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Valve based on novel hydrogels: From synthesis to application

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ABSTRACT

New hydrogels as materials with potential application in the area of actuators have been developed. Hydrogel synthesis was performed using tris[(hydroxymethyl) methyl]acrylamide (NAT) and itaconic acid (ITA) as monomers and (+)N,N′-diallyltartradiamide (DAT) as crosslinker. The hydrogels NAT–ITA were prepared using different molar fraction of monomers and characterized by FTIR-ATR, rheology, swelling properties and mechanical force. The hydrogel prepared with 80% and 20% of NAT and ITA, respectively, has the lowest equilibrium swelling ratio (ESR = 16) in water but the highest elastic modulus (10 ± 1 kPa) and strength (2.2 ± 0.1 N h^{-1}). The gel strength increased 0.5 N in a half hour, while the volume increased 4 times when passed from an acid medium to a basic medium. This hydrogel was chosen to prepare a pH-sensitive valve to control the flux in a capillary tube. The valve was tested using a system to control the formation of Fe^{3+}–EDTA complex. The response time was 3 and 15 min to open and close the valve, respectively. The flow of the solution through the valve was 11 μL min^{-1}. The pressure of the solution during the closing of the valve was 10 kPa. The continuous opening and closing of the valve involves repetitive expansion and collapse of the network that could damage the structure of the network. However, the valve produced a reproducible and stable response. The dynamic hydrogen bonding existing in the polymeric chains of NAT–ITA products could assist in the reversible process when the hydrogels were subjected to repetitive work. The mechanical properties of the gels and self-healing capacity of the networks indicated that the products could be applicable in the development of systems for controlled drug release.

1. Introduction

The conventional solid state actuators are manufactured using complex systems and require an electrical source, which limits the use in many applications [1]. Stimuli-sensitive hydrogels are materials that respond to environmental stimuli, such as temperature, pH or an electric field, by abruptly changing their volume and hence hold or release a large amount of water [2]. Those hydrogels sense a change in those stimuli and expand or contract based on the stimulus [3]. By their capability to reach a large yet reversible volume change, hydrogels have been used as novel drug delivery systems, scaffolding materials for tissue engineering and sensors and actuators for microfluidics channels. In the case of microfluidics valve, the volume change permits an actuation to control or modulate the flow of fluids from a reservoir by the pH sensitive expansion or contraction. So, pH sensitive hydrogels allow the use of microfluidic systems by regulating the flow automatically [4].

Beebe et al. studied the fabrication of active hydrogel components inside microchannels via direct photopatterning of a liquid phase. So, the system construction was simplified since the functional components are fabricated in situ. The stimuli-responsive hydrogel components perform both sensing and actuation functions. The study focused on the response time of the volumetric change of the hydrogel [5]. Eddington and Beebe [1] gave an overview on studies using hydrogel actuators for flow control such as resistance based valves, hydrogel jacket valves, hybrid hydrogel membrane valve, electrically triggered valves, and biomimetic valves. Besides, they reviewed various hydrogel flow control systems such as a flow sorter and pH-regulation system as well as glucose sensitive hydrogel valves. In the review report [1], it was concluded that flow control in microfluidic devices using hydrogel actuators is a very simpler autonomous method.

In general, stimuli-sensitive hydrogels may directly translate chemical energy to mechanical energy, without need of an external power, making them advantageous in applications where the cost of an external power source is critical, when the action needs to be performed for extended periods of time in a portable system, or for controlling the fluids flow [1,3,6–11].

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Well now, the charge in hydrogels sensitive to changes in the pH, depends on protonation or deprotonation of the functional groups (e.g. carboxylic or amine) present in the chains [12–14]. When the molecule contains carboxylic acid groups, protonation or deprotonation occurs in acidic or basic media, respectively. At high pH, the polyelectrolytes exhibit high electrostatic repulsion between the chains [15]. For this reason, acrylic acid (AA) and 2-hydroxyethylmethacrylate (HEMA) were commonly used as functional monomers to prepare pH sensitive gels [1,5,16]. Hydrogels should also meet certain characteristics to be used as actuators [8,13,17]. First, they need to respond in a reproducible and predictable period of time [18]. The cycles of swelling and deswelling of pH-sensitive materials have shown different grades of reversibility [19], thus, it is necessary to determine the relationship between swelling and mechanical properties [20]. The elastic modulus of the hydrogels is an important property to the development of actuators [21–23], because it is related to the capacity of a material to return to the original state when is strained [24]. Hydrogel actuators submitted to repetitive work may also suffer stress that can alter their mechanical properties [25]. To address this, the improvement of the mechanical properties and self-healing by dynamic bonds such as hydrogen bonding of new polymeric materials has been described [26]. Theoretical studies have concluded that these interactions can act as physical crosslinking points that may break under stress and then be partially regenerated [27]. The carboxylic acid and hydroxyl groups might interact in this manner when they are present into the hydrogel structure. Blends of polyvinyl alcohol (PVA) with polyAA were used as pH sensors [28]. These blends have shown strong interactions of hydrogen bridge type, which were characterized by FTIR and other techniques [29].

Due to the presence of carboxylic acid groups, itaconic acid (ITA) can be used to synthesize hydrogels with pH-dependent swelling [8]. ITA is a non-toxic vinyl monomer [30] and commercially obtained from corn starch fermentation using *Aspergillus terreus* [31] among other natural sources [32]. With respect to the use of ITA derivatives for the preparation of polymer blends, Goh et al. reported the synthesis of blends based on poly(dialkyl itaconate) and poly(4-vinylphenol) where the interactions between the polymeric chains were mainly due to hydrogen bonding [33]. Others dicarboxylic acids such as succinic acid, suberic acid or dodecanedioic acid also interact with poly(N-vinyl-2-pyrrolidone) and poly(2-vinylpiridine) by hydrogen bonding [33].

