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Morphology and water affinity of superabsorbent hydrogels composed of methacrylated cashew gum and acrylamide with good mechanical properties

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Abstract

This paper comprises the characterization of superabsorbent hydrogels based on methacrylated cashew gum (CGMA) co-polymerized with acrylamide (AAm) by measuring of the water uptake, water retention capacity in dependence of time, morphological and mechanical properties. The morphological features of hydrogels were evidenced by SEM images. Stress measurements of hydrogels as a function of temperature were considered as being the necessary force for compressing the hydrogels at 1 mm deformation. Stress–strain modeling was used to obtain the compressive elastic modulus and apparent cross-linking density of superabsorbent hydrogels. Hydrolyzed CGMA-*co*-AAm hydrogels showed highly water absorbing. Another remarkably feature of these hydrogels is the efficiency in the water retaining that was caused by increasing in CGMA content. Higher temperature leads to an enhancement in the stress values of superabsorbent hydrogels because the large content of water that penetrates into superabsorbent hydrogels and expands their polymer network. The increase in the amount of CGMA and AAm were accompanied by an increasing on the apparent cross-linking density of hydrogels. This contributed to increase their elastic modulus, which is inherent to a more rigid structure.

Keywords: Superabsorbent hydrogel; Methacrylated-polysaccharide; Water affinity

1. Introduction

Synthesis of superabsorbent hydrogels has been trended for manufacturing of many products such as disposable diapers, feminine napkins, water blocking tapes and soil conditioner for agriculture [1–4]. For these reasons, superabsorbent polymers are essential to modern life. Non-superabsorbent hydrogels have displayed low swelling and therefore are unsuitable for the applications mentioned above. The development and optimization of superabsorbent hydrogels has been widely investigated in the last decades [5–11]. However, their use in agriculture field is limited by their high cost whereas they should present desired characteristics such as fast water absorption, highly porous and excellent mechanical properties mainly when they are highly swollen. Porous superabsorbent hydrogels display advantageous for using in pharmaceutical field, e.g. as scaffold for cell growth because they present adequate sites for attachment and growth of enough cells to survive in vitro [12–14]. Therefore, porous superabsorbent hydrogels could be applied either in soil conditioning or pharmaceutical field. Majority of publications about superabsorbent gels comprise its high swelling capacity without focus in essential features such as porous morphologies and mechanical properties and water retention capacity.

In this work, superabsorbent hydrogels from cashew gum (CG) and acrylamide, AAm, were synthesized using a method already described in the literature [15]. Cashew gum is a low cost polysaccharide extracted from the cashew tree *Anacardium occidentale* [16–18] that grows in semi-arid

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regions, i.e. it needs low amount of water to survive during the year [19,20]. This polysaccharide is composed of arabinose, glucose, glucuronic acid, galactose, mannose and rhamnose [21,22] and it is designed as branched acidic hetero-polysaccharide of complex structure. The majority of papers have been addressed to polysaccharide-based hydrogels of lesser complex structure.

The aim of this paper is to characterize superabsorbent hydrogels based on AAm monomers and on CG modified with glycidyl methacrylate, GMA. The methodology developed in this work for the modification of CG with GMA to obtain the GCMA and the respective GCMA-*co*-AAm hydrogels was recently applied for a Brazilian Patent [23].

2. Experimental

2.1. Materials

The CG powder was kindly supplied by CNPCa-EMBRAPA, Brazil. The isolation process of the CG is the same used by de Paula et al. [20] and the M_w is 2.6×10^5 g mol^{-1}. Ethanol and nitric acid, both PA, were supplied by Synth (Brazil). Acrylamide (AAm) 99% and dimethyl sulfoxide (DMSO) were purchased from Aldrich (14,866-0) and Mallinckrodt AR® (ACS, M4948-04), respectively. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TEMED) 99% was purchased from Invitrogen (15524-010) and glycidyl methacrylate (GMA) 97% from Across Organics (106-91-2). Buffer solution, at pH = 10, was supplied by Across Organics (25860-0010) and cerium (IV) sulfate by Vetec, Brazil (723).

