Chapter 6
Polymer–Water Interactions in Hydrogels

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Abstract Hydrogels are water/polymer systems that are in high demand due to their broad-spectrum applications in the industrial and bio-medical sectors. A basic hydrogel is a polymer network capable of absorbing a large quantity of water. Water–polymer interactions play a vital role in maintaining the structural integrity, physical properties and overall applicability of the hydrogel system. This chapter focuses on the various water–polymer interactions within the hydrogel matrix, techniques to analyze these interactions and the effects of these interactions on the property of the hydrogels.

keywords Hydrogels · Polymer-water network · Hydrogel matrix · Interactions · Monte Carlo models

1 Introduction

Hydrogels are finding increased applications in various fields such as industry, biotechnology, medicine and environment [1]. They act as building blocks for technological and biological industries, with properties between those of solids and liquids. All these applications exploit various properties of the hydrogel such as integrity, solubility and diffusion of substances [8]. Smart/intelligent hydrogel systems are

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J. Jose et al. (eds.), *Nano Hydrogels*, Gels Horizons: From Science to Smart Materials,
https://doi.org/10.1007/978-981-15-7138-1_6

designed to respond to changes in stimuli [12]. Many applications of hydrogels also make use of their unique mechanical abilities due to random alignment of polymer fibres and large percentage of water within the matrix [28, 29].

Hydrogels are crosslinked water-insoluble polymer networks that are capable of holding a vast amount of water. Depending upon the functional group of the constituent polymer side chains, the hydrogels may be neutral or ionic [23]. The water holding capacity of these three-dimensional polymeric structures is several times their weight (~100 g/g of dry polymer or higher). Integrity of the hydrogels is maintained due to its insolubility in water. Various types of natural macromolecules and synthetic polymers are crosslinked to in order to achieve a stable and water-insoluble network. The crosslinking may be of physical or chemical nature [23]. Some of the natural macromolecules used in preparing hydrogels include alginates, agar, polypeptides and their derivatives. There are a large number of synthetic polymers which can be crosslinked into 3D networks. The selection of a polymer matrix for hydrogel preparation must take into account the hierarchy of water solubilising groups: –OH, –COOH, $–COO^-$, >C=O, $>CHNH_2$, $–CONH_2$, $–SO_3H$, etc., present on the polymer backbone [8]. Water in the hydrogels is essential for maintaining the structure and physical properties of the hydrogel. The interaction between water and polymer is very crucial in determining the overall performance of a hydrogel system. The impact of solvent and polymer on each other is crucial in determining the phase transitions, transport properties and occupancy of water in the hydrogel network [10, 20].

1.1 Ambiphillic and Complex Hydrogel Networks

With the ever-increasing demand for hydrogels, innovative designs have led to the development of hydrogels with superior structural and functional properties. The use of block co-polymers with alternating hydrophilic and hydrophobic polymer domains results in hydrogels with microphase separation. These microphase separated hydrogels find great potential in biological applications. Interpenetrating networks (IPNs) are another way of achieving higher mechanical stability in hydrogel structures [6, 22, 25]. IPNs consist of a binary system in which the polymers are individually crosslinked to achieve microdomains [24]. Poly (ethylene oxide) (PEO) star polymers with a few long arms have been shown to have remarkable swelling abilities [13]. Nanocomposite hydrogels possess nano-sized fillers within the polymer matrix which could impart reinforcement to the polymer network [27].

1.2 Techniques for Investigating States of Components in a Hydrogel

Various experimental methods have been explored to study the physical manifestation of water in polymers. The physical properties and structure of water are usually assessed from binding sites in the polymer and by geometrical confinements [8]. The presence of boundaries and interfaces in the polymer matrix reduces the degrees of freedom as well as the natural order that can be observed in the bulk phase of water. A number of factors are taken into account while evaluating the behaviour of water within the hydrogel system. Bound, unbound/free water as well as freezability and inability to freeze the water is taken into account [11].

NMR studies investigate the difference in property of the various states of water present within the hydrogel matrix [15]. This technique enables detailed investigation of the morphology, molecular organization, interactions and internal mobility of the components of a hydrogel system [26]. Low temperature NMR helps to investigate bound–water dynamics that are closely associated with the hydrogel matrix [8]. NMR and dielectric studies often take into account that the behaviour of water molecules directly bound to the polymer chains (bound water) is significantly different from the behaviour of water that is surrounded by other water molecules (free water).

Raman spectroscopy (RS) has been widely used to study the molecular orientation of water. Molecular vibrations used as a probe in RS have relaxation times ($T = 10$–13–10–‘4 s) that are comparable to the rotational rearrangement of liquid water molecules ($T = 10$–11–10–12 s) [17]. Raman spectrum is sensitive to changes in the structure of water and its small structural domains in the hydrogel network.

Differential Scanning Calorimetry (DSC) provides direct thermal analytic data of the hydrogels. This analysis provides insights into the physical and chemical changes that occur as a result of heat evolved or absorbed during the heating and cooling cycles [16]. The changes in glass transition and crystallization temperatures can be easily followed with the help of this technique [9].

Dilatometry and electrical conductivity measurements are used to study the shrinkage or expansion of hydrogels over a specified range of temperature. It gives an insight into the total volume change as a result of physical or chemical changes [5].

Specific conductivity studies can be carried out using an impedance bridge. The electrical conductivity thus obtained can be used to investigate the correlation between the water content present in the hydrogels and other measurable variables such air permeability [4].