Tris[(hydroxymethyl) methyl]acrylamide monomer (NAT) has three hydroxyl groups and has been copolymerized with AA to yield highly swellable hydrogels, caused by the hydrophilic hydroxymethyl triads [34]. In the later, when the AA content increased into the hydrogels, the swelling in water is high, then decreases and finally increases. The minimum could indicate an optimal proportion for attractive interaction and may have some effect on the mechanical properties of this material.

Taking into account the factors mentioned above, the monomers NAT and ITA could form a copolymer with hydrogen bridged interactions between the network chains. These interactions may influence the swelling and the mechanical properties of the hydrogel. In this case, we focused on the study of the mechanical properties, in the response time under certain conditions and in the force that the hydrogel can generate. In addition, other important focus was to know if the volume change was enough for these materials to properly act as an actuator.

So, we studied hydrogels obtained with different proportions of the monomers ITA and NAT with (+)N,N′-diallyltartradiamide. The mechanical forces, rheology and swelling properties were studied. The composition and hydrogen bond interactions of the hydrogels were studied by FTIR-ATR spectroscopy.

After that preparation and characterization of hydrogels were investigated, one of the poly(NAT–ITA) copolymers was selected since the next step was to incorporate it into a flow control valve system to act as an actuator, testing it within a capillary system. The chosen hydrogel was studied by scanning electron microscopy (SEM) and swelling at different pH. The actuator was configured as a valve to control the passage of a solution (in this particular case, a model solution was chosen to allow the formation of Fe^{3+}–EDTA complex) depending of the open and close, according to changes in the pH, that produce changes in the hydrogel swelling. The polymeric actuator could be used with other solutions and as flow control of drugs.

2. Materials and methods

2.1. Reagents

Tris[(hydroxymethyl) methyl]acrylamide (NAT), itaconic acid (ITA), (+)N,N′-diallyltartradiamide (DAT), N,N,N′,N′-tetramethylethylenediamine sodium (TEMED), sodium hydroxide, and hydrochloric acid were purchased from Aldrich (Milwaukee, WI, USA). All reagents were used as received. Ammonium persulphate (APS), ferric chloride and ethylenediamine tetra-acetic acid disodium salt (EDTA) were purchased from Univar (Ajax Chemicals, Australia). The CH_3COOH, H_3PO_4 and H_3BO_3 reagents were purchased from Cicarelli (Argentina). Britton Robinson (BR) buffers were prepared dissolving 2.3 mL of glacial CH_3COOH, 2.7 mL of H_3PO_4 and 2.4720 g of H_3BO_3 in 1 L of distilled water. Aliquots of 100 mL were taken and the pH of each solution was adjusted at pH 3.0, 5.0, 7.0 and 9.0 with 2 M NaOH solution.

All solutions were prepared with ultra pure water (18 MΩ cm^{-1}) from a Millipore Milli-Q system.

2.2. Hydrogel synthesis

All matrices were prepared by free-radical cross-linking polymerization. The procedure for co-polymerization can be described as follows: the mono vinyl monomers, cross-linker, and APS (47 mg) were dissolved in water (4 mL) in glass test tubes. The mixture was mixed for 5 min and sonicated for 10 min. The polymerization mixture was deoxygenated with N_2 for 10 min. To initiate the polymerization reaction, 0.4 mL of TEMED aqueous solution (0.32 M) was added to the reaction mixture and transferred to disposable syringes. The syringes were put in the water bath and the reaction was allowed to proceed for 4 days at 30 °C. The synthesized hydrogels were cut using a blade in discs of 3 mm thick and 10 mm diameter and thoroughly washed with water. The experimental conditions to prepare the hydrogels poly(NAT–ITA) 1–5 are summarized in Table 1.

2.3. Swelling experiments

After the synthesis, the discs were allowed to equilibrate in water for 3 days at 20 °C. Then, they were placed in an oven at 37 °C and dried overnight until constant weight. The dried polymers were placed in water and re-swelled. The swelling kinetic was studied by measuring the swelling ratio (SR) at different times. This procedure was repeated until constant swelling weight was achieved. The SR of each hydrogel was calculated using Eq. (1) [35]:

$$SR = \frac{m_t - m_d}{m_d} \quad (1)$$

where m_t is the weight of the polymeric sample at different times and m_d is the mass of the dried polymeric sample. The SR values for poly(NAT–ITA) 1–3 were plotted versus time.

Table 1
Experimental conditions used for the synthesis of hydrogels.

Product	NAT %[a] (g)	ITA %[a] (g)	DAT %[a] (g)	Physical state	ESR[b]	ESR[c]
Poly(NAT–ITA) 1	90 (0.882)	10 (0.073)	4 (0.026)	Gel	60	30
Poly(NAT–ITA) 2	80 (0.784)	20 (0.146)	4 (0.026)	Gel	90	16
Poly(NAT–ITA) 3	70 (0.686)	30 (0.219)	4 (0.026)	Gel	200	23
Poly(NAT–ITA) 4	60 (0.588)	40 (0.292)	4 (0.026)	Gel-viscous	–	–
Poly(NAT–ITA) 5[d]	50 (0.490)	50 (0.365)	4 (0.026)	Liquid	–	–

[a] Calculated from the molarities of monovinyl monomers.
[b] Measured after synthesis.
[c] Measured after dried the samples at 37 °C.
[d] Other compositions (ITA ≥ 50%) did not produce gel.