2.2. Preparation of chemically modified cashew gum

The CG was purified and modified using a method reported in the previous paper [15,23]. Fresh prepared solution of CG in DMSO was added to TEMED and after homogenizing it was mixed with the requested amount of GMA and stirred at 40 °C. The modified CG, quoted as CGMA, was purified by precipitation in excess ethanol followed by filtration and lyophilization.

2.3. Synthesis of GCMA-co-AAm hydrogels

GCMA-*co*-AAm hydrogels were synthesized as previous reported [15,23]. Briefly, CGMA and AAm monomers aqueous solutions were added to sodium persulfate and heated at temperature 75 °C for 40 min. The obtained hydrogels, quoted as CGMA-*co*-AAm, were hydrolyzed at pH 10 and dried at 40 °C for 3 and 4.5 h. The hydrogels were labeled as (*A*/*C*/*h*) where *A* and *C* indicate the concentrations at g mL^{-1}of AAm and CGMA, respectively; *h* is the hydrolysis time that taken in hours.

2.4. Water uptake measurements

The water uptake capacities (WU) of CGMA-*co*-AAm hydrogels were determined at temperature 25 °C through the following equation:

$$\mathrm{WU} = \frac{W_\mathrm{w}}{W_\mathrm{d}} \tag{1}$$

where W_w and W_d are weights of swelled hydrogel in water and dried hydrogel, respectively.

2.5. Measures of water retention by the hydrogels

The water retaining capacity of hydrogels was investigated as a function of time of exposure in ambient atmosphere. Pieces of swollen hydrogels of approximately 15 cm^3 of volume were put on Petri plates and dried at 25 °C. The highly swollen hydrogels were weighted and the decreases in their weights measured as a function of time by gravimetry. The values of water retention (WR) were obtained by following equation:

$$\mathrm{WR}(\%) = \left(\frac{M_\mathrm{s} - M_t}{M_\mathrm{s}}\right)100 \tag{2}$$

where M_s is the initial weight of the hydrogel in water and M_t is its weight after lost of water at each time.

2.6. Scanning electron microscopy

Hydrogels morphology was evaluated by scanning electron microscopy, SEM, (Shimadzu, model SS 550), operating at 12 keV. The hydrogels were swollen at 25 °C and freeze dried (Christ gefriertrocknungsanlagen) for 72 h. Thereafter, the dried hydrogels were gold sputter-coated before observation by SEM analysis.

2.7. Compressive tests (gel strength) at different temperatures

Mechanical tests were considered as being the measured force for compressing the hydrogels at 1 mm penetration using a texture analyzer (TAXT$_{2i}$ Stable Micro System, Haslemere, Surrey, UK) equipped with a 5 kg load cell. The apparatus was equipped with a circular probe of 12.7 mm diameter, which it descended on surface of gel moving at a constant speed of 0.2 mm s^{-1}. All hydrogels were cut in pieces of 10 mm height. After adjusting of the experimental parameters, each measurement was performed at less than 1 min to avoid the water losing from the hydrogel during the experiment. All tests were run four times for each gel. Their compressive strength was performed at temperatures of 25, 30, 35, 40, 45 and 50 °C. Before measuring, the gels were maintained in water for 48 h at desired temperature. The force necessary for compressing the hydrogels at 1 mm was recorded and the stress values (σ) were determined using the equation [20]:

$$\sigma = \frac{F}{A} \tag{3}$$

where F is the force and A is the cross-sectional area of the strained specimen.

2.8. Stress–strain measurements

The parameters generated by the instrument are force and displacement. These information were then converted to elastic modulus, E, by the use of the following equation [24,25].

$$\sigma = E(\lambda - \lambda^2) \tag{4}$$

where λ is relative deformation of the specimen.

The $(\lambda - \lambda^2)$ is the strain calculated from the Eq. (5) [25].

$$\lambda = \frac{\Delta L}{L_0} \tag{5}$$

where ΔL is the deformation of the sample and L_0 is initial sample length. The apparent cross-linking density, ν_e, was obtained from the slope of linear dependence of σ vs. $(\lambda - \lambda^2)$ [24,26].

$$\sigma = RT\left(\frac{\phi_{g,0}}{\phi_g}\right)^{2/3} \phi_g \nu_e (\lambda - \lambda^{-2}) \tag{6}$$

where $\phi_{g,0}$ and ϕ_g are the polymer volume fractions of the gel in the relaxed state (just after polymerizing) and swollen state, respectively.

