparatively with commercial polyacrylamide gel and PAMACRYL, a poly(acrylamide-*co*-acrylate) hydrogel without RHA. FT-IR and WAXS were the techniques employed for characterizing a series of hydrogel obtained by varying the percentage of RHA (1, 2, 5, 10, and 20 wt %) and the amount of crosslinking agent (0.05, 0.1, and 0.2 mol %) relative to sum of AAm and AAc. Superabsorbent hydrogel with $W_{eq} > 800$ g H_2O/g gel was obtained with percentage of 10 wt % of RHA and 0.1 of crosslinking agent mol %. The hydrogel showed to be sensitive to the pH variation and to the presence of salts. The hydrogels, even though submitted through cycles of drying and swelling, preserved their superabsorbent characteristics and demonstrated better water absorbance properties when compared with commercial polyacrylamide gel. The composite hydrogels of poly(acrylamide-*co*-acrylate) with RHA presented good characteristics to be applied as soil conditioner for using in agriculture. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 879–887, 2012

Key words: hydrogels; composites; hydrophilic polymers; swelling

INTRODUCTION

The preparation and application of the new materials is one of the most important areas in polymer science. Resulting polymeric materials from the mixture and combination of polymers and inorganic components have received attention from researchers in the last few years, mostly due to a plenty of possibilities for applying such materials in pharmaceutical, medical, technological, and agriculture fields.[1–10]

Hydrogels are polymers that are able to absorb and retain large amounts of water and are used in agricultural activities such as soil conditioners, especially for increasing the water-storage capacity of the soil.[11] Soil conditioner is defined as all organic material, synthetic, natural or natural but chemically modified which, when added to the soil, favorably alters its physical and structural properties and tends to increase the humidity of soil.[12] Soils conditioners based on hydrogels consist of one or more three dimensionally polymer networks, formed by macromolecular chains linked by covalent bonds or physical interactions.[13] Due to these characteristics, the hydrogels present, at same time, hydrophilicity that contributes to retaining large amount of water or polar fluids and insolubility due to the 3D network of matrix.

The swelling process is governed by physical parameters of gel and by external factors. Some of the physical parameters, such as the presence of cohesion forces, hydrophilic groups, low crosslinking density, and flexibility of the polymer chains, are favorable for the swelling process.[14] The presence of hydrophobic groups, higher crosslinking density, and the presence of ions in the environment where the gel is placed does not favor the water absorption by the hydrogel. External factors such as pH, ionic forces, temperature, solvent composition, are some key-parameters that interfere in the water absorption process by the gel.

On the other hand, the search for environmental friendly technology has become a major concern in the last few years. The adequate disposal of recycled material and of waste derived from natural vegetable-raw materials is of great interest from the

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economic and technological point of view. For reaching this, the inclusion of subproducts derived from some transforming industries in new final products with higher aggregated values and in more noble applications has been proposed. The large amount of residues generated by the agro industries is one of the factors that contribute to the current concern in preserving the environment.

The rice husk (RH) is a coating or a protective layer formed during the growth of rice grains. The RH generates combustion ash with varying structural forms (amorphous or crystalline) which depend both on the type of equipment and burns used, as well as the time and temperature of the burn.[15] The rice husk is an residue from agro industry and, as a residue, the greater part of the rice husk generated is discarded, causing pollution. Studies indicate that the rice husk ash (RHA) produced from a controlled combustion (600°C) has in its morphological composition the presence of silica (SiO_2) in the amorphous state.[16–18] It is worth mentioning that there are few studies on using of such ash as a filler in polymers.[19–22]

In this study, superabsorbent hydrogels of acrylamide–acrylate copolymer and RHA, as composites, were synthesized and some of its characteristics were compared with commercial polyacrylamide (PAMCOM). The effect of RHA on acrylamide–acrylate copolymer hydrogel was evaluated by comparison of composite matrices (RHAG) behavior with the matrix without RHA (PAMACRYL). FTIR and X-ray diffraction were techniques used to characterize the gel structure. The effect of RHA on the swelling–drying capabilities of hydrogels was also investigated.

EXPERIMENTAL

Materials

Acrylamide (AM), acrylic acid (AA), *N*,*N*,*N*′,*N*′-tetramethylenodiamine (TEMED), as accelerator of the reaction, and the potassium persulfate ($K_2S_2O_8$), as catalyst, were purchased from SIGMA ALDRICH. *N*,*N*′-methylenobisacrylamide (MBAAm), as crosslinker, was obtained from PHARMACIA BIOTECH.

The used rice husk originates from the city of Mucambo/CE, Brazil. Ashes were produced through calcination in a muffle furnace at 600°C for 2 h. The ashes were previously ground and sieved through a 325 mesh (44 μm) sieve prior using in hydrogel synthesis.