The equilibrium swelling ratio (ESR) was calculated using Eq. (2) [35]:

$$\mathrm{ESR} = \frac{m_s - m_d}{m_d} \tag{2}$$

where m_s is the weight of the polymeric sample at equilibrium. The ESR was measured before and after drying the samples (Table 1). Also, the ESR at different pH (1.0, 3.0, 5.0, 7.0, 9.0 and 13.0) was determined on dried samples of poly(NAT–ITA) 2 using BR buffers (for pH 3.0–9.0) and 0.1 M HCl or 0.1 M NaOH for pH 1.0 and 13.0, respectively.

The water diffusion rate within the hydrogels was determined using Eq. (3) [35]:

$$F = \frac{M_t}{M_8} = kt^n \tag{3}$$

where M_t is the mass of water that diffused into the matrix at time t, M_∞ is the mass of water that diffuses into the matrix at the equilibrium, k is a constant associated with the network structure, and the exponent n is a number that is related to the type of diffusion. This equation is applicable during the initial stages of swelling (<60%). The diffusion type (n) and k were calculated from the slope and intercept of the straight line, respectively, obtained from the plot of $\ln F$ versus $\ln t$.

2.4. Rheological characterization

The rheological characterization was performed in a rotational rheometer (Anton Paar-Physica MCR 301). The different tests were carried out using a 10 mm parallel plate geometry diameter. First, each dried disc was swollen in water to reach the equilibrium and then placed between the plates and allowed to thermal conditioning for 5 min before testing. All assays were performed at 20 °C using a 2 mm gap. The viscous and elastic modules were measured using small amplitude oscillatory experiments. The start delay was 4 ± 1 s, while the recovery time was 15.6 ± 0.1 s. Each material was submitted to a range between 0.01% and 50% strains at frequencies of 1 Hz. The sweep of the deformation was performed seeking the range of amplitudes that can work in the linear viscoelastic region. The data obtained were used to determine the strain in experiments of frequency sweeps between 0.1 and 20 Hz.

2.5. Measurements of force

The time dependent normal force N (Newton) on samples of poly(NAT–ITA) was measured using a rotational rheometer (Anton Paar-Physica MCR 301). The normal forces during the oscillatory shear in linear viscoelastic region were obtained [36].

2.5.1. Measurements of force in water

Dry samples of poly(NAT–ITA) 1–4 of 7.0 mm diameter and 2.5 mm thick were placed between the parallel plate geometries of 25 mm diameter. The space between the plates was filled with water and during the swelling process, the normal force produced for each hydrogel was recorded. The force exerted by the gels, produced a small displacement in the separation of the plates (<0.01 mm). All assays were performed at 20 °C.

2.5.2. Measurements of force in alkaline medium

Samples of poly(NAT–ITA) 2 equilibrated in 0.1 M HCl of 7.0 mm diameter and 2.5 mm thick were placed between the parallel plate geometries of 25 mm diameter. The space between the plates was filled with 0.1 M NaOH and during the swelling process, the normal force produced for the samples was recorded. The force exerted by the gels, produced a small displacement in the separation of the plates (<0.01 mm). The assays were performed at 20 °C.

2.6. Scanning electron microscopy

The surface morphology of different samples of poly(NAT–ITA) 2 were analyzed by scanning electron microscopy (SEM) using a FEI Quanta 600 MLA ESEM in the Central Science Laboratory, University of Tasmania. After swelling in H_2O, one sample was directly vacuum dried and analyzed. In order to evaluate the porous structure in the swelling state at different pH values, hydrogels were swollen at room temperature for 3 days in different solutions [water, 0.1 M HCl or 0.1 M NaOH solutions] and freeze-dried. The dried samples were sputter coated with platinum (Pt) for 40 s at 35 kV and 40 mA using a BalTec SCD050 system before imaging.

2.7. Infrared spectroscopy

Samples of poly(NAT–ITA) 1–3 were dried at 37 °C and then powdered. The infrared spectra were measured using ZnSe Cristal in Bruker Vertex 70 Single Refraction ATR. The data were processed by Atmospheric Compensation, extended ATR correction and Vector Normalization.

2.8. Valve system equipment

The valve was constructed using a glass sheet of 1 mm thickness. Fig. 1 shows the schematic diagram of the polymeric valve. The hydrogel [poly(NAT–ITA) 2; (II) in Fig. 1] has a disc shape of 2 mm in diameter and 1 mm thickness. It was confined between two membranes: on one side of the hydrogel an elastic and waterproof membrane of Parafilm M® (Pechiney Plastic Packaging Inc., USA) (IV) was placed while on the other side of the polymer, it was supported on a porous and rigid membrane [steel grid with 140 μm mesh size; Bopp (Switzerland)] (III). The pH of the solution that flows by the capillary channel (200 and 150 μm of external and internal diameters, respectively) (I) controlled the swelling of the hydrogel; the pH changes were monitored with the electrodes (VI and VII) and measured as changes in the potential (ΔE). Fig. 1 shows the scheme of the valve developed. At low pH, the hydrogen potential is near to 0.4 mV, the gel is collapsed (II) and the capillary tube is open (V). When change to high pH, the hydrogen potential