3. Results and discussion

3.1. Water uptake (superabsorbing properties of hydrogels)

The dependence with time of WU capacity of CGMA-*co*-AAm hydrogels hydrolyzed at 3 and 4.5 h is displayed in Fig. 1. CGMA-*co*-AAm hydrogels showed WU capacity highly dependent on the hydrolysis time and concentrations of CGMA and AAm used for hydrogels synthesis. The (0.4/0.1/*h*) hydrogel swells more than (0.4/0.4/*h*) hydrogel due to its smaller polymer density and consequent smaller cross-linking density. More concentrated AAm in hydrogel decreases the space between the polymer chains in the hydrogel. This yields a tighter structure that cannot be easy expanded hindering the efficiency water absorption [27,28]. Higher amount of CGMA (vinyl groups from GMA coupled to CG) in (0.4/0.4/*h*) hydrogels produces more cross-linked points in polymer network. It is well known that the cross-linking density is one of the most essential factors that affect the water absorption of hydrogel. Tighter structure that hinders the mobility of the polymer chains minimizes their exposure to the water molecules. This explains the lower WU values presented by the (0.4/0.4/*h*) hydrogels.

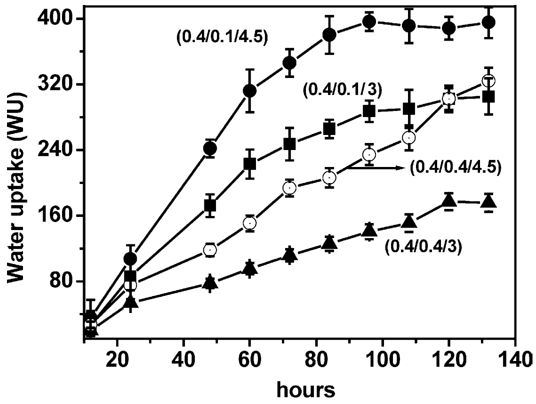

Fig. 1. Water uptake capacity of CGMA-*co*-AAm hydrogels composed of methacrylated cashew gum (CGMA) and acrylamide at room temperature as a function of time.

The influence of hydrolysis time on WU capacity of hydrogels was connected to modification of chemical structure of hydrogel or electric charge of co-polymer chain. The hydrolysis process generates carboxylic groups from amide groups that are present in structure of AAm [29]. They increase the electrostatic repulsion inter and intra-polymer chains and consequently increase the exposure of polymer chains to the water molecules. Moreover, hydrolyzed hydrogels contain more hydrophilic groups compared with the same non-hydrolyzed hydrogels, which strongly interacts with the water molecules leading to water absorption enhancement.

3.2. Water retention in hydrogels

The water retention, WR, capacity of hydrogels to lose water was measured as function of time. Kinetics curves of WR of the (0.4/0.1/3), (0.4/0.4/3) and (0.4/0.4/4.5) hydrogels are displayed in Fig. 2. The WR values for (0.4/0.4/3) and (0.4/0.4/4.5) hydrogels are in the same order of magnitude. This indicates that the effect of the time of hydrolysis on the water retention capability of hydrogels is

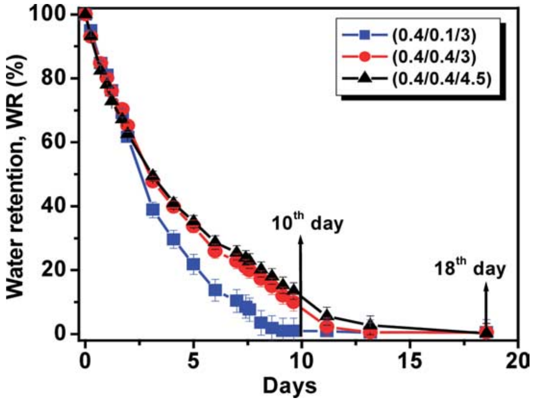

Fig. 2. Water retention of (0.4/*C*/*h*) hydrogels composed of methacrylated cashew gum (CGMA) and acrylamide at temperature 25 °C in dependence of time.

not as important as it was on the water uptake. The hydrogel hydrolyzed for 4.5 h absorbs almost two times more water than that hydrolyzed for 3 h [15].