Synthesis of hydrogel copolymer of acrylamide–acrylate (PAMACRYL)

For every 30 mL of distilled water, after stirring and nitrogen gas bubbling (to reduce the inhibiting effect of the oxygen in the radical polymerization reaction), 2.1 g of acrylamide and 3.3 g of acrylate were added. After 10 min, 16.2 mg of $K_2S_2O_8$ were added. Then MBAAm (0.05, 0.1, and 0.2 mol % related to the amount of monomers) and 100 micro L of TEMED solution 0.57 g L^{-1} were added. The system was closed and maintained stirred under nitrogen flow until the gel formation, which was then left to rest for further 15 h. The material was divided into small pieces and washed with distilled water for removing the excess of non reacted monomers. The obtained material was then oven-dried at 70°C and then the sizes of particles fall within 9–24 mesh (2–0.71 mm) range.

Synthesis of hydrogel copolymer of acrylamide–acrylate and rice husk ash (RHAG)

For the synthesis of the RHAG hydrogels, the same procedures used for the PAMACRYL obtainment were followed, excepting that the monomers were dissolved in a dispersion of mineral (1, 2, 5, 10, and 20 wt % in related to the amount of monomers).

Fourier transform infrared spectroscopy

The IR spectra were obtained with a Shimadzu FTIR-8300 equipment. The dried material was blended with KBr powder and pressed into tablets before spectrum acquisition.

X-ray diffraction

The X-ray diffractograms were obtained through a powder diffractometer, Shimadzu, model XRD-6000, with Cu-Kα radiation source −40 kV and 30 mA.

Swelling experiments

The hydrogels obtained were initially characterized by their water absorption capacity, through swelling tests. In this way, 15 mg of the gels were placed in 30 mL filter crucibles (porosity n° 0) premoistened and with a dry outer wall. This set was inserted in water in such a way that the gel was completely submerged.

The crucible/gel set was removed at various time intervals, with the external wall of the set dried and the system weighed. Each experiment was performed in triplicates. The swelling capacity of gels was determined from eq. (1), where W is the gained water mass per gram of gel, m is the mass of the swollen material and m_0 is the mass of the dry material.[22] It was possible to follow the kinetics of the swelling in each studied medium. The size of the gels, after drying, remained in 2–0.71 μm.

$$W = [m/m_o] - 1 \tag{1}$$

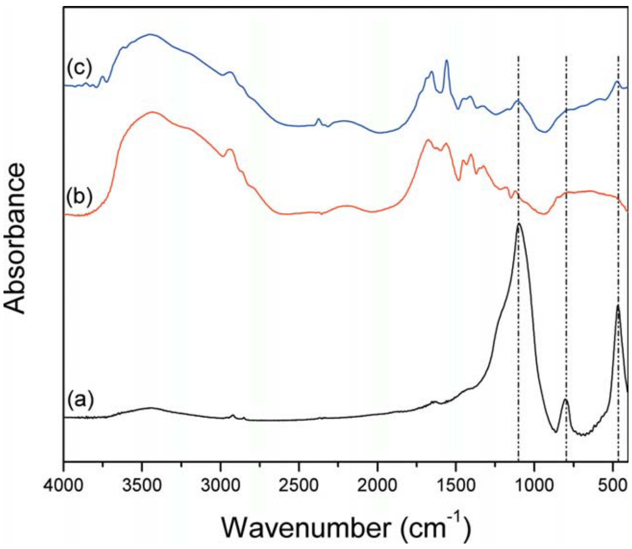

Figure 1 Infrared Spectra: RHA (a), PAMACRYL (b), and RHAG10 (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The effect of the ionic force and type of metallic ions

The hydrogels were immersed in aqueous NaCl solutions of different concentrations (0.001, 0.01, 0.05, and 0.10 *M*) and the swelling capability of gels determined through the previously described procedures.[22] For studying the effect of the type of ions as counter-ion of salt, solutions of NaCl and $NaHCO_3$ were used for seeing the anion effect; NaCl and $CaCl_2$ were used for evaluating the cation effect, being all at fixed ionic force ($I = 0.1$ *M*).

Evaluation of pH effect on swelling capability of gels

The effect of the pH was also verified using solutions at pHs 2.4, 9.4, and 7.4 (using phosphate buffers), maintaining the ionic force equal to 0.1 *M*.

Effect of drying–swelling cycles on hydrogel swelling capability

The effect of the repetition of the drying and swelling processes of gels was verified in aqueous environment. The dried hydrogel was immersed in water at ambient temperature (30°C) and the absorption was determined as previously described. The swollen material was then dried at 70°C for 24 h, and again submitted to the swelling process. This cycle was repeated five times.