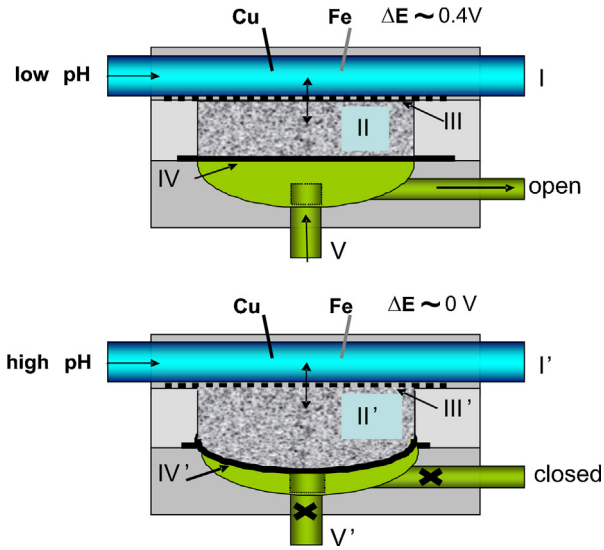

Fig. 1. Scheme of the developed valve. Capillary channel (I), hydrogel (II), porous and rigid membrane (III), elastic and waterproof membrane (IV), capillary tube (V), Cu electrode (VI) and Fe electrode (VII). At low pH, the hydrogen potential is near to 0.4 mV, the gel is collapsed (II) and the capillary tube is open (V). When change to high pH, the hydrogen potential is near to 0 mV, the gel is expanded (II′) and the capillary tube is blocked (V′).

is near to 0 mV, the gel is expanded (II′) and the capillary tube is blocked (V′).

To study the behavior of the valve, an experimental system was constructed. This system was designed to control the formation of a complex between EDTA and Fe^{3+} by switching the valve with solutions of different pH. Fig. 2 shows the schematic diagram of the system used to evaluate the behavior of the polymeric valve. A syringe pump was used to control the valve operation. This pump has two channels to control the passage of acid (0.1 M HCl) or alkaline (0.1 M NaOH) solutions. The flow rate of these solutions was 40 μL min^{-1}. As mentioned above, to measure the change in the pH near to the polymer, two electrodes were placed (copper and iron) in a cell of 20 μL. An electrometer (RE 357 TX Microprocessor PH meter, England) registered the changes in the potential of the redox couple ($Fe + 2H^+ \leftrightarrow H_2 + Fe^{2+}$) as a function of time. Note that this part of the actuator was not in contact with the fluid to be

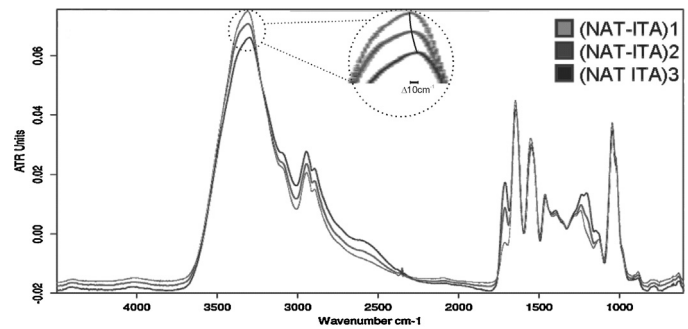

Fig. 3. ATR spectra of dry samples of poly(NAT–ITA) 1-3. The expansion zone (inset) shows the displacement of $\Delta\nu = 10\,cm^{-1}$ associated with the occurrence of more hydrogen bonding interactions.

controlled. The polymeric valve controls the flux of the solution of Fe^{3+}, while the solution of EDTA circulates via the other capillary to the detector. The flow of the Fe^{3+}–EDTA solution through the valve was 11 μL min^{-1}. The pressure of the solution during the closing of the valve was 10 kPa. The presence of the complex was detected by determining the absorption of the solution flowing through the UV detector (K-2001 KNAUER, Germany) at 254 nm. The electrometer and the UV detector were connected to a digital analog converter (eDAQ Power Chrom, Pty Ltd., Australia) and the data were stored on a computer.

3. Results and discussion

The synthesis of the new hydrogels was performed by copolymerizing different proportions of NAT and ITA monomers with 4% DAT (with respect to the total molarity of monovinyl monomers) as crosslinking agent.

Some properties of the new materials are shown in Table 1. Poly(NAT–ITA) 1–3 produced hydrogel-like products. Poly(NAT–ITA) 4 was obtained as a viscous soft gel while poly(NAT–ITA) 5 and other compositions with more than 50% of ITA (not shown) yielded liquid products.

Fig. 3 shows the FTIR-ATR spectra of poly(NAT–ITA) 1–3. The following absorption bands were assigned to NAT: 1043 cm^{-1} (C—O), 3300–3310 cm^{-1} (O—H), 1643 cm^{-1} (C=O amide) and 1548 cm^{-1} (N—H). The signals assigned to ITA were: a shoulder at 3100 cm^{-1}

