ISSN (Online) 2456 -1304

International Journal of Science, Engineering and Management (IJSEM)
Vol 5, Issue 9, September 2020

Synthesis of Poly (Acrylamide-Co-Acrylic acid) Hydrogel: Study of its Swelling Kinetics

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Abstract: **- Hydrogels are an important material for drug delivery, tissue engineering and numerous other applications. They constitute a 3D network with a hydrophilic part and can swell upto 20 times their dry weight. In this review, a hydrogel of Acrylamide and Acrylic acid is developed and a review of its swelling kinetics and swelling behaviour is discussed. The effect of pH on the swelling content and swelling ratio has also been studied.**

Keywords: Acrylamide, Acrylic acid, diffusion mechanism, hydrogels, kinetics, pH, Poly(Acrylamide-Co-Acrylic acid), swelling behaviour

INTRODUCTION

Hydrogels were first applied for industrial use in 1960 by Wichterle and Lim[1]. Since then, they have been utilized as novel materials for a large number of processes. Some major applications are drug delivery and drug administration in biomedical engineering, super absorption in disposable sanitary products, matrices in tissue engineering, calcium alginate microcapsules for cell encapsulation[2], enriched oil recovery, etc.

Controlled drug delivery and controlled agriculture fertilisers require high water retention properties. Among the different polymeric and inorganic materials examined for the purpose, hydrogels have gained considerable interest due to their high rate and degree of swelling.

Hydrogels constitute a three dimensional network of hydrophilic polymeric chains that contain a large amount of aqueous solvent within. This property arises from the hydrophilic functional groups like -NH2, -COOH, -OH, -CONH2 and So3H present in the polymeric backbone of the hydrogel and the difference in osmotic pressure between the solvent phase and gel phase. The macromolecular network is insoluble in the solvent, if it is crosslinked. Studies have proven that the swelling property of hydrogels in water is due to the hydrophilic groups, while its mechanical resistance is the result of physical or chemical network cross-linking[3].

They can be classified as natural or synthetic based on their occurrence, crosslinked gums and collagens are two materials which are fabricated to form hydrogels. Poly (hydroxyalkyl methacrylates), poly (acrylamide) and poly (acrylic acid) are few examples of synthetic hydrogels.

It is possible to prepare hydrogels with significant amounts of hydrophobic content by blending or copolymerization of hydrophilic and hydrophobic polymers.

The level of hydrophobic and hydrophilic content in a hydrogel, the degree of crosslinking and the degree of ionization are the most crucial parameters in determining the equilibrium swelling and dimensional modifications. The study of swelling kinetics and swelling behaviour has been widely discussed. This review aims to shed light on the mathematical theory of kinetics and rheology pertaining to the Poly(Acrylamide-Co-Acrylic acid) hydrogel.

SYNTHESIS OF HYDROGELS

Hydrogels are prepared mainly by two methods: Polymerization of homopolymers or copolymers or Modification of existing functional polymers[4]. They may be divided into the categories of homopolymer, copolymer and interpenetrating polymer network.

Homopolymers contain a single monomer species and they might have a crosslinked structure depending on the nature of the monomer. Examples of widely applied homopolymer monomers are 2-Hydroxyethyl methacrylate (HEMA) and Poly(2-hydroxyethyl methacrylate) (PHEMA). Copolymers constitute two monomers of which one is necessarily hydrophilic. Examples of monomers include Methacrylic acid (MMA) and PEG-PEGMA.

Semi - Interpenetrating Polymer Network (Semi - IPN) and Interpenetrating Polymer Network (IPN) are a class of hydrogels that have found extensive use in biomedical and pharmaceutical applications. The heightened interest in this class of hydrogels is due to the possibility of combining with each other to form an enhanced product with favourable

ISSN (Online) 2456 -1304

International Journal of Science, Engineering and Management (IJSEM)
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properties[5]. A Semi - IPN is prepared by the penetration of a linear monomer into a crosslinked network without any chemical reaction. Similarly, an IPN is formed by the combination of monomers of which one has been deposited in the solution. A hydrogel is first pre - polymerized and then mixed with a solution of monomers and initiators. However, a large number Interpenetrating Polymer Networks (IPNs) do not interact on a molecular level. An example of an IPN is the combination of Chitosan with Poly(*N*-isopropyl acrylamide) (PNIPAM)[6].