Measurements of swelling of the hydrogels in simulated soil

The capacity of the hydrogel to swell in simulated soil solution[23] (KCl, 5 mM; $MgCl_2$, 1 mM; $CaCl_2$, 0.25 mM) was evaluated. The hydrogels were immersed in the solution and the amount of absorbed fluid was determined as previously described.

Study of release of water by the swollen hydrogel

The gels were swelled in distilled water till the equilibrium has been reached. Then, the samples of the swollen material were left for drying at room temperature (30 ± 1°C) or placed in an oven at 35, 40, and 45°C. The mass of lost water was monitored in each case over a time period necessary to reach the equilibrium in weight loss. For each sample, the percentage of gel-remaining water was calculated as a function of time based on initial masses of the swollen hydrogels. All experiments were performed in triplicates.

RESULTS AND DISCUSSION

Analysis of RHA, PAMACRYL and composite (RHAG) structures through FTIR

Figure 1 shows the FTIR spectra of the RHA and the synthesized gels (PAMACRYL and RHAG10). In the RHA spectrum, the bands related to the main vibrational modes in the Si—O—Si bonds in the region of 1100, 800, and 471 cm^{-1} were observed, being attributed to the asymmetric stretching, symmetric stretching, and angular deformation, respectively.[24] The broad band in the region of 3548 cm^{-1} is attributed to the vicinal silanol with hydrogen bonded water. The spectrum of the PAMACRYL, Figure 1(b), demonstrated the formation of the copolymer due to the appearance of the bands at 1670 and at 1564 cm^{-1}, referring to the C=O stretching and to the *N*—O stretching, respectively. The spectrum of the RHAG10, Figure 1(c), confirms the formation of the composite by the appearance of the bands at 1100, 800, and 471 cm^{-1}, representing the SiO_2 and Si—O—Si[25,26] bonds, as is shown in Table I.

TABLE I
Assignments of Infrared Frequency of RHA and the Synthesized Hydrogels

RHA	PAMACRYL (cm^{-1})	RHAG10 (cm^{-1})	Assignments
3548			υ, O—H
	3436	3434	υ, H_2O e NH_2
	2947	2939	υ_{as}, CH_2
	1670	1632	υ, C=O
	1564	1556	δ, NH_2
	1456	1450	δ, CH_2
	1408	1406	υ, C—N
	1328	1320	δ, CH
	1176	1171	ω, NH_2
1100		1110	υ_{as}, Si—O—Si
800		800	υ, Si—O—Si
471		471	δ, Si—O

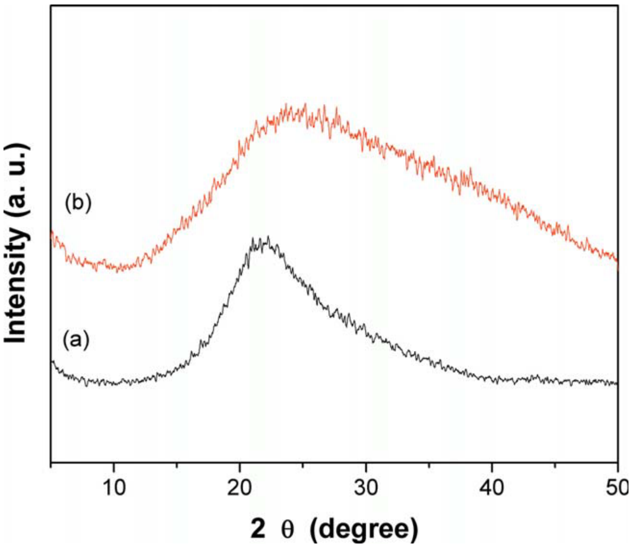

Figure 2 X-Rays Diffractograms: RHA (a) and RHAG10 (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

X-ray diffraction

Figure 2(a) presents the X-ray diffraction profile of the RHA calcined at 600°C for 2 h and cooled to room temperature within the muffle for 24 h. The analysis showed that this ash presented similar X-ray profile as compared to that calcined at 700°C for 4 h.[27] In both, no well defined peaks appear in respective X-ray profiles, except the one that appears at $2\theta = 22°$, which indicated the no occurrence of the crystalline phases on the ash, meaning the predominance of noncrystalline silica.[26–31] The characteristics of the amorphous silica of the RHA in the RHAG [Fig. 2(b)] is maintained but signal is enlarged due to the presence of copolymer. It suggests also that the RHA was completely dispersed during the gelling process (Fig. 3), being the RHA present in the polymeric matrix and confirming the formation of a composite as observed through FITR spectra analysis.

