Sensors and Actuators B 254 (2018) 519–525

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

# Thermally induced reversible and reprogrammable actuation of tough hydrogels utilising ionoprinting and iron coordination chemistry

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A R T I C L E I N F O

*Article history:*
Received 20 April 2017
Received in revised form 3 July 2017
Accepted 14 July 2017
Available online 17 July 2017

*Keywords:*
Ionoprinting
Hydrogel
Interpenetrating polymer network
Actuation
Temperature responsive

A B S T R A C T

Ionoprinting has proven itself as a technique capable of enabling repeated post-synthesis programming of hydrogels into a variety of different shapes, achieved through a variety of different actuation pathways. To date, the technique of ionoprinting has been limited to conventional brittle hydrogels, with reversible actuation requiring a change in submersion solution. In this study, ionoprinting has been combined for the first time with a tougher interpenetrating network polymer (IPN) hydrogel with dual pH and temperature responsiveness. This new methodology eliminates the brittle material failure typically occurring during shape change programming and actuation in hydrogels, thus allowing for the realisation of more highly strained and complex shape formation than previously demonstrated. Critically, the temperature responsiveness of this system enables actuation between an unfolded (2D) and a folded (3D) shape through an external stimuli; enabling reversible actuation without a change in submersion solution. Here, the reversible thermally induced actuation is demonstrated for the first time through the formation of complex multi-folded architectures, including an origami crane bird and Miura folds, from flat hydrogel sheets. The robustness of the IPN hydrogel is demonstrated through multiple reprogramming cycles and repeated actuation of a single hydrogel sheet formed into 3D shapes (hexagon, helix and zig-zag). These advancements vastly improve the applicability of ionoprinting extending its application into areas of soft robotics, biomedical engineering and enviro intelligent sensors.

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## 1. Introduction

Hydrogels are three-dimensional polymer networks which are able to absorb large amounts of water [1]. They have current and potential uses in biomedical, agricultural and waste treatments applications [2]. Hydrogels often possess comparable mechanical properties to biological tissue, but with significantly reduced toughness [3]. A number of approaches have been shown to significantly increase the toughness of these materials, the most widely demonstrated has been the utilisation of multiple polymer networks [3,4]. Such additional polymer networks may involve covalent crosslinking (double, triple etc. network hydrogels), ionic crosslinking (ionic-covalent network (ICE) hydrogels) or secondary bonds (interpenetrating polymer network (IPN) hydrogels) [4].

Depending on their molecular composition, hydrogels can also show stimuli-responsiveness to a range of stimuli including light, pH and temperature, undergoing large volume changes in response [5]. Stimuli-responsive hydrogels have the potential to be used in sensing, actuating and drug delivery applications [6–8]. The ability to induce shape change, not simple volume change, further extends the application of stimuli responsive hydrogels [9]. Single composition hydrogel i.e. homogenous hydrogels, will only undergo inhomogeneous volume change i.e. shape change, when exposed to inhomogeneous stimuli [10]. For a hydrogel to undergo shape change in response to a uniform (homogenous) stimuli, the introduction of an embedded inhomogeneity is required. This has conventionally been achieved during the synthesis/manufacture of the hydrogel through the use of bilayers, aligned reinforcements and spatially variable crosslinking [11–18]. Ionoprinting introduces inhomogeneity into a hydrogel after synthesis, by ionically crosslinking localised regions of the hydrogels [19–26]. The increasing ionic crosslinking causes a reduction in hydrogel water content and thus volume, while increasing hydrogel stiffness; which when localised to specific areas of the hydrogel can cause inhomogeneous

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http://dx.doi.org/10.1016/j.snb.2017.07.095
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shape change. Ionoprinting achieves this localised ionic crosslinking by surface injection of metal cations, which are generated in situ via an oxidative bias generated by an electric field. The dynamic nature of the ionic crosslinks allows them to be formed after manufacturing through the introduction of metal cations and destroyed on demand by removal of the metal cations through a competing coordinating species. This dynamic nature allows for post-synthesis shape change programming and subsequent removal of the cations, returning the hydrogel to its originally synthesised state, allowing for new re-programming of further shape changes. However, the shape changes demonstrated to date have been very limited and simplistic, which is believed to be due to the inability to create complex reversible shape changes derived from brittle hydrogels (due to material failure during ionoprinting and actuating conditions).

In this study, a dual pH-temperature responsive interpenetrating polymer network hydrogel is programmed to undergo reversible shape change and actuation through ionoprinting of hinges. This work explores the factors controlling the hinge formation through an investigative study of the ionoprinting input variables and the conductivity of the hydrogel. A variety of thermally induced reversible shape changes are then demonstrated, all showing 2D (hot) to 3D (cold) transformations.

## 2. Materials and methods

### 2.1. Materials

*N*-isopropylacrylamide (NIPAAm), phosphoric acid 2-hydroxyethyl methacrylate ester (PHMA), *N*,*N*′-methylenebisacrylamide (MBAA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), Lithium chloride (LiCl), iron(III) chloride hexahydrate, disodium ethylenediaminetetraacetic acid (EDTA) and triethylamine (TEA) were obtained from Sigma-Aldrich (Poole, UK). 2-(methacryloyloxy)ethyl phosphate (MOEP) was extracted from PHMA with n-hexane, all other chemicals were used as supplied without further purification. Polyurethane (PU HydroMed D3) was supplied by AdvanSource biomaterials and was used as a 10% w/v solution in reagent grade ethanol.