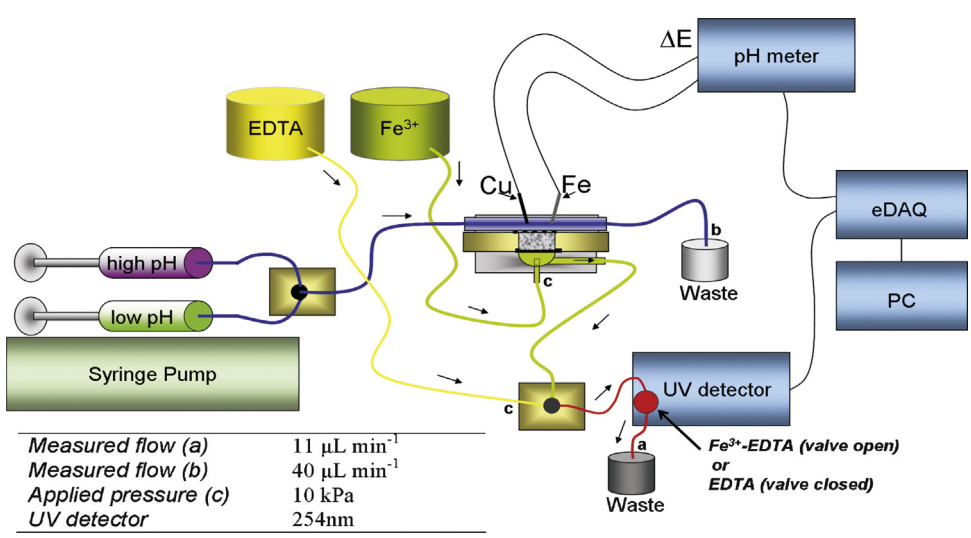

Fig. 2. Valve system equipment and solutions used to evaluate the behavior of the valve. The system controlled the formation of the complex between EDTA and Fe^{3+} by switching the valve with solutions of different pH. The measured flow for Fe^{3+}–EDTA and acid/basic solutions were 11 and 40 μL min^{-1}, respectively. The pressures applied by solutions of Fe^{3+} and EDTA were 10 kPa. The Fe^{3+}–EDTA complex was detected at 254 nm.

(O—H) and the band at 1716 cm^{-1} (C=O carboxylic acid). The relative absorption intensity of carboxyl group increased from poly(NAT–ITA) 1–3 according to the proportion of ITA into the polymers. These characteristic bands confirmed the presence of NAT and ITA in the samples.

The absorption signals of the NAT hydroxyl groups showed characteristic shifts for hydrogen bonding interaction. The presence of a very broad band between 3200 and 3600 cm^{-1} belonging to the OH group has been associated with hydrogen bonding [37]. More specifically, the band of the hydroxyl group (–OH) shifts from 3310 in poly(NAT–ITA) 1–3300 cm^{-1} in poly(NAT–ITA) 3. The figure shows an expansion of the zone, (into the inset) to facility the observation. The displacement of $\Delta\nu = 10\,cm^{-1}$ could be associated with the occurrence of more hydrogen bonding interactions. Displacements of similar magnitude ($\Delta\nu = 8–10\,cm^{-1}$) have been found by other authors in bands from hydroxyl groups present in different epoxy resin–silica nanocomposites [38].

The swelling studies performed in the relaxed state (ESR^b – Table 1), demonstrated that incorporating higher amounts of ITA into the gels yielded major swelling. This behavior could be due to the increased potential for ionization of the hydrogels by the increase in the proportion of carboxylic groups into the gels.

When the gels were dried and then re-hydrated in water, the behavior was different compared to the studies performed in the relaxed state (ESR^c – Table 1). In this case, the ESR was minor in all cases compared to ESR measured after synthesis. This is possibly related to the lower space between the chains in the networks after drying, possibly due to the presence of a significant amount of crosslinks by secondary interactions as hydrogen-bridged type. Similar behavior was observed in NAT–AA copolymers studied previously [34].

The presence of new covalent bonds in the samples was discounted because there were no differences in the infrared spectra of the samples freeze-dried after synthesis and those obtained after drying at 37 °C (data not shown).

Samples of poly(NAT–ITA) 1–3 were dried and then re-hydrated with water to study the swelling kinetic, shown in Fig. 4(a). A lower SR value was observed for poly(NAT–ITA) 2 compared to poly(NAT–ITA) 1 and 3. Poly(NAT–ITA) 4 presented very poor mechanical properties and therefore it was not possible to study the swelling kinetics.

The data of swelling studies were used to determine the type of mechanism for diffusion of water within the hydrogels and k. For cylindrical shaped hydrogels, Eq. (3) predicts that if $0 < n < 0.5$, it corresponds to a Fickian diffusion type mechanism (only diffusion is present); if $0.5 < n < 1$, it represents non-Fickian diffusion (diffusion and relaxation polymer chains are present); if $n = 1$, it corresponds to type II mechanism (only relaxation polymer chain is present) [39]. The type of diffusion in the gels was non-Fickian since n resulted (0.78 ± 0.02), (0.75 ± 0.02) and (0.82 ± 0.05) for poly(NAT–ITA) 1, 2, and 3, respectively, which indicates that the diffusion rate of water is similar to the rate of relaxation of the chains. Similar results were observed in other hydrogels from NAT [40]. The average value for k was 2.2 ± 0.2.

Actuators need to produce a force when they make a mechanical action for which the measurement of this property is really important. Fig. 4(b) shows the mechanical force (N) performed as function of time for each gel when it was hydrated in water. It was observed that poly(NAT–ITA) 2 produced a higher and faster force. This can be correlated with the swelling behavior since in this case, the gel may develop more strength with lower displacement. In contrast, the more swellable poly(NAT–ITA) 1 and 3 presented a lower ability to produce force. The inset in Fig. 4(b) shows the quasi linear increase in the mechanical force (N) as function of time, for poly(NAT–ITA) 2 when it was equilibrated in 0.1 M HCl and later swelled with 0.1 M NaOH.

To confirm this tendency, the mechanical properties were studied by rheology. Fig. 5(a) shows the elastic modulus (G') versus strain (γ) reached during sweeps at 20 °C using a frequency of 1 Hz for the products. This assay determines the strain range of linear response of polymeric materials [25]. The graph shows that the hydrogels present a similar linear viscoelastic range although this is slightly shorter in the case of both poly(NAT–ITA) 1 and 4. The inset of Fig. 5(a) shows the relationship between the elastic modulus (G') and the NAT molar fraction [$\chi = m_{NAT}/(m_{NAT} + m_{ITA})$] for 1% strain. The elasticity of the hydrogels presented a peak function shape dependence of the molar fraction with a maximum at $\chi = 0.8$, corresponding to poly(NAT–ITA) 2. A similar dependence of elasticity on the stoichiometry was also observed for gel-type polymeric networks from xanthan gum with the addition of aluminum ions (Al^{3+}) [41].