Kinetics of swelling

Figure 4 shows the kinetics of swelling in water for the RHAG10 hydrogel and of the PAMACRYL and commercially (PAMCOM) hydrogels used for comparison. The observed trends in the swelling kinetics are very similar. There were quick increasing in the degree of swelling during the first 20 min of immersion, reaching about 90% of the equilibrium value in this time range, followed by a slower process until the equilibrium was reached (W_{eq}) at around 30 min, whose values depend on the gel (see the insertion on Fig. 4). It is observed that the synthesized gels presented an equilibrium time (t_{eq}) of 24 and 10 min for PAMACRYL and RHAG10, respectively, while the PAMCOM had a $t_{eq} = 31$ min. Thus, the synthesized gels (PAMACRYL and RHAG10) show higher velocity in the swelling when compared with the commercial one (PAMCOM). The PAMACRYL and PAMCOM gels presented practically the same

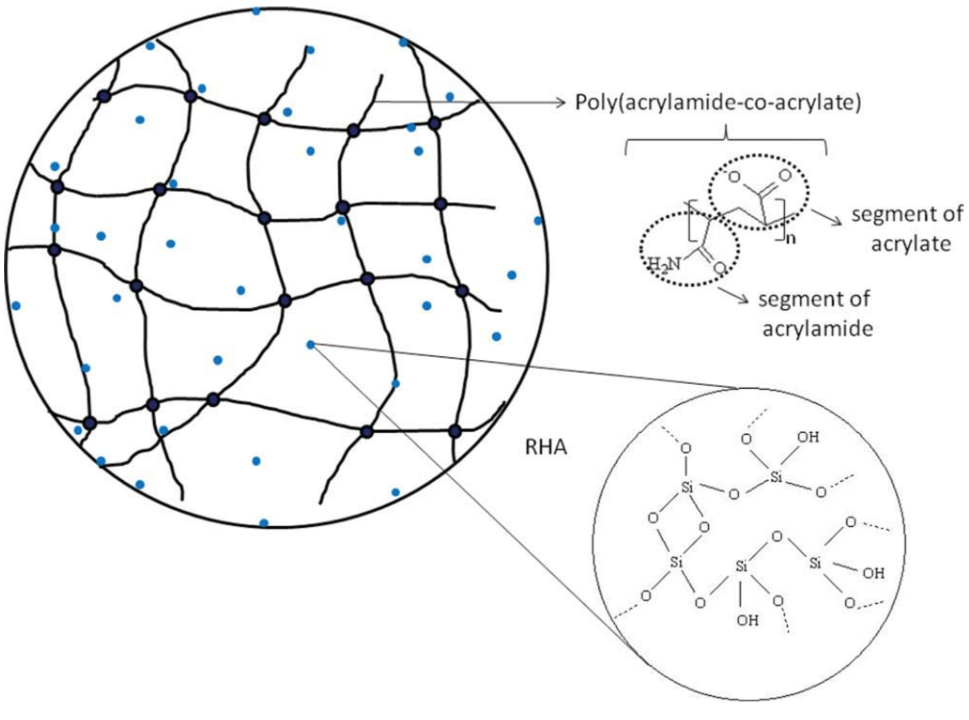

Figure 3 Proposed model for the structure of RHAG superabsorbent composite network. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

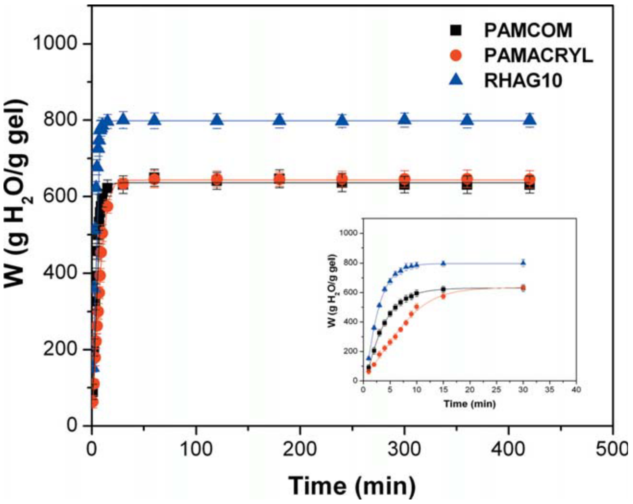

Figure 4 Swelling of the synthesized gels and a commercial gel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

water-absorption capacity at equilibrium (W_{eq}), 645 and 634 g/g, respectively, although the gel RHAG10 presented higher water absorption capability (W_{eq} = 802 g/g) when compared with the PAMACRYL and PAMCOM gels. The used units g/g mean gram of water by gram of hydrogel.

