

# Synthesis of pullulan graft polyacrylamide porous semi ipn hydrogel biology essay...

[Science](#), [Biology](#)



Samaneh Saber-Samandari\*, Mustafa Gazi  
Department of Chemistry, Eastern  
Mediterranean University, Gazimagusa, TRNC via Mersin 10, Turkey

## Abstract

The porous P(NIPAAm-co-DPAM) hydrogel exhibited much faster swelling/deswelling rates, absorbing 90wt% in 240min, and losing 95wt% of water in just 1min.[10]Corresponding Authors: samaneh. saber@gmail. com +90 392 630 3053 (Samaneh Saber-Samandari),

## 1. Introduction

Superabsorbent hydrogels are three-dimensional hydrophilic polymer networks that absorb a large amount of water or biological fluids without dissolving and retain water under pressure [1]. Among them the natural-based super-absorbent hydrogels have created extensive interest because of their biocompatibility, biodegradability and non-toxicity. They have widely applied in many fields such as medicine, pharmacy, and biotechnology, absorbent sanitary goods, agriculture, and waste water treatment. Despite of their advantages they have two important deficiencies: low mechanical properties and slow rate of swelling. For improving the mechanical properties, the synthesis of interpenetrating network (IPN) and semi-interpenetrating network hydrogels was one of the options. The interpenetrating networks (IPN) are a combination of two or more polymers which one (in semi-IPN case) or all of them (in IPN case) cross-linked independently in network form. Also, formation of porous structure provides a certain way to improve the absorption rate by increase diffusion of water into the glassy matrix of dried hydrogel [2]. Porous hydrogel are structurally

crosslinked hydrophilic polymers, besides they have super-porous structure and can absorb considerable amounts of water in relatively short periods of time [3]. The three main functional properties of porous hydrogel: absorption capacity, absorption rate and the swollen gel strength are related to the degree of porosity and the pore size which play the multiple role of enhancing the total water sorption capability and the rate of response by reducing the transport resistance [4, 5]. Unique physical properties of porous hydrogel provided them with a variety of applications such as water treatment [6], tissue engineering [7], drug delivery [8] cosmetics [9] and food industry [10] and agriculture [2]. Various methods, such as the phase inversion technique [11], freeze-drying and hydration technique [12], the water-soluble porogens [13] and the foam technique [14, 15], have been used to create the porous structure of hydrogels [9]. To the best of our knowledge, preparation of pullulan-graft-polyacrylamide hydrogel as well as porous hydrogel has not yet been reported. Thus, in the present study, the novel porous semi-IPN hydrogel through graft polymerization of acrylamide onto pullulan in the presence of a crosslinking agent was synthesized. Besides that, the effect of reaction variables affecting the swelling behavior and porosity of the hydrogel were investigated.

## **2. Experimental Procedures**

### **2.1 Material**

The synthesis of the semi-IPN hydrogel was achieved using pullulan (Freda) and acrylamide (Aldrich) as a monomer. The crosslinker N, N'-methylene-bis-acrylamide (Aldrich), potassium persulphate (Aldrich) as an initiator and

calcium carbonate ( ) were used as received. The ethanol ( ) was used without further purification. Finally, .....were used for .... purposes as received.