Rheological characterization was also performed with dynamic frequency sweeps, realized at 20 °C using strain (γ) of 1%. The elastic and viscous modulus (G' and G'') versus frequency is shown in Fig. 5(b). The rheological behavior of all samples was characteristic of low crosslinking degree polymers. The elastic modulus was greater than the viscous modulus and practically constant in the range studied. G' of poly(NAT–ITA) 4 decreases at low frequency which indicates that the lax network has been formed with lower crosslinking degree. The elastic moduli of these gels were similar to copolymers synthesized using NAT and N-isopropyl acrylamide (NIPA) with similar concentrations of monomers and crosslinking

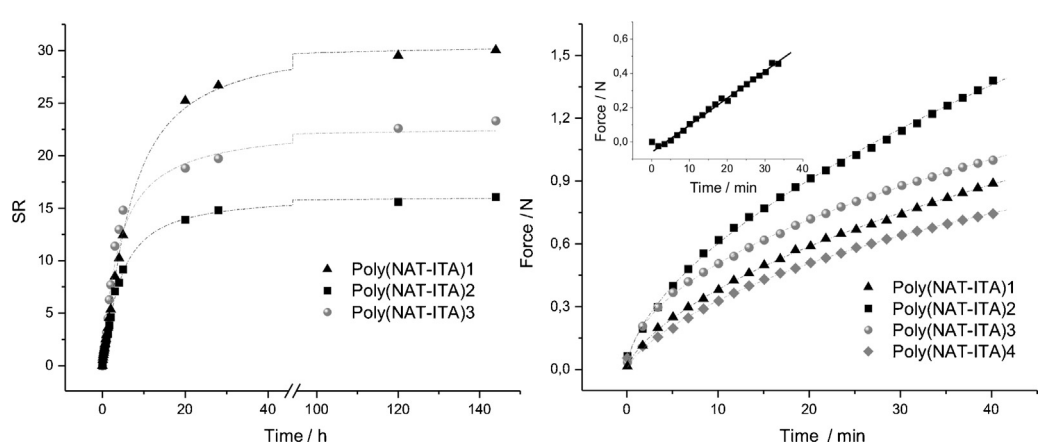

Fig. 4. (a) Equilibrium of swelling in water of poly(NAT–ITA) 1–3 hydrogels; (b) Force (N) of poly(NAT–ITA) 1–4 versus time in water. Inset: Force of poly(NAT–ITA) 2 versus time in alkaline medium. The sample was previously equilibrated in acid medium. Poly(NAT–ITA) 1 ▲, 2 ■, 3 ●, 4 ♦.

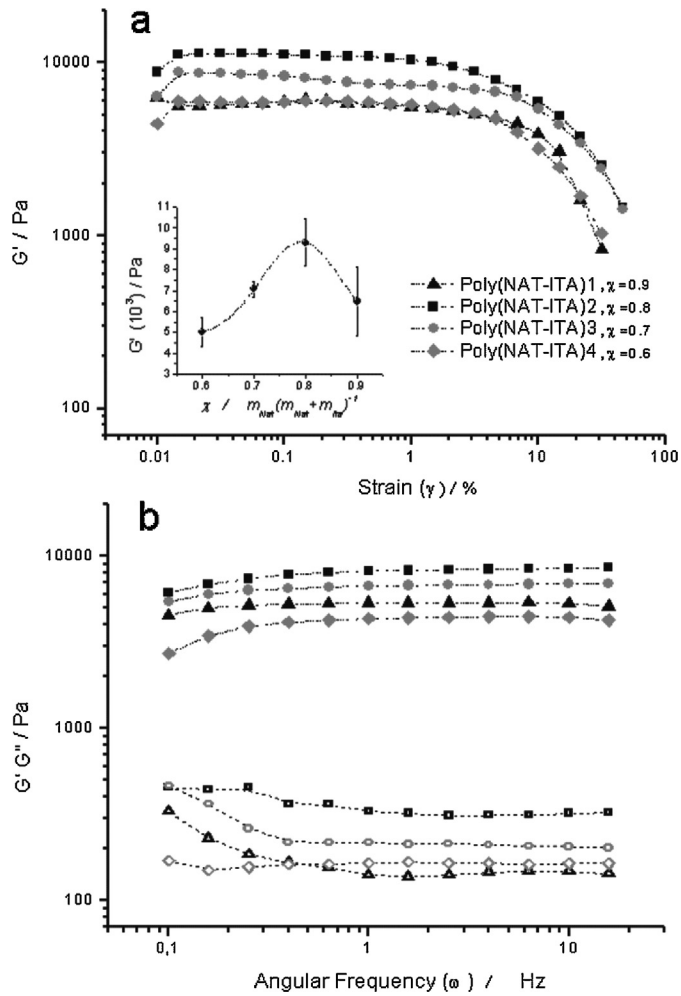

Fig. 5. (a) Elastic component (G') versus strain (γ) of poly(NAT–ITA) 1–4. Inset: dependence of elastic component (G') versus NAT molar fraction (χ) at strain 1%. (b) Elastic (G') and viscous (G'') component versus angular frequency (ω). Poly(NAT–ITA): 1 ▲, 2 ■, 3 ●, 4 ♦. Filled shapes indicate G' and empty G''.

agent, although, those swelling ratio values were lower (SR ≤ 6) [40].