Determination of the constant swelling velocity

Some of the characteristics collected from the swelling curves through the relations proposed by Karadag et al.[32] are showed in Table II

$$t/W = A + Bt \tag{2}$$

where

$$A = 1/k_s W_t^2 \text{ and } B = 1/W_t \tag{3}$$

Parameter A corresponds to an initial swelling rate $[(dW/dt)_0]$ of the hydrogel, k_s is the constant rate for swelling and W_t is a theoretical swelling value at equilibrium. k_s and W_t were calculated by fitting experimental data shown in Figure 3 to eqs. (2) and (3).

TABLE II
Parameters Obtained in the Kinetics of Swelling

Hydrogel	W_{eq}[a]	W_t[b]	t_{eq} (min)[c]	k_s (min^{-1})[d]
RHAG10	802 ± 19	800	10 ± 1	1.42×10^{-3}
PAMACRYL	645 ± 21	649	24 ± 3	6.54×10^{-4}
PAM COM	634 ± 23	633	31 ± 1	9.78×10^{-4}

[a] Equilibrium swelling (g H_2O/g gel).
[b] Equilibrium theoretical swelling (g H_2O/g gel).
[c] Necessary time (min) to reach the equilibrium swelling.
[d] Rate of swelling (g gel/g H_2O)/min.

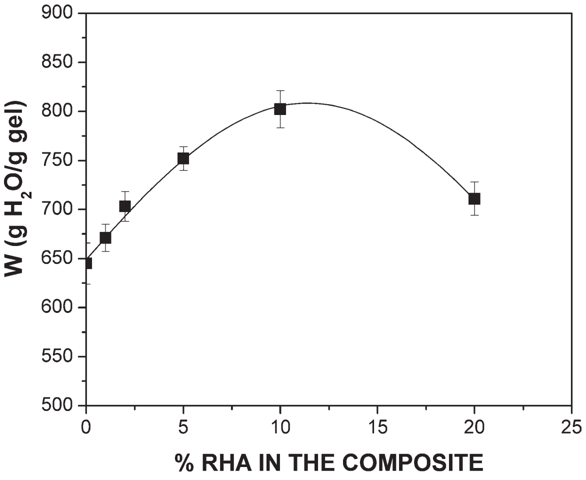

Figure 5 Effect of the quantity of RHA in the swelling process of RHAG10 hydrogels containing three different amount of RHA.

Effect of the RHA amount in the swelling properties of RHAG hydrogels

Figure 5 shows that the presence of RHA in the hydrogel increases the swelling capability of gel in ~ 24% related to PAMACRYL and 26% related to PAMCOM, considering W_{eq} = 334 g/g for PAMCOM. The dependence of water absorption to the amount of RHA in the RHAG hydrogels is shown in Figure 5. It can be observed that the incorporation of 10 wt % of RHA leads to a maximum in the water uptake property of composite hydrogel. The addition of RHA in 20 wt % resulted in a significant reduction compared to maximum swelling of composite. This behavior can be attributed to the presence of more crosslinking points in the polymeric chain and such increase in the density of the crosslinking in the composite leads to a reducing the elasticity of the matrix.

The RHA probably acts as a support in the gel acting between the layers of the polymer chains, increasing the quantity of the load of the material and consequently the absorption of the water too. It should also

TABLE III
W(g H_2O/g gel) in as a Function of the Quantity of RHA for Hydrogels

Hydrogel	W_{eq}	W_t	t_{eq} (min)	k_s (min^{-1})
RHAG20	711 ± 17	714	56 ± 5	2.71×10^{-4}
RHAG10	802 ± 19	800	10 ± 1	1.42×10^{-3}
RHAG5	750 ± 12	752	14 ± 2	1.47×10^{-3}
RHAG2	703 ± 15	709	25 ± 2	4.33×10^{-4}
RHAG1	670 ± 14	680	52 ± 4	2.19×10^{-4}
PAMACRYL	645 ± 21	649	24 ± 3	6.54×10^{-4}

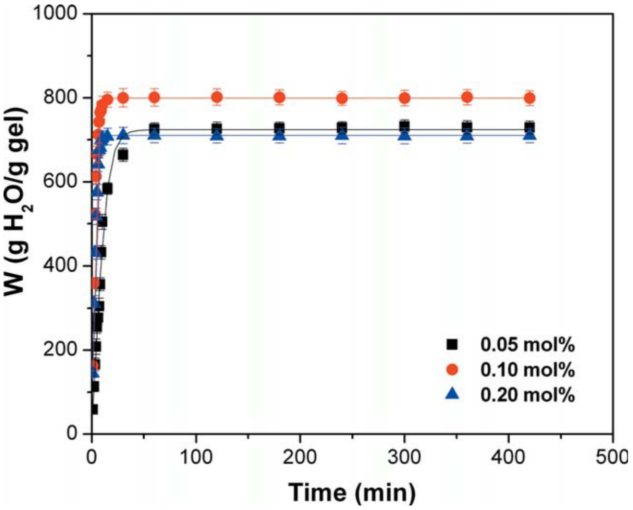

Figure 6 Effect of crosslinking concentration on the kinetics of swelling in water for the RHAG10 hydrogel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to increase the mechanical resistance and the crosslinking degree of composite compared to PAMACRYL. This explains the increase in the water absorption of the RHAG related to the PAMACRYL, mainly the RHAG10, as showed in Table III.