On the other hand, the water retention is dependent on the amount of CGMA The complete water losing from the (0.4/0.4/3) hydrogel was observed after ca. 18 days of exposure at room temperature improves the water retention in hydrogel. Otherwise, the (0.4/0.1/3) hydrogel containing smallest amount of CGMA was fully dehydrated at above 10 days on the same ambient. The authors suggested that the branch chains of raw CG [21] which are formed of hydrophilic carbohydrates, e.g. galactose, arabinose and glucuronic acid, create a hydrophilic environment that minimizes the loss of water from the hydrogel, leading to WR enhancement. This argument was strengthened through WR results shown in Fig. 3, where the WR capacity of (0.2/C/3) hydrogels is dependent on the CGMA amount in the polymer matrix. The full dehydration of (0.2/0.1/3) hydrogel at ca. 3 days, compared to the ca. 7 days necessary for the (0.2/0.2/3) hydrogel, was attributed to the smallest amount of CGMA included in the first gel. The WR enhancement of hydrogels by increasing in the amount level of CGMA might be attributed to the properties of water retaining inherits from cashew tree gum, which grows in semi-arid regions.

3.3. Hydrogels morphologies

For that purpose, the superabsorbent hydrogels swollen to equilibrium at 25 °C were first frozen in liquid nitrogen then freeze dried at −55 °C. In those conditions it can be assumed that the morphologies of the swollen samples were preserved. The SEM micrographs of (0.1/0.1/4.5), (0.2/0.2/4.5) and (0.4/0.4/4.5) GCMA-*co*-AAm hydrogels after lyophilization are shown in Figs. 4–6. It was observed that they displayed highly porous structure due to the formation of gaps. When the hydrogel is immerged in an aqueous media, the water molecules easier diffuse into hydrogel through these gaps leading to WU enhancement.

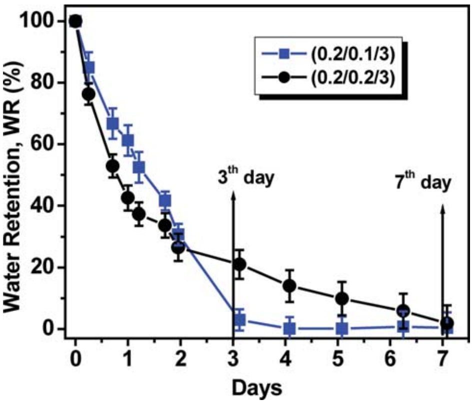

Fig. 3. Water retention of from (0.2/*C*/*h*) hydrogels composed of methacrylated cashew gum (CGMA) and acrylamide at temperature 25 °C in dependence of time.

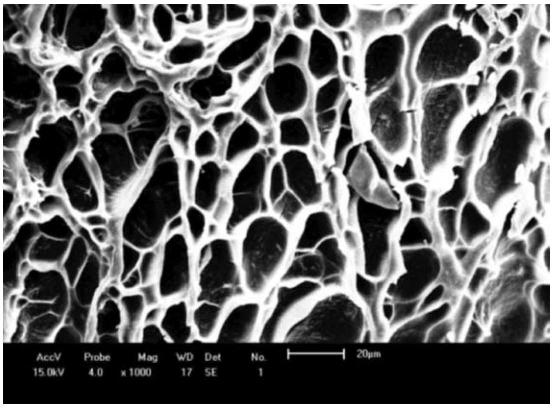

Fig. 4. SEM image of (0.1/0.1/4.5) superabsorbent hydrogel composed of methacrylated cashew gum (CGMA) and acrylamide. Micrograph of the hydrogel freeze dried after swelling to equilibrium at temperature 25 °C.