## **2. 2 Synthesis of Pullulan-graft-Polyacrylamide Porous Semi-IPN Hydrogel**

First, pullulan solution (0. 25 g, 1. 66 % w/v) was prepared by dissolving pullulan powder in distilled water. The pullulan solution was placed in a three-neck round-bottom flask fitted with a condenser and an argon gas inlet in water bath at 60 °C with continuous stirring. Then, the potassium persulphate as an initiator was dissolved in the pullulan solution and allowed to stir for 10 minutes. During this time the exact amount of calcium carbonate as a progen was added to the solution. Subsequently, acrylamide and N, N-methylene-bis-acrylamide were added to the above solution and the mixture was continuously stirred for one hour. The original amount of components and the designations of the systems are summarized in Table 1. Finally, the obtained hydrogels were cut in several pieces and washed with distilled water. Then, the hydrogels were immersed in 10 % wt hydrochloric acid solution for a day with stirring at room temperature. It is worth to note that immediately, the newly formed CO<sub>2</sub> bubbles will rise up though the porous medium. For removing the calcium chloride and the other remained substrate like homo-polymer or unreacted acrylamide, the hydrogels kept under bidistilled water overnight and then dried in an oven at 50 °C. As control the characterization of porous hydrogels, the pullulan-graft-polyacrylamide semi-IPN hydrogel without CaCO<sub>3</sub> as progen under the same procedure as described above was synthesized.

## 2.3 Density and Porosity (%) Measurement

Porosity (%) of synthesized hydrogels was determined by using liquid replacement method [16-17]. For this purpose the ~0.5 g of dried porous hydrogel (W1) was immersed in a graduated cylinder containing a known volume (V1) of ethanol overnight till no air bubbles were seen emerging from the hydrogel. The volume difference (V2–V1) represented the volume of hydrogel. Then the water-impregnated hydrogel was removed from the cylinder and after removing the excess amount of ethanol from the surface of hydrogel by the filter paper, weighed (W2). The volume of the cylinder after removing hydrogel was recorded as (V3). Therefore the volume of porous hydrogel was calculated by summation of the volume of water held by the hydrogel or void volume (V1–V3) and the volume of hydrogel (V2–V1). The porosity (%) of porous semi-IPN hydrogel was calculated from the Equation 1:(1) where,  $\rho$  is the density of ethanol ( $\text{g. cm}^{-3}$ ) and  $V_S$  is the volume of hydrogel (V2-V3) which attained during density measurement.

## 2.4 Swelling and Deswelling Behavior

The swelling property of the porous semi-IPN hydrogel was investigated by immersing 0.5 g of hydrogel in 50 mL of distilled water at 20 °C in atmospheric conditions until swelling equilibrium was reached. Then, the swelling percentage was calculated using the Equation 2. In addition, for measuring the deswelling behavior of swollen hydrogel, the water retention capacity at constant temperature (80 °C), was considered. First, the swollen and equilibrated hydrogel weighed and then were put into an oven through which passed a current of hot dry air at constant 80 °C. The weights of the

porous hydrogel were measured regularly until 24 hours. Then, the water retention capacity was calculated using the following Equation 3:(2)(3) where  $W_2$  (g),  $W_3$  (g) and  $W_4$  (g) are weights of the dried, swollen and deswelled hydrogels, respectively.

### **3. Results and Discussions**

#### **3. 1 Characterization of Pullulan-graft-Polyacrylamide Semi-IPN Hydrogel**

3. 1. 1 Fourier Transform Infrared Spectroscopy (FTIR) 3. 1. 2 Scanning Electron Microscopy (SEM) The formation of porous hydrogel can be schematically illustrated by figure... 3. 1. 3 Differential Scanning Calorimetry (DSC)

#### **3. 2 Porosity and Swelling behavior of Semi-IPN Hydrogel**

Different variables (i. e. pullulan/acrylamide ratio, progen content, crosslinker and initiator amounts) affecting directly the structure of porous hydrogel were studied to achieve the porous hydrogel with optimized physical and chemical properties. Among the several properties, porosity (%) as physical and swelling (%) as chemical property were investigated.

##### **3. 2. 1 Effect of Monomer Concentration**

The effect of acrylamide concentration on porosity and swelling (%) were studied by varying the amount of acrylamide, while the rest of variables kept constant. As indicated in Figure 6 A, the porosity percentage decreased as the acrylamide amounts was increased and the maximum porosity (%) was achieved at 0. 11 mol. L<sup>-1</sup> of acrylamide. This result can be due to the

greater number of homo-polyacrylamide chains, which can hinder the presence and movement of progen inside of the network. However, this diminishing in the porosity of hydrogels cannot eliminate the hydrophilic nature of acrylamide that can offer considerable hydrogen bonding with hydrophilic groups. Thus, in spite of decreasing the porosity, the swelling capacity of hydrogels was not decreased. It is therefore should not be concluded generally that the porosity and swelling percentage have positive and direct relation in every case.

