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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.