The most distinguish feature evidenced by SEM images is from (0.4/0.1/4.5) hydrogel (Fig. 6) that shows a foliaceous-type morphological characteristic. This is indicative that higher amount of AAm inside hydrogel leads to formation of a more homogenous porous structure. Moreover, more amount of AAm inside hydrogel did not contribute to change its average porous sizes that were similar order of magnitude. In this sense, we would suggest that water absorbing of GCMA-*co*-AAm hydrogels is also connected with their highly hydrophilic chains that were originated from hydrolysis process.

3.4. Mechanical properties

All mechanical tests were carried out on fully hydrated hydrogels free from air bubbles or physical imperfections. In Fig. 7 is shown the photo of (0.4/0.4/4.5) superabsorbent hydrogel cut as a membrane to compressive stress measurements. Fig. 8 shows the applied stress for compressing at 1 mm the (0.2/0.2/3), (0.2/0.1/3) and (0.2/0.05/3) hydrogels in dependence of temperature. The lowing in the values of stress observed for CGMA-*co*-AAm

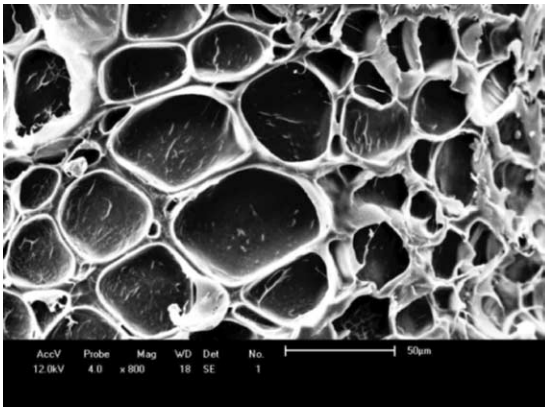

Fig. 5. SEM image of (0.2/0.2/4.5) superabsorbent hydrogel composed of methacrylated cashew gum (CGMA) and acrylamide. Micrograph of the hydrogel freeze dried after swelling to equilibrium at temperature 25 °C.

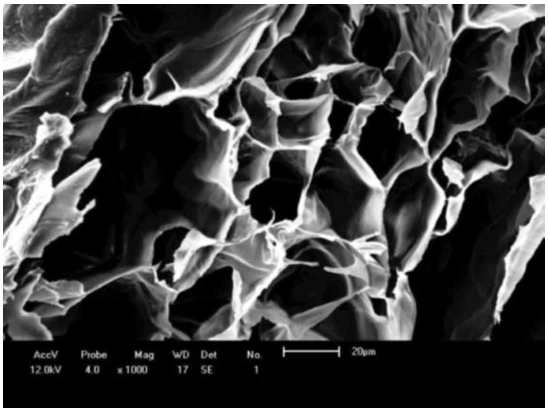

Fig. 6. SEM image of (0.4/0.1/4.5) superabsorbent hydrogel composed of methacrylated cashew gum (CGMA) and acrylamide. Micrograph of the hydrogel freeze dried after swelling to equilibrium at temperature 25 °C.

hydrogels was attributed to their properties of water superabsorbing, compared to the non-superabsorbent hydrogels. When a hydrogel becomes highly swollen, it presents a softer network leading to the lowing in the values of compressive stress. Other relevant feature is the slightly increases of stress values of all hydrogels when heated from 25 up to 50 °C. Higher temperature requests an additional stress for compressing at 1 mm the hydrogels. This is due to the superabsorbing properties of hydrolyzed CGMA-*co*-AAm hydrogels. For instance, when a hydrogel is immersed in water, it swells until the osmotic forces that help to extend to polymer network are balanced by the elastic forces from the stretched segments of network polymer. These elastic retractive forces are inversely proportional to swelling capacity of a hydrogel [30]. If the hydrogel has superabsorbing properties, the water molecules easier penetrate into its polymer network than into non-superabsorbent one. Increasing the temperature, this effect becomes still more pronounced due to the larger amount of water that penetrates into hydrogel causing the highly expansion of its polymer network. As a result, the polymer segments of superabsorbent hydrogel become more stretched leading the enhancement of the resistance force to the deformation.