A. Acrylamide/ Acrylic Acid Hydrogel

In this review paper, a Semi - IPN of Acrylic acid and Acrylamide was prepared with Ammonium persulfate as initiator. The monomers Acrylic acid (99.0%) LR grade from Central Drug House (P) Ltd. Delhi, Acrylamide from Central Drug House (P) Ltd. Delhi and Initiator APS (98.0%) from Thermo Fisher Scientific, U.S. were used. A calculated amount of monomers and initiator were mixed with Deionised Water to form a solution (Table 1). The solution was heated at 70 degree Celsius for an hour in a round bottom flask kept in a water bath. A Nitrogen atmosphere was maintained throughout the process to prevent oxygen from interfering with the free radical polymerisation. The sample formed was washed with a Methanol - DI Water mixture in the ratio of 1:1.

Table I: AAm/ Aac Hydrogel Composition

Component	Amount
Acrylamide	0.7 g
Acrylic acid	0.72 mL
Ammonium persulfate	0.5 g
Methanol	25 mL
DI Water	35 mL

The sample obtained was then dried in an oven at 40 degree celsius overnight. The dry weight of the hydrogel formed was 0.62 g.

SWELLING BEHAVIOUR OF HYDROGEL

When solvent molecules come in contact with the hydrogel, they penetrate into the polymeric network by getting through the surface. As the meshes of the network in the rubbery phase expand, more solvent molecules enter the network. The forces acting on the system are the favorable osmotic pressure and the opposite elasticity forces. At equilibrium, the swelling discontinues and maximum swelling is obtained. The elasticity forces play the role of balancing the network stretching and preventing its deformation[7].

As per the Flory-Rehner theory, in the case of an ionic hydrogel the osmotic pressure P of the gel is a combination of three parts[8]:

$P = P_s + P_e + P_i$

Where P_s represents the mixing tendency of solvent and polymer, P_e is the elastic response of the network opposing dissolution and P_i is the osmotic pressure resulting from difference in gradient between the gel phase and external surroundings[9].

An important parameter is the rate of swelling which has been widely researched and reported in available literature. The Lowman definition provides a correlation between the ratio of the diffusion coefficient of the solute in the membrane and pure solvent phase[10].

Various studies of reversible volume changes in response to pH, ionic concentration, etc. have been carried out for several kinds of polymeric networks [11]. However, in the case of ionic networks, swelling kinetics depends upon mass transfer limitations, ion exchange and ionic interaction[12].

The hydrogels exhibiting pH-sensitive swelling behavior exhibit this property due to the presence of acidic or basic groups in their ionic setup. When these groups are ionized, a swelling osmotic pressure inside the polymer is generated, and fixed charges are trapped in the gel. The electrostatic repulsion generated by the interaction leads to a higher ingestion of solvent in the network.

Results from various studies indicated that the strong interaction in the Acrylamide/Acrylic acid hydrogel resulted in the formation of a more stable copolymer. The presence of a single glass transition temperature (*Tg*) for both the polymers of the hydrogel indicates a high miscibility between the two in the hydrogel.

SWELLING KINETICS & MATHEMATICAL MODELS

Hydrogels can swell to profitable rates when placed in a solution. Many polymer- solvent systems do not conform to the classical model of diffusion with respect to sorption processes[13]. Two categories of swelling kinetics may arise due to the slow orientation of polymer molecules which can be classified as diffusion-controlled (Fickian) or relaxation-controlled (non-Fickian)[14].

Case 1: Fickian Transport: When the glass transition temperature (Tg) of polymer is below the medium temperature there is high mobility and the solvent diffuses quickly and easily into the hydrogel, the swelling kinetics is

ISSN (Online) 2456 -1304

International Journal of Science, Engineering and Management (IJSEM)
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said to be diffusion controlled.

Case 2: Non- Fickian Transport: When the Tg is well above the experimental temperature, the polymer chains do not permit mobility adequately thus hindering the fast penetration of water into the network[15].

Case 3: Anomalous transport: When the diffusion and relaxation rates are comparable.

Different mathematical models are available in literature that describe the kinetics of hydrogel swelling. An empirical equation called the Power Law equation is a useful explanation of the diffusion mechanism in polymeric networks[16]:

$M_t/M_\infty = kt^n$

M_t is the amount released at any given time, M_∞ is the maximum amount (weight) available for release, t is the release time. The diffusional constant, 'n' depends on the device geometry and solute uptake mechanism. 'k' is a characteristic constant of the system. By determining the diffusional constant, one can understand the solute uptake mechanism by a particular device (Table 2).

