**Comprehensive steady state behavior modeling of polyelectrolyte hydrogels**

Raffaella De Piano1\*, Diego Caccavo1,2, Anna Angela Barba2,3, Gaetano Lamberti1,2

*1 Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II,132, 84084 Fisciano (SA), Italy; 2 EST Srl, University spin-off, https://est.srl, 83100 Avellino, Italy; 3 Department of Pharmacy, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy*

*\*Corresponding author E-Mail: rdepiano@unisa.it*

**1. Introduction**

Hydrogels are a class of polymeric material whose main characteristic is to absorb a large quantity of water and swell due to presence on their chains of hydrophilic groups such as -OH, -CONH, -CONH2 [1, 2]. The huge family of hydrogels comprehends a particular category of them called smart hydrogels which are sensible to variation of the external stimuli such as mechanical forces, temperature, light or electric fields. In this class, particularly interesting are the so-called polyelectrolytes, long chained polymers characterized by the presence, on their chain, of ionizable groups. These groups lead the hydrogel to be sensible to variation of pH of the external surrounding since, changing the external conditions, they dissociate in a fixed part that remain on the chain and in a mobile part that goes in solution. These hydrogels are important in different fields from pharmaceutical to medical and polymeric applications. To fully understand the behavior relates to the hydrogel swelling, during years several mathematical models have been studied. Starting from the work of Caccavo et al. on the PoroViscoElastic behavior of neutral hydrogel[3-5], aim of this work is to extend the model to a polyelectrolyte in a steady state condition. In addition, to tune the model, a first series of experimental data has been obtained monitoring the swelling behavior of an anionic copolymer gel of Acrylamide in aqueous solution at different pH [6].

**2. Methods**

As regard the modeling part a monophasic approach, which relies on a strong thermodynamic basis, has been used. Starting from the dissipation inequality and using the Helmholtz Free Energy for polyelectrolytes the constitutive equations have been derived. The Helmholtz Free Energy in this case is formed by four terms: the one related to the elastic part, the one related to the mixing, and the terms related to the ionization and the dissociation of the charges. The system is formed by six variables (the deformation and the concentrations of the species together with the pressure) and so six equations are needed. The deformation and the pressure are calculated using the linear momentum balance and the volumetric constraint, while the concentrations are calculated considering the thermodynamic criterion for the phase equilibrium according to which when two phases are in equilibrium the chemical potential are equal. These equations are solved numerically through the software MATLAB R2020b.

To observe swelling phenomena under experimental point of view, an anionic copolymer gel of Acrylamide was prepared. In particular, a solution of Acrylamide (632 mM), N,N’-MethylenBis (Acrylamide) (8.6 mM), Sodium Acrylate (71.2 mM) were dispersed in 50 mL of solution, then Ammonium Persulfate (1.75 mM) and Sodium Betafisulfite (2.1 mM) were added as initiator and accelerator respectively. The solution was transferred into cylinders molds for 24 hours and then the original mass M0 of each sample was determined. The degree of swelling was measured by soaking a sample of gel in 100 mL of solution of known pH. After equilibration for 48 h, the swollen gel was removed from the solution, drained and weighed. The swelling ratio was defined as the ratio of swollen mass, M, to the original mass M0. The measurements of each sample were performed in triplicate.

**3. Results and discussion**

The system is mainly based on five parameters: salt concentration, acidic dissociation constant, elastic modulus, number of ionizable groups and enthalpic Flory Huggins parameter. With the aim of understanding the mechanism of swelling of anionic hydrogels, a first parametric study, assuming a free swelling experiment, has been done. The general behavior of an anionic hydrogel is well described by the model in a range of pH from 1 to 7 together with the degree of ionization as depicted in the figure below:



**Figure 1.** Swelling ratio and degree of ionization as a function of pH

As it can be seen from the Figure 1 the model describes a completely association of the charges and a lower swelling for lower pH, and a completely dissociation increasing the swelling of the matrix for higher pH, as also reported in literature.

Figure 2 shows the experimental data of the anionic gel at equilibrium in aqueous solutions at different pH, while the solid line represents the swelling curve obtained from the model fitting the parameters for the examined system.



**Figure 2.** Comparison of model and experimental swelling data

**4. Conclusions**

Using a monophasic modeling approach the steady state behavior of polyelectrolyte was modeled. It was shown that, for a simple experiment, the system of equations to be solved is constituted by six equations. These equations were used to perform a study to understand the general behavior of the hydrogel. Furthermore, a first set of experimental data was obtained soaking hydrogels of known initial mass in solution at different pH and the behavior of the system is well described by the model. The proposed model can describe the general behavior of the hydrogel in a steady state condition and it could be seen as an important tool to develop a transient model, extending the description to unsteady state problems.

**References**

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