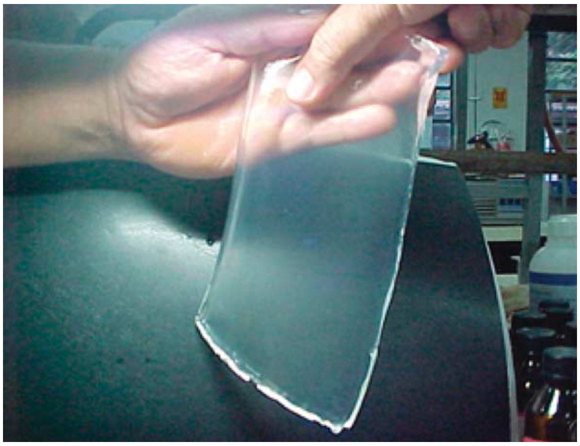

Fig. 7. Photo of (0.4/0.4/4.5) superabsorbent hydrogel composed of methacrylated cashew gum (CGMA) cut as a membrane to compressive stress measurements.

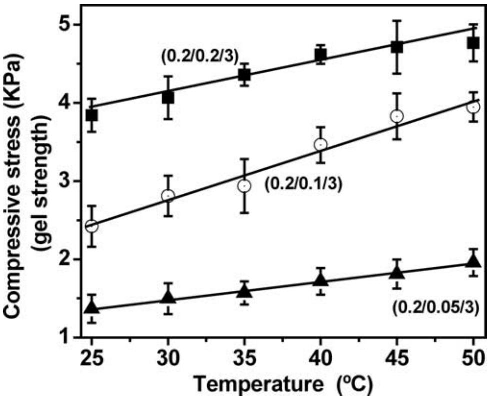

Fig. 8. Applied stress for compressing at 1 mm the (0.2/*C*/3) hydrogels composed of methacrylated cashew gum (CGMA) and acrylamide in dependence of temperature.

The increasing of CGMA amount in the hydrogels, shown in Figs. 8 and 9 reflected in an increase in the values of their compressive stress. This effect may be explained by the formation of denser hydrogels in polymer chains. These matrixes have tighter structure, hence are more rigid and request an additional compressive force to be deformed at 1 mm. Then, it could be point out that the addition of more CGMA molecules in the co-polymer network produces a stronger hydrogel.

As reported above, changes on the content of AAm and CGMA help to achieve the desired mechanical properties of superabsorbent hydrogels. However, if the polymer density of the system becomes higher a denser hydrogel will be formed and this affects the water absorption.

Some important parameters as compressive elastic modulus, E, and apparent cross-linking density, ν_e, were determined by mechanical experiments and summarized in Table 1. The values of ν_e were obtained from the Eq. (6),

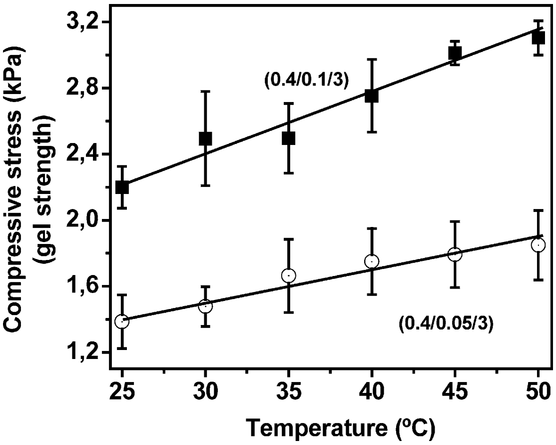

Fig. 9. Applied stress for compressing at 1 mm the (0.4/*C*/3) hydrogels composed of methacrylated cashew gum (CGMA) and acrylamide dependence of temperature.

Table 1
Values of elastic modulus, E, and apparent cross-linking density, ν_e, for superabsorbent CGMA-*co*-AAm hydrogels. The samples vary in amount of methacrylated cashew gum (CGMA) and acrylamide and time of hydrolysis

Hydrogel	E (kPa)	$\nu_e \times 10^{-3}$ (mol m^{-3})[a]
[0.1/0.1/3]	1.48	196
[0.2/0.05/3]	1.67	338
[0.2/0.1/3]	2.20	605
[0.4/0.4/3]	2.94	1400
[0.4/0.4/4.5]	2.24	830

[a] Apparent cross-linking density.