Table II. Solute uptake mechanism and diffusional constants for hydrogels [17].

Type of Transport	Diffusional constant (n)	Time dependence
Fickian Diffusion	0.5	$t^{1/2}$
Anomalous transport	0.5< n <1	t^{n-1}
Non-Fickian	1	Time independent

Several researchers have studied the swelling of pH-sensitive Poly(Acrylamide-Co-Acrylic acid) hydrogel and the influence of this parameter in chemical, biological and physiological systems.

The hydrogel's swelling characteristics that include swelling content, swelling rate, diffusion of water, and activation energy have been widely studied by the Tanoka-Fillmore model[18] according to which:

$$t = R^2/D$$

Where, t, R and D are the characteristic time for swelling of gel, size of the gel and the diffusion coefficient respectively.

Swelling Content: The quantitative measure is given as,

$S = (W_s - W_d)/W_d$

Where S is the Swelling Content, W_s is the swollen weight of the hydrogel and W_d is the dry weight of the hydrogel.

The other models which have been used in literature to study the Acrylamide/Acrylic acid copolymer are Peleg model, first-order and second-order absorption kinetic model.

The Peleg model is a two parameter model that describes the water absorption[19]:

$S = S° + t/(k_1 + k_2t')$

Where, $S_\circ$ is the swelling content at t= 0, S is the swelling at any time t, k_1 is the kinetic constant and k_2 is the characteristic constant of the model.

The first-order absorption kinetic model uses the exponential association equation[20, 21]. Consider,

$S = S_e + (S_\circ - Se)\exp(-k_{R1}t)$

Where k_{R1} is the swelling kinetic constant (h−1). Consider,

$S = S_e[1 - \exp(-k_{R2}t)]$

where k_{R2} is the kinetic constant (h−1).

Using these models, the best fitted model for the swelling kinetics of Poly(Acrylamide-Co-Acrylic acid) can be determined by regression and be simultaneously compared with the experimental data. Model analysis has indicated that the swelling transport followed a non-Fickian mechanism. Acrylic acid contains carboxyl groups (–COOH) and the ionization of these groups above its pKa causes the swelling to increase which results in a high swelling ratio.

As the pH decreases, the solvent transport mechanism becomes non-Fickian as gel ionization becomes prominent[23].

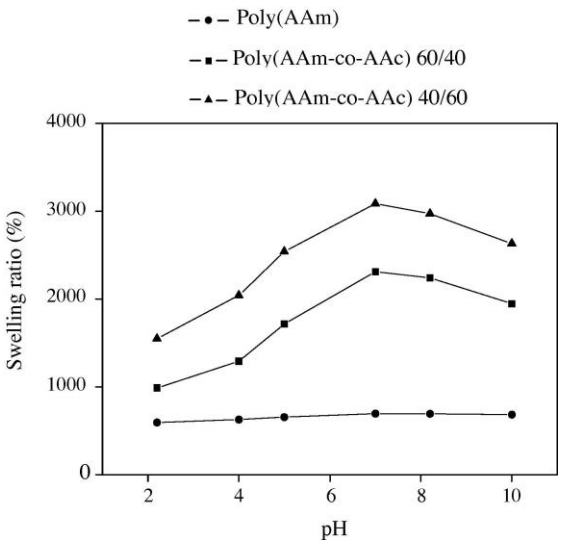

Figure 1: Influence of pH on the water uptake of the poly(AAm)-co-poly(AAc) hydrogels[22].

I. CONCLUSION

In this review, the swelling behaviour and swelling kinetics of poly(Acrylamide-co-Acrylic acid) hydrogels prepared by free radical polymerization has been studied. The important parameters that determine the swelling kinetics are crosslinking, pH of the solution and temperature. It is well-known that poly(acrylic acid) is a typical pH-responsive polyelectrolyte and with increase in its concentration, the swelling content of the hydrogel increases.

Different models have studied the solvent uptake mechanism and the diffusion mechanism. Equilibrium swelling data were studied for the evaluation of swelling parameters like diffusional exponent (*n*) and swelling coefficient (*k*). From literature, it is evident that the hydrogel exhibits a Non- Fickian diffusion mechanism as the value of the diffusional exponent (n) was above 0.5. The value displayed an inverse relationship with decreasing pH and increasing time.