The morphological characterization of poly(NAT–ITA) 2 was performed by scanning electron microscopy (SEM). Fig. 6 shows the SEM images of poly(NAT–ITA) 2 under different drying conditions and magnifications. On the left, the hydrogel is shown in the dry state. This shows a stratified laminar structure and numerous zones of fracture at the different magnifications. The other images were taken using freeze-dried samples from gels previously swollen in water, alkaline and acid media, to keep the structure as in its swollen state. The sample prepared from hydration in water shows pores with average size lower than 20 μm. In the case of the freeze-dried sample prepared from swelling in alkaline solution, very large pore of about 100 μm were observed, but only few smaller pores were observed at very high magnification on the walls of the larger pores. The lyophilized sample prepared from acid medium showed few large pores. At high magnification, fracture characteristic as in the dried state can be observed. These changes in porosity observed in different media mean that these materials could have potential for use as ion permselective membranes [42].

As observed by SEM, the pores of the sample changed significantly when the acidity of the medium varied. When ESR of poly(NAT–ITA) 2 at different pH was measured, an increase of nearly 3 times in alkaline solution compared to in acid medium was observed in Fig. 7(c) [pH = 1.0, ESR = (2.4 ± 0.1); pH = 3.0, ESR = (3.6 ± 0.1); pH = 5.0, ESR = (7.5 ± 0.3); pH = 7.0, ESR = (9.3 ± 0.3); pH = 9.0, ESR = (9.6 ± 0.3) and pH = 13.0, ESR = (12.5 ± 0.1)]. The hydrogel volume of poly(NAT–ITA) 2 increased approximately 300% from acid medium to basic; it was enough to ensure the desired switch. The change of approximately 300% arises from the ESR ratio of 9.6 (at pH 9.0) respect to 3.6 (at pH 3.0). While, the expansion needed to perform the change in the gel volume of the designed valve is nearly 20%. The last, was calculated from the gel thickness, 1 mm, and the expansion to 1.2 mm. Therefore, the selection was based on the strength of the network.

After the physicochemical characterization, poly(NAT–ITA) 2 was evaluated in an actuator system. Fig. 7(a) shows the potential variation of the electrodes (Cu/Fe) when the pH changed inside of the valve. When the pH is basic, the hydrogen ion concentration is low and the potential becomes close to zero, while when the pH is acid, the proton concentration is high and the potential increases to approximately 400 mV. Fig. 7(b) shows the analytical response of the polymeric valve. Changes in the pH of the solution

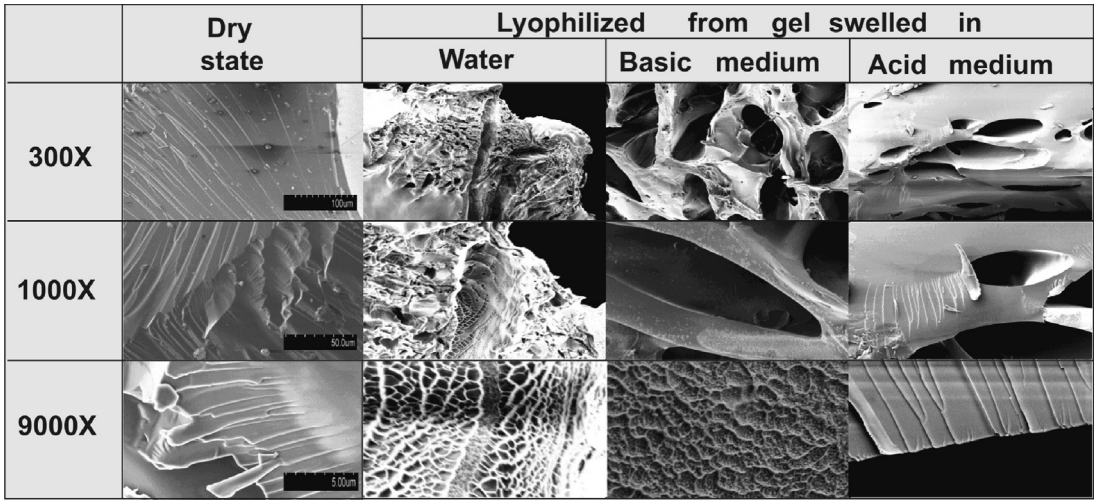

Fig. 6. SEM images of poly(NAT–ITA) 2 at magnifications of: 300×, 1000×, and 9000×. The samples were analyzed in the dry state and lyophilized from acid, basic and neutral medium.