E is the slope obtained by plotting stress vs. $(\lambda - \lambda^2)$, shown in Fig. 10.

The ν_e of (0.2/C/3) hydrogels increases with the content of CGMA. This indicates that the material becomes more rigid, leading to E enhancement. The increases on the ν_e of hydrogels by increasing the amount of CGMA was attributed to vinyl groups coupled to CG (originated from GMA), which produce more cross-linked points in polymer network after co-polymerizing with AAm monomers. It was suggested that the non-covalent interactions among polymer chains caused by the content effecting of CGMA may also have an additional contribution to the increasing on the ν_e, which help to increases the strength of the hydrogel.

Increase in AAm content in (AAm/0.1/3) hydrogels also led to an increase in ν_e, as verified with the augment of cashew gum amount. However, the effect of AAm seems to be more intense than that of CGMA. The increase in ν_e was 3.1 times when AAm amount was increased twice and only 1.8 for the same CGMA content augment.

Increasing the time hydrolysis of hydrogels from 3 to 4.5 h induces a decreasing on the ν_e. This was concluded by comparing the ν_e from (0.4/0.4/h) hydrogels. Hydrolyzed hydrogel for 4.5 h contains more hydrophilic groups and swells much more than the hydrolyzed for 3 h. As the superabsorbent hydrogel is extremely swollen, its polymer network tends to be highly expanded and hinders the formation of non-covalent interactions. As a result, a softer polymer network and a weaker hydrogel were formed. These aspects contribute to an increased on the elastic modulus of (0.4/0.4/4.5) hydrogel, which is inherent to its less rigid structure.

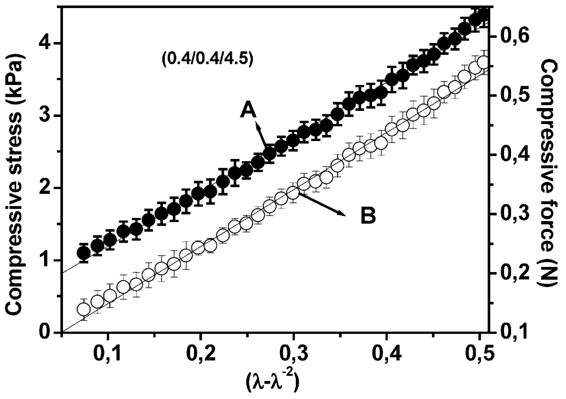

Fig. 10. (A) Applied stress and (B) applied force in dependence of $(\lambda - \lambda^2)$ of the (0.1/0.1/3) hydrogel composed of methacrylated cashew gum (CGMA) and acrylamide.

The dependence of water absorption and ν_e could be confirmed by (0.4/0.4/h) hydrogels data from Table 1 and Fig. 1. Decreasing 1.7 times ν_e induces an increase of more than two times in maximum water absorption. Taking in account that (0.1/0.1/3) hydrogel swells at about 1900 (data not show here) and comparing with (0.4/0.4/3) one, a decreasing of 7.1 times in apparent cross-linking density led to an increase of more than 12.5 times in water absorption. The effect of ν_e over the swelling becomes more important as less cross-linked is the polymer network in the hydrogel.

Often the majority of superabsorbent hydrogels present poor mechanical properties in highly swollen state due to low densely polymer networks. The co-polymerization of chemically modified cashew gum (CGMA) and acrylamide (AAm) resulted in a superabsorbent hydrogel with good mechanical performance and, to the best of our knowledge, this has not yet been reported in the literature.

4. Conclusions

Hydrolyzed CGMA-*co*-AAm hydrogels showed highly water absorption. This effect was attributed to the hydrolysis process and highly porous structure of hydrogel. Another remarkably feature of these hydrogels is the dependence of the efficiency in the water retention with the CGMA content. The fully dehydration of hydrogels may be extending from 3 to 18 days by increasing the content of CGMA from 0.1 to 0.4 g mL^{-1}.

