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Department of Industrial Engineering

Degree course in Food Engineering

Modelling Behaviour of anionic hydrogels

Thesis in

Transport phenomena

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To my Family

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Abstract

Anionic polysaccharides polymers are class of polyelectrolyte hydrogels. They have a wide range of application in the food industry, such as shelf-life extension, flavour release, nutraceutical preservation, and food packaging. Polyelectrolyte hydrogels are linear, slightly crosslinked polymers containing ionizable groups on their backbone. Additionally, they are sensitive to pH changes.

In this work, the monophasic model is used to describe the steady-state behaviour of polyelectrolyte hydrogels. As a result of ionizable groups' existence, there are four contributions in the Helmholtz free energy: the elastic ones, the term of mixing of the solvent with the network, the term of mixing of the ions with the solvent, and the term of dissociation of acidic groups. Electroneutrality assumption also has been considered in this work.

In the comparative study, the model has been used to simulate hydrogels' behaviour reported in the literature. From the results, it can be established that the model's swelling ratios can be calibrated to fit the actual behaviour of the literature findings. This conclusion is evident from the simulation results, as the initial concentration of the ionizable groups present in the polymer chain increased with an increase in the PAA concentration of each gel reported. Comparing the model's results and literature showed a proportional dependence of the swelling behaviour on the number of dissociation groups, indicating the model's realistic results.

Bibliography

1. *Alupei, I.C., et al., Superabsorbant hydrogels based on xanthan and poly (vinyl alcohol): 1. The study of the swelling properties. European Polymer Journal, 2002. 38(11): p. 2313-2320.*
2. *Klein, M. and E. Poverenov, Natural biopolymer-based hydrogels for use in food and agriculture. Journal of the Science of Food and Agriculture, 2020. 100(6): p. 2337-2347.*
3. *Zarrintaj, P., et al., Thermo-sensitive polymers in medicine: A review. European Polymer Journal, 2019. 117: p. 402-423.*
4. *Thakur, S., et al., Recent approaches in guar gum hydrogel synthesis for water purification. International Journal of Polymer Analysis and Characterization, 2018. 23(7): p. 621-632.*
5. *Peppas, N.A., et al., Hydrogels in pharmaceutical formulations. European journal of pharmaceutics and biopharmaceutics, 2000. 50(1): p. 27-46.*
6. *Okamoto, T., et al., Self-assembly of colloidal nanocomposite hydrogels using 1D cellulose nanocrystals and 2D exfoliated organoclay layers. Gels, 2017. 3(1): p. 11.*
7. *Rudzinski, W.E., et al., Hydrogels as controlled release devices in agriculture. Designed monomers and polymers, 2002. 5(1): p. 39-65.*
8. *Mao, L., et al., Design of gel structures in water and oil phases for improved delivery of bioactive food ingredients. Critical reviews in food science and nutrition, 2020. 60(10): p. 1651-1666.*
9. *Shit, S.C. and P.M. Shah, Edible polymers: challenges and opportunities. Journal of Polymers, 2014. 2014.*
10. *Chen, L., G.E. Remondetto, and M. Subirade, Food protein-based materials as nutraceutical delivery systems. Trends in Food Science & Technology, 2006. 17(5): p. 272-283.*
11. *Farris, S., et al., development of polyion-complex hydrogels as an alternative approach for the production of bio-based polymers for food packaging applications: a review. Trends in food science & technology, 2009. 20(8): p. 316-332.*

12. *Abaee, A., M. Mohammadian, and S.M. Jafari, Whey and soy protein-based hydrogels and nano-hydrogels as bioactive delivery systems. Trends in Food Science & Technology, 2017. 70: p. 69-81.*

13. *Catley, B.J. and W.J. Whelan, Observations on the structure of pullulan. Archives of biochemistry and biophysics, 1971. 143(1): p. 138-142.*

14. *Ridley, B.L., M.A. O'Neill, and D. Mohnen, Pectins: structure, biosynthesis, and oligogalacturonide-related signaling. Phytochemistry, 2001. 57(6): p. 929-967.*

15. *Morris, E.R., D.A. Rees, and D. Thom, Characterization of alginate composition and block-structure by circular dichroism. Carbohydrate Research, 1980. 81(2): p. 305-314.*

16. *Suckow, M.A., et al., Alginate microparticles for vaccine delivery. 1999, ACS Publications.*

17. *Souguir, Z., L. Picton, and D. Le Cerf, Anionic polysaccharide hydrogels with charges provided by the polysaccharide or the crosslinking agent. Drug Delivery Letters, 2012. 2(4): p. 240-250.*

18. *Liu, G., et al. The pH-responsive alginate hydrogel prepared through solution extrusion and the release behavior for different drugs.*

19. *Bignami, A.F., Effects of NaCl and alginate concentrations on the rheological properties of aqueous solutions and hydrogels. 2020.*

20. *Casas, J.A., V.E. Santos, and F. Garcıa-Ochoa, Xanthan gum production under several operational conditions: molecular structure and rheological properties ☆. Enzyme and microbial technology, 2000. 26(2-4): p. 282-291.*

21. *Bueno, V.B., et al., Synthesis and swelling behavior of xanthan-based hydrogels. Carbohydrate polymers, 2013. 92(2): p. 1091-1099.*

22. *Piga, A., et al., Interventi tecnologici per la valorizzazione delle olive da tavola della varietà" Manna". 2001.*

23. *Saunders, J.R., et al., Modeling theories of intelligent hydrogel polymers. Journal of Computational and Theoretical Nanoscience, 2008. 5(10): p. 1942-1960.*