REFERENCES:

1. Morteza Bahram, Naimeh Mohseni and Mehdi Moghtader (August 24th 2016). An Introduction to Hydrogels and Some Recent Applications, Emerging Concepts in Analysis and Applications of Hydrogels, Sutapa Biswas Majee, IntechOpen, DOI: 10.5772/64301.
2. Yahia LH, Chirani N, Gritsch L, et al. History and Applications of Hydrogels. J Biomedical Sci. 2015, 4:2. doi:10.4172/2254-609X.100013
3. Almdal K., Dyre J., Hvidt S., Kramer O.: What is a gel? Macromolecular Symposia, 76, 49–51 (1993).
4. Graham N B, in Hydrogels in Medicine & Pharmacy, Vol. 3, edited by N A Peppas (CRC Press, Boca Raton, FL), 1987, p.95
5. Matricardi P, Di Meo C, Coviello T, Hennink WE, Alhaique F (2013) Interpenetrating polymer networks polysaccharide hydrogels for drug delivery and tissue engineering. Adv Drug Deliv Rev 65:1172–1187
6. Sougata Jana, Arijit Gandhi and Kalyan Kumar Sen, Chitosan-Based Interpenetrating Polymer Networks: Drug Delivery Application, Functional Chitosan, 10.1007/978-981-15-0263-7_9, (269-295), (2020).
7. Fariba, Ganji, S. Vasheghani Farahani and E Vasheghani Farahani. "THEORETICAL DESCRIPTION OF HYDROGEL SWELLING: A REVIEW." (2010).
8. Flory P J & Rehner J (Jr), J Chem Phys, 11 (1943) 521.
9. Bajpai SK. Swelling studies on hydrogel networks—A review. Journal of Scientific and Industrial Research. 2001;60(6):451–462.
10. Lowman A M, Smart Pharmaceuticals, www.gatewaycoalition.org/files/NewEH/htmls/lowman.doc, 7 September 2008
11. Almdal K., Dyre J., Hvidt S., Kramer O.: What is a gel? Macromolecular Symposia, 76, 49–51 (1993).
12. Peppas N. A., Huang Y.: Polymer and gels as molecular recognition agents. Pharmaceutical Research, 19, 578–587 (2002). DOI: 10.1023/A:1015389609344
13. Gao D, Xu H, Philbert MA, Kopelman R, Ultrafine hydrogel nanoparticles: synthetic approach and therapeutic application in living cells, Angew Chem Int Ed, 46, 2224-2227, 2007
14. Bajpai AK, Shukla SK, Bhanu S, Kankane S, Responsive polymers in controlled drug delivery, Prog Polym Sci, 33, 1088-1118, 2008
15. Li H, Ng TY, Lam KY, Modeling and simulation of the swelling behaviour of pH-stimulus-responsive hydrogels, Biomacromolecules, 6, 109-120, 2005.
16. Ganji F, Vasheghani-Farahani E, Hydrogels in controlled drug delivery systems, Iran Polym J, 18, 63-88, 2009.
17. Lowman A M, Smart Pharmaceuticals, www.gatewaycoalition.org/files/NewEH/htmls/lowman.doc, 7 September 2008
18. Tanaka T & Fillmore D J, J Chem Phys, 70(1979) 1214.
19. M. Peleg, "An empirical model for the description of moisture sorption curves," *Journal of Food Science*, vol. 53, no. 4, pp. 1216–1217, 1988.
20. K. G. Kaptso, Y. N. Njintang, A. E. Komnek, J. Hounhouigan, J. Scher, and C. M. F. Mbofung, "Physical properties and rehydration kinetics of two varieties of cowpea (Vigna unguiculata) and bambara groundnuts (Voandzeia subterranea) seeds," *Journal of Food Engineering*, vol. 86, no. 1, pp. 91–99, 2008.
21. K. Górnicki, A. Kaleta, R. Winiczenko et al., "Chapter 16: some remarks on modelling of mass transfer kinetics during rehydration of dried fruits and vegetables engineering," in *Mass Transfer—Advances in Sustainable Energy and Environment Oriented Numerical Modeling*, H. Nakajima, Ed., 2013.
22. Seddiki Nesrine, Aliouche Djamel, Synthesis, characterization and rheological behavior of pH sensitive poly(acrylamide-co-acrylic acid) hydrogels,
23. A. THAKUR et al., Structural Parameters and Swelling Behavior of pH Sensitive ..., *Chem.*

Biochem. Eng. Q. **25** (2) 181–194 (2011)