Increasing in the temperature leads to enhancement in stress values of superabsorbent hydrogels. The increase in the amount of CGMA and AAm was accompanied by an increasing on the apparent cross-linking density of hydrogels. This contributed to increase their elastic modulus, which is inherent to the more rigid structure. According to the results of this work, it may be concluded that superabsorbent hydrogels based on cashew gum chemically modified and acrylamide displayed excellent conditions to be further applied as soil conditioner and scaffold for culture of cells.

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References

[1] Kabiri K, Omidian H, Hashemi SA, Zohuriaan-Mehr MJ. Eur Polym J 2003;39:1341–8.

[2] Kost J. Encyclopedia of controlled drug delivery. vol. 1. New York: Wiley; 1999.

[3] Buchholz FL, Graham T. Modern superabsorbent polymer technology. New York: Wiley; 1998, p. 1 and 152.

[4] Sannino A, Nicolais L. Polymer 2005;46:4676–85.

[5] Chatzoudis GK, Rigas F. Commun Soil Sci Plant Anal 1999;30: 2465–74.

[6] Lionetto F, Sannino A, Maffezzoli A. Polymer 2005;46:1796–803.

[7] Xue W, Champ S, Huglin MB. Polymer 2001;42:2247–50.

[8] Anbergen U, Oppermann W. Polymer 1990;31:1854–8.

[9] Chatzoudis GK, Rigas F. J Agric Food Chem 1998;46:2830–3.

[10] Chatzoudis GK, Valkanas GN. Commun Soil Sci Plant Anal 1995;26: 3099–111.

[11] Omidian H, Zohuriaan-Mehr MJ. Polymer 2002;43:269–77.

[12] Shapiro L, Cohen S. Biomaterials 1997;18:583–90.

[13] Schneider GB, English A, Abraham M, Zaharias R, Stanford C, Keller J. Biomaterials 2004;25:3023–8.

[14] Drury JL, Mooney DJ. Biomaterials 2003;24:4337–51.

[15] Reis AV, Cavalcanti OA, Rubira AF, Muniz EC. Int J Pharm 2003; 267:13–25.

[16] Zakaria MB, Rahman ZA. Carbohydr Polym 1996;91:25–7.

[17] Maia JGS, Andrade EHA, Zoghbi MGB. J Food Comp Anal 2001;13: 227–32.

[18] Silva DA, De Paula RCM, Feitosa JPA, De Brito ACF, Maciel JS, Paula HCB. Carbohydr Polym 2004;58:163–71.

[19] Menestrina JM, Iacomini M, Jones C, Gorin PAJ. Phytochemistry 1998;47:715–21.

[20] de Paula RCM, Rodrigues JF. Carbohydr Polym 1995;26:177–81.

[21] Sarubbo LA, Oliveira LA, Porto ALF, Duarte HS, Carneiro-Leão AM A, Lima-Filho JL, et al. J Chromatogr B Analyt Technol Biomed Life Sci 2000;743(1–2):79–84.

[22] Paula HCB, Gomes FJS, de Paula RCM. Carbohydr Polym 2002;48: 313–8.

[23] Guilherme MR, Rubira AF, Feitosa JPA, Muniz EC. Brazil Patent, INPI, PI 0404265; deposited on September 29, 2004.

[24] Muniz EC, Geuskens G. Macromolecules 2001;34:4480–4.

[25] Ferruzzi GG, Pan N, Casey WH. Soil Sci 2000;165:778–92.

[26] Gutowska A, Bae YH, Jacobs H, Feijen J, Kim SW. Macromolecules 1994;27:4167–75.

[27] Muniz EC, Geuskens G. J Membr Sci 2000;172:287–93.

[28] Guilherme MR, da Silva R, Rubira AF, Geuskens G, Muniz EC. React Funct Polym 2004;61:233–43.

[29] Mahdavinia GR, Purjavadi A, Hosseinzadeh H, Zohuriaan MJ. Eur Polym J 2004;40:1399–407.

[30] Kulkarni AR, Soppimath KS, Aminabhavi TM. Pharm Acta Helv 1999;74:29–36.