Dielectricrelaxation spectroscopy (DRS) can be used to study the correlation between structural and physical properties of the hydrogel. This technique is very sensitive in determining the critical water contents in the hydrogel system. These values can be obtained from the changes in water or the hydrogel matrix behaviour [14].

Thermally stimulated depolarization current (TSDC) technique is useful in determining the transitions that occur as a function of changes in mobility at the molecular

scale. It is favoured over other thermal analyses due to its high sensitivity. The electrical properties of the hydrogel can be determined through the measurement of thermal relaxation effects [3].

Microscopy especially electron microscopy provides valuable information on the surface morphology and pore structures present in the hydrogels [8].

Studies on diffusion and swelling characteristics of hydrogels can be studied in order to fine tune the design of a hydrogel matrix in order to obtain ideal diffusion control of solute diffusion.

Theoretical methods are employed for hydrogels when the needs for exploring details in an experiment are limited by the resolving ability of the experimental set up. Network structure formation is usually determined by using kinetic models, statistical models and Monte Carlo simulations. Kinetic models, which are mean field models usually, determine the overall properties of the system [21]. The statistical and Monte Carlo models predict in-depth, the network properties and provide detailed insights into the sol and gel states [2, 7].

Such theoretical simulation experiments help to determine the stability, degradation and failure of hydrogel structure. Molecular dynamics (MD) simulation methods have been carried out extensively to determine various aspects of state, structure and dynamics of the binary hydrogel system [30].

1.3 Properties of Water in Hydrogels

Water is primarily responsible for determining the macroscopic states and properties of hydrogels. The state of water in hydrogels in not uniform as it is constrained by the polymer. In the hydrogels matrix, a fraction of water exists in at least three known states such as water bound to the polymer which is non-freezing, another fraction exists as weakly bound which can freeze and another fraction exists as unbound water which is capable of freezing at 0 °C [11]. All these states of water are in turn dependent on the type and amount of solute present. Salinity, pH and the structural property of the solutes affects water behaviour in the hydrogels. The physicochemical attributes of hydrogels depend on the properties of water such as its domain size (including micro and nano-sized domains), electroconductivity and density [8, 11].

The hydrogen bond network among water molecules has been shown to lead to anomalous behaviour in the static and dynamic properties within the polymer network. Such anomalies are investigated using simulation studies such as molecular dynamics (MD) or Monte Carlo (MC) methods. The swelling behaviour of hydrogels is governed by a variety of non-ideal thermodynamic schemes. Swelling in a hydrogel matrix is a complex play between the thermodynamic compatibility between the polymer and water which is counteracted by the crosslinks in the hydrogel, which tries to prevent water absorption by the system [23].

1.4 Properties of Polymer in Hydrogels

The polymer in a hydrogel network comprises about 5–10% of the total hydrogel volume and it acts as a structural scaffold to hold the water inside the network [14]. Some of the properties of the hydrogels are attributed to their pendant polymeric group such the polarity, crystalline nature and supramolecular structure [23]. The transport properties of the hydrogels are influenced by the changes induced in the solvent due to the presence of polymer [20]. The polymer is known to enhance the viscosity of the solvent within the hydrogel matrix and it is dependent on the nature of the solvent [18]. Various simulation and diffusion experiments indicate that water has limited mobility in hydrogels due to the modification of H-bond network structure and dynamics by the polymer [20]. A study involving PVA-water system indicated that the solvation depended on the hydrogen bonds between the polymer and water molecules and the polymer also induced water clustering within hydrogel networks [19]. Raman spectroscopy studies have revealed that the presence of ionic groups in the polymer side chains tends to disrupt the H-bonding between the water molecules leading to unfavourable orientations around the ionic groups of the polymer. However, the presence of hydrophobic side chains tends to make H-bonding between the water molecules stronger and leads to the formation of a stable hydration shell around the hydrophobic polymer chains [17].

It has been observed that polymers of synthetic origin show better mechanical properties due to their complex structural conformations. These conformations lead to higher glass transition temperatures and chain motion is usually restricted below these temperatures [31]. MD simulations of a binary system involving PVA and water indicated that both the components played a crucial role in determining the glass transition properties [30].

2 Conclusion

The design and development of hydrogels has been evolving and continues to reflect the fast paced developments in various fields of science and technology. The simpler hydrogels of yesterday are being replaced by stimuli sensitive and complex structured hydrogels which can perform countless physical, chemical and biological functions. Chemical modification of existing materials to attach or detach various functional groups from the polymer backbones can help create innumerable variations of hydrogels. These complex hierarchical structures are the future for various biomedical applications such as tissue engineering and targeted drug delivery. The complexity of the hydrogel network and their thermodynamic states determines various properties such as diffusivity, chemical/biological interactions, molecular sieve diameter and overall stability.

It is expected that there will be advancements in this field to churn out hydrogels that are technological superior to the currently available ones. The ease of production

and modification will be considered as the benchmark for future applications; this will enable fast and easy synthesis of tailor made hydrogels to suit individual needs. With the increasing complexity in the design of hydrogels, sophisticated analysis techniques will also develop simultaneous to thoroughly investigate such complicated networks. This will also witness the fine tuning of existing models for network predication and probably the development of newer simulation models for studying complex hydrogel structures. Research and development in this field is likely to lead to marked improvement in the quality of life for a worker in an industry as well a patient suffering from a chronic illness.

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