Effect on the crosslinking degree

Hydrogels were synthesized using different concentrations of *N*′,*N*-methylenebisacrylamide (MBAAm), which presents an important role in the swelling characteristics of the hydrogel.[33–35] The MBAAm concentration range handled in this work was of 0.05–0.20 mol %. The dependence of W_{eq} to the MBAAm concentration is shown in Figure 6 and Table IV. It can be observed that the capacity of water absorption by the gel obtained at concentration of MBAAm of 0.10 mol % is superior to that obtained at MBAAm 0.05 mol %. Clearly the increase in the concentration of the crosslinking agent MBAAm beyond 0.1 mol % caused a pronounced decrease in the absorption of water in the hydrogels.

Polymeric networks formed with high concentration of MBAAm are strongly crosslinked and this fact reflects in a smaller expansion of matrix and, consequently, smaller volume of water diffuses into the interior of the matrix.[36] The hydrogels studied by Pourjavadi et al.[37] presented similar behavior and the increase in the MBAAm concentration resulting in highly crosslinked polymeric networks, resulting in decreased W_{eq}.

TABLE IV
Effect of Crosslinking Concentration on the Kinetics of Swelling in Water for the RHAG10 Hydrogel

RHAG10 (mol %)	W_{eq}	W_t	t_{eq} (min)	k_s (min^{-1})
0.05	724 ± 17	736	32 ± 4	1.83×10^{-4}
0.10	802 ± 19	800	10 ± 1	1.42×10^{-3}
0.20	710 ± 14	715	14 ± 2	2.87×10^{-3}

Effect of the ionic force

It has been confirmed, through theoretical and experimental considerations, that the presence of ions has great effect on the hydrogels swelling behavior.[38,39] In this work, the influence of ions in the swelling capability of hydrogels was tested by the addition of NaCl (0.001–0.1 *M*) or $NaHCO_3$ (0.1 *M*) or $CaCl_2$ (0.1 *M*) in the surrounding solution.

Tables V and VI present the data collected in swelling measurements for the hydrogels in NaCl solution. The sensitivity of hydrogel to presence of salts can be related by the dimensionless factor *f* defined[40] as:

$$f = 1 - \{(W_s/W_w)\} \qquad (4)$$

where W_s and W_w are the swelling in saline solution and in deionized water, respectively. The *f* values (Tables V and VI) indicate that the RHAG10 gels suffer less influence to the presence of salt than the PAMACRYL gel. The increase in the ionic force reduces the difference in the concentration of movable ions between the polymer matrix and the external solution (osmotic swelling pressure) and leads to an immediate contraction of gel.

Amounts of divalent and trivalent cations drastically reduce the swelling capacity of the hydrogels. This is due to the complexing ability of the carboxymide or carboxylate groups and the formation of inter and intramolecular complexes.[41,42] The RHAG hydrogels presented greater W_{eq} values in saline solution (Table VI) when compared with the PAMACRYL one.

TABLE V
***W*(g H_2O/g gel) as Function of the Ionic Force for the Hydrogels**

	H_2O	NaCl 0.001 *M*		NaCl 0.01 *M*		NaCl 0.05 *M*		NaCl 0.1 *M*	
	W_{eq}	W_{eq}	*f*	W_{eq}	*f*	W_{eq}	*f*	W_{eq}	*f*
RHAG10	802 ± 19	459 ± 4	0.43	253 ± 2	0.68	123 ± 2	0.85	87 ± 1	0.89
PAMACRYL	645 ± 21	361 ± 4	0.44	195 ± 2	0.70	85 ± 1	0.87	63 ± 1	0.91

TABLE VI
W(g H_2O/g gel) as Function of the Type of Anion and Metal for I = 0.1

	H_2O	NaCl		$NaHCO_3$		$CaCl_2$	
	W_{eq}	W_{eq}	f	W_{eq}	f	W_{eq}	f
RHAG10	802 ± 19	87 ± 1	0.89	79 ± 1	0.90	24 ± 1	0.97
PAMACRYL	645 ± 21	63 ± 1	0.91	69 ± 1	0.89	17 ± 1	0.97