### 2.2. Hydrogel synthesis

IPN hydrogels were prepared by combining the monomers (NIPAAm and MOEP, 80:20 molar ratio) followed by neutralisation with TEA. This mixture (40.0% weight) was dissolved in PU solution prior to the addition of the photoinitiator (DMPA, 1:750 photoinitiator:monomer molar ratio) and the crosslinker (DMPA, 1:500 crosslinker:monomer molar ratio). For single network (SN) hydrogels the same procedure was followed however monomer mixtures were dissolved in ethanol instead of PU stock solution. All the solutions were cured in either 1 ml syringes (internal diameter of 5 mm) or between two glass slides separated by a spacer (1.0 mm thickness). Samples were cured under a UV lamp (365/425 nm, 4 W) for 4 h. Hydrogels were submerged into DI water after curing to precipitate the PU out of solution to form the second interpenetrating network. Pure hydrogel samples were air dried prior to submersion into water to prevent brittle failure.

### 2.3. Ionoprinting & actuating conditions

Prior to ionoprinting hydrogel samples were equilibrated in 0.1 M LiCl solution, unless otherwise stated, for a minimum of 48 h. Immediately prior to ionoprinting the hydrogels were removed from their equilibration solution and pat dried. Ionoprinting was performed using an iron wire anode (diameter 2.8 mm) and a flat aluminium sheet (surface area greater than the hydrogel) with pressure onto the hydrogel controlled by a spacer (thickness 1.0 mm). The variables tested ranged from 0.5 to 5.0 min for duration, 2.0–10.0 V for input voltage and 0.05–1.00 M for LiCl solutions. The standard baseline conditions used throughout this study were 5.0 V for 1 min for ionoprinting of a hydrogel swollen in 0.1 M LiCl solution. Samples used to investigate ionoprinting variables were 20 mm by 5 mm by 0.6 mm (water swollen dimensions) hydrogels. The voltage measured through the entire system was assumed to be the voltage occurring through the hydrogel (i.e. the only significant resistive element in the circuit), whilst the current was measured in series (range up to 200 mA with an accuracy of 0.1 mA or a range up to 5.00 A with an accuracy of 0.01 A) recorded every 5 s and integrated to determine moles of electrons through the circuit. Final out-plane-angle was measured immediately after ionoprinting and were repeated 3 times.

Actuation was performed in the equilibration solution, samples were heated to 50 °C (for 1 h) to enable unfolding of the ionoprinted hinges and cooled to 25 °C (for 1 h) to enable folding of the ionoprinted hinges. Cations were extracted with EDTA overnight and re-equilibrated in 0.1 M LiCl solution before further ionoprinting.

### 2.4. Hydrogel characterisation

The hydrogel's response to a range of environmental stimuli was investigated by submersion for 24 h in different solutions, including various concentrations of iron(III) chloride (0.0 M–5.0 M) and buffer solutions (0.1 M NaCl and 0.01 M buffer) over a range of temperatures (10–90 °C).

Compressive testing was performed between two parallel plates on disc samples, diameter 7.0 mm (0.1 mm standard deviation (STD) by 3.7 mm (0.6 mm STD) thickness for SN hydrogels and diameter 7.6 mm (0.1 mm STD) by 4.1 mm (0.6 mm STD) thickness for IPN hydrogels) at a rate of 100% $\text{min}^{-1}$ until failure. Compressive modulus (up to 20% strain), energy absorbed until failure and stress and strain at failure were determined.

## 3. Results and discussion

### 3.1. Ionoprinting fundamentals

The process of ionoprinting employs an oxidative bias generated by an electric field to produce metal cations, these are utilised for ionic crosslinking within a hydrogel [19]. For the hydrogel to be successfully ionically crosslinked by the cations, coordinating groups must be present within the hydrogel. The ionic bridging of these coordination groups triggers the explosion of the water molecules leading to the shrinking of the hydrogel. Throughout this study a flat aluminium sheet was employed as the cathode whilst an iron wire was used as the anode, as shown in Fig. 1a. When a potential is applied across the system a number of simultaneous electrochemical processes are established; at the anode the oxidation of the iron metal to iron(III) cations ($Fe^{3+}$) and at the cathode the reduction of protons to hydrogen. While the metal cations become bound within the hydrogel, forming the ionic crosslinks, the hydrogen gas leaves the system.

The ionic crosslinking is locally concentrated near the anode-hydrogel interface, with the concentration decreasing with increasing distance from this interface. The ionic crosslinking results in localised shrinking of the hydrogel (see supplementary Fig. S1), while leaving the remaining hydrogel swollen, the internal stresses generated by this swelling differential is relieved through the out-of-plan folding of hydrogel along the ionoprinted line, as shown in Fig. 1b. The ionoprinted hinge can be unfolded back to the original configuration by de-swelling the non-ionoprinted regions of the hydrogel, i.e. removing the differential in swelling within the specimen, by heating the hydrogel above its lower critical solution

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