### **3. 2. 2 Effect of CaCO<sub>3</sub> (Progen) Content**

The porosity and swelling values for porous hydrogels with various progen contents are comparatively given in Figure 6 B. According to the Figure, increasing the amounts of CaCO<sub>3</sub> during synthesis of hydrogels and subsequently acid treatment causes the high number of produced pores. Therefore, increase the porosity % leads to decreasing density and increasing water uptake of hydrogels due to the enhancing the contact area between polymeric network and external solution that facilitate to speed up the diffusion rate [18]. Nevertheless, further increase in the amount of progen with the aim of making more pores cannot increase considerably the porosity % when the structure of hydrogel reaches to the highest capacity of porosity.

### **3. 2. 3 Effect of Crosslinker Amounts**

Figure 6 C demonstrates the effect of the crosslinker amount on the above-mentioned physical and chemical properties of porous hydrogel. The porosity and water absorbency of hydrogel decreased as the crosslinker amount was

increased. This leveling off can be attributed to highly crosslinked rigid structure which will be difficult to expand and open a spaces for  $\text{CaCO}_3$  inside of network. Therefore, the porous structure could be observed in just surface not in its cross-section and consequently, the porosity decreased but because of the vicinity to solution still have water adsorption. Increase in crosslinker content more than 0.01 mol. L<sup>-1</sup> leads to very inflexible semi-IPN network that exhibit less porosity in both the surface and cross-section, which can lead to impressive decrease in swelling (%).

### **3. 2. 4 Effect of Initiator**

In this series of experiments, the effect of the initiator amount on water absorbing capacity, and porosity (%) were investigated. As seen in Figure 6 D, maximum swelling and porosity (%) was obtained at 0.012 mol. L<sup>-1</sup> of initiator concentration. More or less than this concentration gives porous hydrogels with decreased porosity and swelling capacity. This behavior can be originated from the fact that increasing the proportion of initiator in the feed mixture increases the number of active free radicals which, in turn, resulting in higher graft polymerization extent and consequently greater semi-IPN networks. This explains the elevating in the porosity and swelling ratio of the hydrogel. However, much higher concentration of KPS leads to fast termination step by the collision of the active ends causes to increase in density of network chains. Therefore, decrease in the porosity and swelling (%) would be expected by reducing the network space inside and the diffusion of solvent molecules simultaneously. A similar trend was reported by Sadeghi et al. [19] in the preparation of salt- and pH- sensitive



carrageenan-graft-poly (acrylamide-co-itaconic acid) superabsorbent hydrogel

### **3. 2. 5 Kinetic of Swelling**

Figure 4 shows the effect of time on the swelling and deswelling behavior of the pullulan-graft polyacrylamide porous hydrogel. As indicated in the Figure, at the beginning the rate of water uptake sharply increases up to 1975 % after 90 min and then begins to level off. Initially, the water molecules are in contact with the hydrogel. Then, they attack to the surface of hydrogel and penetrated inside of network. By the way, the pores of rubbery region of hydrogel will start to expand after separating unsolvated glassy region of hydrogel from rubbery region with a moving boundary [20]. Obviously, this swelling system cannot continue forever and by the increasing hydrogel-water interaction, the osmotic pressure difference will be reduced. Finally, at the equilibrium, the osmotic force will be balanced with elasticity force. It should be noted that the elasticity force prevents from deformation of hydrogel network by the stretching balance of the network. Water retention ability of hydrogels is one of the important features of hydrogel in view of practical applications. Figure 4 which represent this ability of swollen hydrogel at 80 °C shows that the rate percentage of retained water in hydrogel decreased as the time passes. As Aizawa and Suzuki reported, water inside of the swollen hydrogel can be classified into free water, bound water and half-bound water. It is obvious that free water compared to the other has high mobility thus can be removed easily. But, the bound water and half-bound water may have some hydrogen bonds with the hydrophilic