Effect of the pH on swelling properties of gels

The effect of pH on the kinetics of hydrogel swelling was observed by the use of buffer solutions at pHs 2.4, 7.4, and 9.4, maintaining the ionic force equal to 0.1 (Fig. 7). An increase in the value of W_{eq} was observed as the pH of the external solution is increased.[10,43] In acidic medium, the carboxylate anions are protonated and the anion–anion repulsive forces vanishes; this will lead to a minimum swelling of the hydrogel. For greater pH values, the carboxylate groups become ionized and the electrostatic repulsion between COO^- groups causes expansion of matrix and, consequently, increasing W_{eq}.[44]

At pH 9.4 buffer the hydrogel swells much more due to the repulsion of the COO^- groups, while at pH 2.5, it collapses in minutes due to the shielding effect of excess cations. The semi-IPN hydrogels studied by Aouada et al.[45] presented similar behavior of pH-responsive. This behavior makes the RHAG hydrogels strong candidates to be utilized in controlled release systems.

Effects of the drying swelling cycles

If a material is undergoing a soil application, it should be subjected to water absorption and drying cycles and, even that, it must maintain its water absorption characteristics. The effect of the repetition of the drying–swelling processes was verified for hydrogels with 0.10 mol % of crosslinking (Fig. 8). As in contact with water or aqueous solution, the particles of the dried-absorbent material suffer swelling and expand many times over its initial volume. The repetition of the swelling and drying cycle affects the water absorption capacity. An initial decrease in the W_{eq} value is observed for all the hydrogels and it is only stabilized after four cycles of drying–swelling. The RHAG10 hydrogel presented the smallest reduction (29%) while the PAMACRYL hydrogel presented a moderate reduction (46%) and the PAMCOM hydrogel the greater reduction (49%).

Swelling measurements of the hydrogels in simulated soil solution

The value of W_{eq} for RHAG10 in simulated soil solution was evaluated and compared to PAMACRYL and PAMCOM (Table VII). The RHAG10 hydrogel presented greater swelling ratio, nearly twice as compared to the commercial gel, indicating that the presence of RHA leads to smaller reduction in its swelling capacity when the immersion media is changed from distilled water to simulated soil

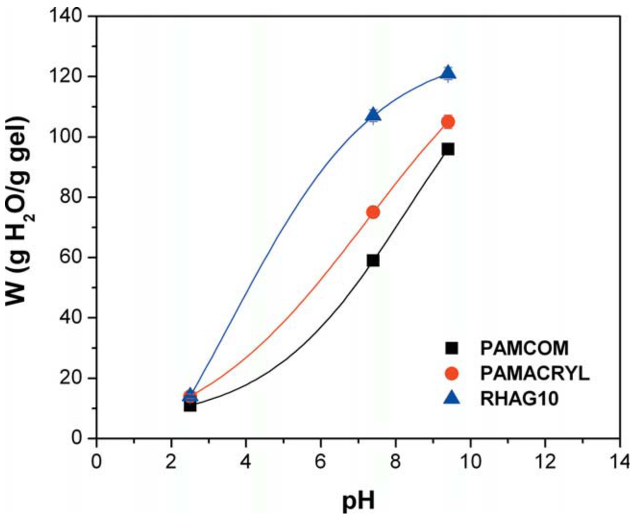

Figure 7 pH effect on the swelling of hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

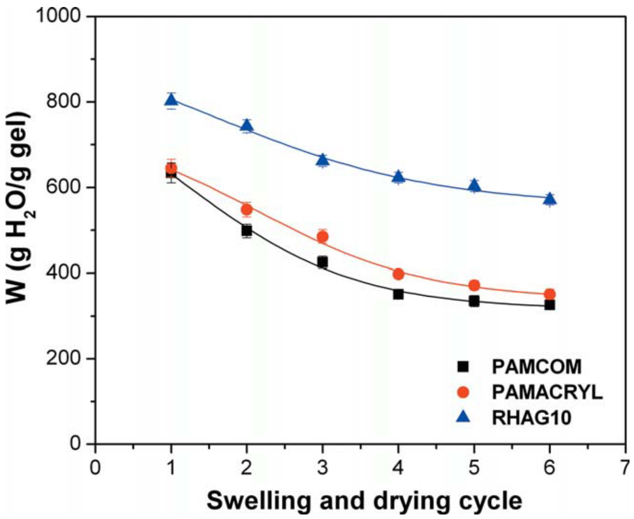

Figure 8 Effect of drying cycle and swelling in the capacity of water absorption. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VII
Swelling of Hydrogels in Simulated Soil Solution

	W_{eq}		
Medium	RHAG10	PAMACRYL	PAMCOM
Water	802 ± 19	645 ± 21	645 ± 21
Soil	232	168	129
Water/soil	3.5	3.8	4.9

solution. Therefore, the RHAG10 proved to be the best gel considering the three different analyzed materials.