24. *Bahram, M., N. Mohseni, and M. Moghtader, An introduction to hydrogels and some recent applications, in Emerging concepts in analysis and applications of hydrogels. 2016, IntechOpen.*

25. *Sundararajan, A., Synthesis and Analysis of Anionic Hydrogel Scaffolds for Endothelial Cell Tissue Engineering. 2005.*

26. *Marcombe, R., et al., A theory of constrained swelling of a pH-sensitive hydrogel. Soft Matter, 2010. 6(4): p. 784-793.*

27. *Hong, W., X. Zhao, and Z. Suo, Large deformation and electrochemistry of polyelectrolyte gels. Journal of the Mechanics and Physics of Solids, 2010. 58(4): p. 558-577.*

28. *Caccavo, D., et al., Modeling the mechanics and the transport phenomena in hydrogels, in Computer Aided Chemical Engineering. 2018, Elsevier. p. 357-383.*

29. *Hong, W., et al., A theory of coupled diffusion and large deformation in polymeric gels. Journal of the Mechanics and Physics of Solids, 2008. 56(5): p. 1779-1793.*

30. *Caccavo, D., et al., Drug delivery from hydrogels: a general framework for the release modeling. Current drug delivery, 2017. 14(2): p. 179-189.*

31. *Drozdov, A.D. and J.d. Christiansen, Modeling the effects of pH and ionic strength on swelling of anionic polyelectrolyte gels. Modelling and Simulation in Materials Science and Engineering, 2015. 23(5): p. 055005.*

32. *Caccavo, D. and G. Lamberti, PoroViscoElastic model to describe hydrogels' behavior. Materials Science and Engineering: C, 2017. 76: p. 102-113.*

33. *Lucantonio, A., P. Nardinocchi, and L. Teresi, Transient analysis of swelling-induced large deformations in polymer gels. Journal of the Mechanics and Physics of Solids, 2013. 61(1): p. 205-218.*

34. *Holmes, D.P., et al., Bending and twisting of soft materials by non-homogenous swelling. Soft Matter, 2011. 7(11): p. 5188-5193.*

35. *Gurtin, M.E., E. Fried, and L. Anand, The mechanics and thermodynamics of continua. 2010: Cambridge University Press.*

36. *Allen, R.J., T.R. Rieger, and C.J. Musante, Efficient generation and selection of virtual populations in quantitative systems pharmacology models. CPT: pharmacometrics & systems pharmacology, 2016. 5(3): p. 140-146.*

37. *Flory, P.J., Principles of polymer chemistry. 1953: Cornell University Press.*

38. *Gronski, W., E. Mark, B. Erman: Rubberlike Elasticity, A Molecular Primer, John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore 1988. 196 Seiten, Preis:£ 23.70. Berichte der Bunsengesellschaft für physikalische Chemie, 1989. 93(10): p. 1149-1149.*

39. *Lee, E.H. and D.T. Liu, Finite-strain elastic—plastic theory with application to plane-wave analysis. Journal of applied physics, 1967. 38(1): p. 19-27.*

40. *Horkay, F. and G.B. McKenna, Polymer networks and gels, in Physical properties of polymers handbook. 2007, Springer. p. 497-523.*

41. *Brannon-Peppas, L. and N.A. Peppas, Equilibrium swelling behavior of pH-sensitive hydrogels. Chemical Engineering Science, 1991. 46(3): p. 715-722.*

42. *Smith, J.M., Introduction to chemical engineering thermodynamics. 1950, ACS Publications.*

43. *Huang, Y., H. Yu, and C. Xiao, pH-sensitive cationic guar gum/poly (acrylic acid) polyelectrolyte hydrogels: Swelling and in vitro drug release. Carbohydrate Polymers, 2007. 69(4): p. 774-783.*

44. *Chen, L.-G., Z.-L. Liu, and R.-X. Zhuo, Synthesis and properties of degradable hydrogels of konjac glucomannan grafted acrylic acid for colon-specific drug delivery. Polymer, 2005. 46(16): p. 6274-6281.*

45. *Dehbari, N., et al., In situ polymerized hyperbranched polymer reinforced poly (acrylic acid) hydrogels. Materials Chemistry Frontiers, 2017. 1(10): p. 1995-2004.*

46. *Hossain, M.A., et al., Improvement of the strength of poly (acrylic acid) hydrogels by the incorporation of functionally modified nanocrystalline Cellulose. Materials Advances, 2020. 1(6): p. 2107-2116.*

47. *Thakur, A., R.K. Wanchoo, and P. Singh, Structural parameters and swelling behavior of pH sensitive poly (acrylamide-co-acrylic acid) hydrogels. Chemical and Biochemical Engineering Quarterly, 2011. 25(2): p. 181-194.*

48. *Safronov, A.P., et al., Enthalpy of Swelling of Potassium Polyacrylate and Polymethacrylate Hydrogels. Evaluation of Excluded-Volume Interaction. Macromolecular Chemistry and Physics, 2004. 205(11): p. 1431-1438.*

49. *Prudnikova, K. and M. Utz, Electromechanical equilibrium properties of poly (acrylic acid/acrylamide) hydrogels. Macromolecules, 2012. 45(2): p. 1041-1045.*

50. *Safronov, A.P., et al., The Influence of Counterion Type and Temperature on Flory-Huggins Binary Interaction Parameter in Polyelectrolyte Hydrogels. Macromolecular Chemistry and Physics, 2009. 210(7): p. 511-519.*

51. *Ricka, J. and T. Tanaka, Swelling of ionic gels: quantitative performance of the Donnan theory. Macromolecules, 1984. 17(12): p. 2916-2921.*

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