groups in the structure of hydrogels (such as -OH, -CONH<sub>2</sub>, -COOH in this study). The pullulan-graft-polyacrylamide swollen hydrogel lost free and partly half-bound water very fast until first five hours and then decreased. It can be concluded that, the synthesized hydrogel can be very useful to apply in the dry and desert region due to saving 24.6 % of adsorbed water even after 24 hours. According to the some applications such as water treatment, which is the aim of next study, high swelling rate in addition to high swelling capacity is an important property which can be determined by several physicochemical parameters particularly the extent of porosity and the type of porous structure [20]. As stated by Voigt-based Equation:(3) Where  $S_e$  (g. g<sup>-1</sup>) is equilibrium swelling and  $S_t$  (g. g<sup>-1</sup>) stand for the swelling at time  $t$  (min). In addition,  $\tau$  the rate of swelling (min) can be calculated from rearrangement of above equation [21]. The slope ( $-\tau^{-1}$ ) of fitted line from the plot of  $\ln[1-(S_t/S_e)]$  versus  $t$  (min) leads to finding 35.33 min rate of swelling for this porous hydrogel. As described by Ganji et al., this fast diffusion of water and filling the pores, in addition to SEM result confirm the synthesis of macro-porous (0.1-1  $\mu$ m) hydrogels [20].

### **3. 2. 6 Effect of Temperature on Swelling**

The effect of temperature on the swelling capacity of the hydrogel was studied by varying the temperature from room temperature, 18 to 80 °C as shown in Figure 8. Increasing the temperature leads to the increasing the water absorbency until it is considerably decreased with a further increase in the temperature. The maximum swelling (2920.2 %) was achieved at 60 °C. The initial increase in water uptake capacity could be attributed to the

necessary activation energy to open up the network structure and making it more accessible to water [22]. The swelling loss beyond the optimum temperature is due to the disruption of hydrogen bonding and therefore degradation of crosslinked network.

### **3. 2. 7 Effect of pH on Swelling**

Figure 8, represents the pH dependence of water uptake by the porous hydrogel at room temperature. The swelling behavior of hydrogel in different buffer solution with the pH ranging from 1.8-12.3 is characterized by a curve with two maximum water uptakes at pHs 4.2 and 9.4. The remarkable swelling changes are due to the ionization of functional groups such as carboxamide (-CONH<sub>2</sub>) in acrylamide and hydroxyl (-OH) groups in the structure of pullulan. The involving species are COOH and OH<sub>2</sub><sup>+</sup> (pH less than 4.9), CONH<sub>3</sub><sup>+</sup> and OH<sub>2</sub><sup>+</sup> (pH= 4.9), CONH<sub>2</sub><sup>+</sup> and O<sup>-</sup> or CONH<sub>2</sub> and OH (at pH 4.9-9.4), CONH<sub>2</sub> and O<sup>-</sup> (pH= 9.4). Under basic condition the electrostatic repulsion of COO<sup>-</sup>-COO<sup>-</sup> and/or O<sup>-</sup>-O<sup>-</sup> and in acidic condition the electrostatic repulsion of CONH<sub>3</sub><sup>+</sup>-CONH<sub>3</sub><sup>+</sup> and/or OH<sub>2</sub><sup>+</sup>-OH<sub>2</sub><sup>+</sup> increases the osmotic pressure inside the hydrogel which can be balanced by water uptake from swelling medium. However, under very acidic conditions, the acrylamide converted to acrylic acid and swelling is decreased and with a pH above 9.4, the network structure began to collapse and the swelling ratio decreased sharply.

## **4. Conclusions**