Study of releasing water from swollen hydrogels

Beyond the water absorption capacity, the capacity to release water is another important characteristic of the superabsorbent hydrogels to be used as soil conditioners or with the potential for this purpose. Figure 9 illustrates the drying curves for the RHAG10 gel that were swelled in water and dried at room temperature (30 ± 1°C) and in an oven at 35, 40, and 45°C. The curves were built from the percentage of remaining-gel water in relation to the initial mass of the swollen material (at time zero).

When the water is evaporated from the swollen gels, the occurrence of three straight lines with different slopes can be observed, indicating three drying rates and, presumably, different mechanisms of drying would be evolved. Similar behavior was observed in 1995 by Salem et al.,[46] performing studies on a hydrogel soil conditioner (EVERGREEN 500) prepared from polyacrylamide after-modified with sulfonic groups.

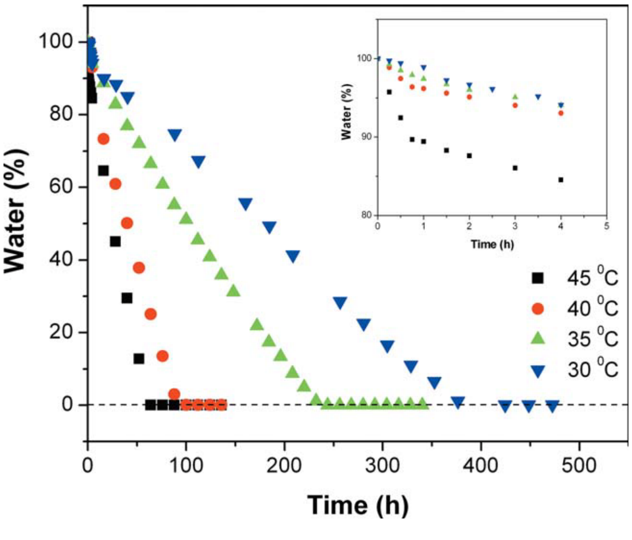

Figure 9 Loss of water from the RHAG10 hydrogel which were swollen in water and dried in different temperatures. Values expressed as percentages of water retained in relation to the initial mass of the system in time zero. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VIII
Drying Rates for the Three Events and Drying Times of Equilibrium as a Function of Drying Temperature

Temperature (°C)	Rate (%/h)			
	1° Event	2° Event	3° Event	t_{eq} (h)
30	1.09	1.03	0.25	376
35	2.58	1.04	0.41	233
40	4.89	1.04	0.97	88
45	13.68	1.59	1.31	64

Table VIII shows the values of drying rates for the three events, calculated from the slope of the straight lines. Two of them are clearly seen in the insert on Figure 9 in which the time-scale ranges from 0 to 4 h. Also, in the insert the values for the time required for the systems to reach the equilibrium as a function of drying temperature can be observed. For all the straight lines, correlation coefficients (R^2) were never lower than 0.99 and the respective slopes were used for calculating the drying rates.

For all the hydrogels, it could be observed that the first drying rate were always superior to the corresponding values of the other stages. The highest drying rates for the first event are related to the water molecules weakly bounded to the gel, mainly those localized at the gel surface. The lowest values of the drying rates of the second and third events are related to the water molecules more strongly linked through the hydrogen bonds with carboxylate and/or amide groups. It was observed that the composite hydrogel prepared by blend RHA with acrylamide and acrylate (RHAG10) has higher potential to retain water at room temperature compared to PAMACRYL and PAMCOM.

CONCLUSION

Composites of acrylamide–acrylate copolymer and RHA were formed, as observed by FTIR and X-ray techniques. The RHAG hydrogels synthesized in this work proved to be more efficient in the water absorption than the commercial or poly(acrylamide–acrylate) hydrogels without RHA particles, used for comparison. The presence of RHA on acrylamide–acrylate polymeric matrix improved the water-absorption properties of material, providing an increase of 24% in the W_{eq} values when compared with hydrogel without RHA particles. The water absorption capacity by the gel depends on the RHA and MBAAm contents, and the maximum values observed were of 10 wt % and 0.10 mol %, respectively. The RHAG10 presented more rapid and more efficient water absorption than the commercial gel.

The hydrogels synthesized using RHA and acrylamide–acrylate monomers proved to be adequate for the use as soil conditioner. These preliminary results indicate that the synthesized gels have great potential for their utilization in the agronomic area.

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