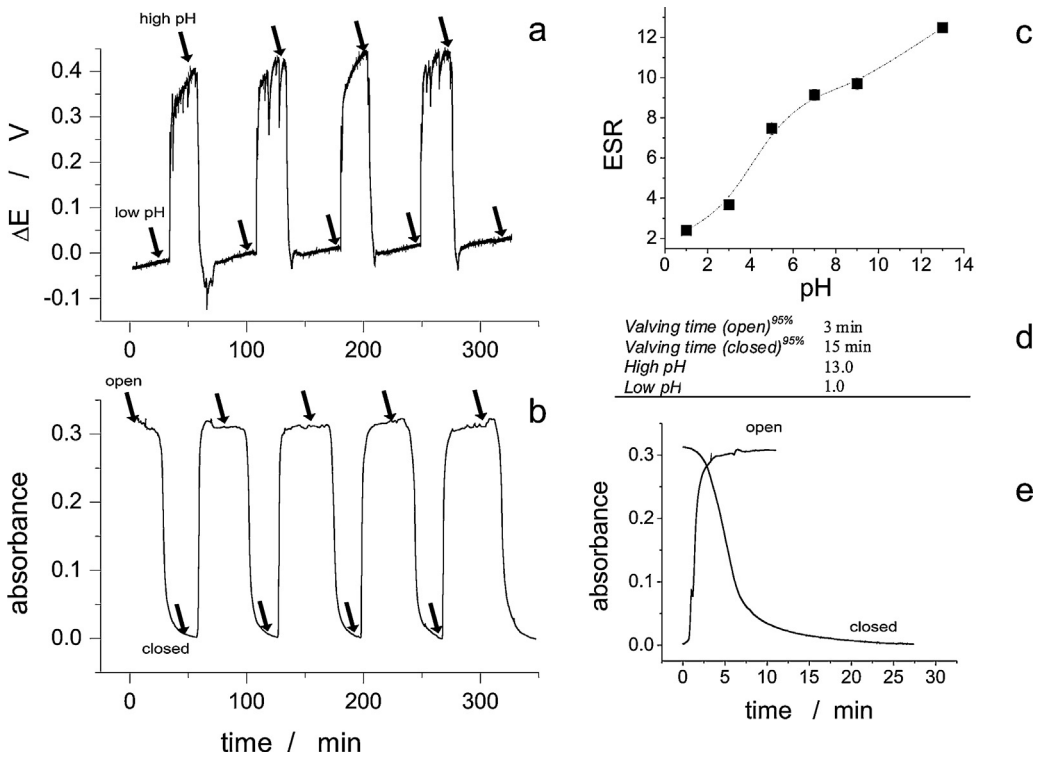

Fig. 7. Analytical response of polymeric valve: (a) Potential of the control solution versus time. The potentials were 0.4 and 0.0 V when the solutions were acidic or basic, respectively; (b) absorbance at 254 nm of Fe^{3+}–EDTA complex versus time. The acidic solution collapsed the gel allowing the valve to open permitting the passage of Fe^{3+} to form the complex (monitored by the increase of absorbance); (c) ESR versus pH of poly(NAT–ITA) 2; (d) kinetics of the valve response and pH of the solutions utilized to start the actuation; (e) absorbance versus time showing the kinetics of open/closed of the valve.

according to Fig. 7(a) [from pH = 1.0 (low pH) to pH = 13.0 (high pH)] modified the volume and expansion of the polymer, which in turns opens or closes the valve and regulates the flow of the solution of Fe^{3+}. The switching was monitored spectrophotometrically by the change of the absorbance observed due to the formation of Fe^{3+}–EDTA complex at 254 nm. Under these experimental conditions, the absorbance of a solution of EDTA is essentially zero. When the basic solution has been flowing for half an hour, the polymer swells and closes the valve and the passage of Fe^{3+}. For about 30 min, the absorption drops from 0.3 to about zero because the absorption of EDTA is only detected when the valve is completely closed. When the acid solution is flowing, the valve opens since the polymer collapses and permits the passage of the Fe^{3+} to form the Fe^{3+}–EDTA complex. In this way, an increase in the absorption is detected, which can be directly connected to the actuation of the valve. When the gel is into the valve, remains in contact with solutions (HCl and NaOH) that control the actuation, while Fe^{+3}–EDTA solution do not take in contact with the hydrogel because there is a waterproof membrane that protects it. Furthermore, the solution composed of Fe^{+3}–EDTA can be replaced by other solutions (depending on the requirements of each case).

As it was verified for other systems [1], the valve coupled the volume expansion of the hydrogel to deform the membrane and occlude the orifice. In this case, the system was reproducible and the polymer was capable of switching 10 times without significant change in the response. Moreover, the reproducibility of the response could indicate that the hydrogel has adequate mechanical properties for repetitive opening and closing, indicating reversibility.

The response time was 3 and 15 min to open and close the valve, respectively, as shown in Fig. 7(e) and summarized in the table in 7(d). The opening and closing speed was calculated as 95% of the maximum response obtained.

We could not get valve commute when poly(NAT–ITA) 1 and 3 were used to construct actuators, probably caused by their poor mechanical properties.

4. Conclusions

New hydrogels from tris[(hydroxymethyl) methyl]acrylamide and itaconic acid as monomers and (+)N,N′-diallyltartradiamide as crosslinker, were developed. They were characterized by FTIR, swelling, mechanical properties and SEM. The selection of the material to be used as an actuator was the main objective proposed. The criteria for selection of poly(NAT–ITA) 2 (prepared with 80% and 20% of NAT and ITA, respectively) to be used in the actuator system, were based on mechanical properties and in the force that can produce. This hydrogel has the lowest equilibrium swelling ratio (ESR = 16) in water but the highest elastic modulus (10 ± 1 kPa) and strength (2.2 ± 0.1 N h^{-1}). Poly(NAT–ITA) 2 was chosen to prepare a pH-sensitive valve to control the flux in a capillary tube. The valve was tested using a system to control the formation of Fe^{3+}–EDTA complex.

The developed hydrogel valve was reproducible and capable of switching various times without significant changes in the response. The structural damage of the network was avoided by the hydrogen dynamic bonds occurred in the polymeric samples which allowed the repetitive expansion and collapsing of the network. Furthermore, it assisted in the reversibility when the hydrogel poly(NAT–ITA) 2 were subjected to repetitive process, such as, the continuous opening/closing of the valve.

At the moment, we are working in the development of an actuator using this useful material to control the soil moisture in irrigation systems. This type of actuators could be constructed in larger dimensions and properly switch. Although the soil moisture conditions can change daily or seasonally, the switching time of

these devices would be sufficient to achieve an efficient humidity control in this application.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2013.06.086.

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