# Chapter 7
# Functional Crosslinked Hydrogels

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**Abstract** In this chapter, the science, technology and applications of functional hydrogels are considered. A brief discussion on fundamental network properties, such as fractal dimensions, network relaxation and stiffness, are given. A large number of synthesis approaches for the manufacture of functional hydrogels are discussed here. The key synthesis approaches which underpin a series of hydrogel variants and their applications are also discussed. An overview of the composition, structure, functionality, characterization and application of a range of functional hydrogels is offered in this chapter, as well as relevant rheological approaches in the synthesis and characterization of these materials are discussed here, paying particular attention to the gelation, sol-gel transitions and multiwave mechanical spectroscopy.

**Keywords** Applications · Characterization · Critical gel · Crosslinking

## 7.1   Introduction

The behavior of functional hydrogels arises from their (micro) structure, which is a three-dimensional (3D) network, created by the chemical and physical crosslinking of monomers/polymers. There are several applications of functional hydrogels, and therefore, any information that can lead to (or promote) an understanding of its fundamental structure, synthesis routes and characterization pathways is essential. Functional hydrogels are often classified from the extent and type of crosslinking, the mechanical properties, the network characteristics, the point of view of their constituent materials and the presence of entanglements and other physical forces. These essential factors control the micro- and macro-behavior of functional

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hydrogels. The structure of functional hydrogels has defined characteristics. This can also be dynamic, depending on the conditions that the material is subject. As a basis for the application of the hydrogel, essential properties such as insolubility, optical clarity, rigidity/stiffness, stimuli responsiveness, swelling and viscoelasticity (tendency or resistance to deformation) are often considered and targeted during synthesis (Tomadoni et al. 2019). The swelling of the material is based on properties such as crosslinking, hydrophilicity and mesh size. The hydrophilicity of the hydrogel network arises due to the presence of hydrophilic functional groups such as amido, amino, carbonyl, carboxylic, hydroxyl, phosphonic and sulfonic functional groups.

## 7.2 Fundamentals of Hydrogel Structure

The structure of the hydrogel is an important property that defines its application. The structure can be made using hydrophilic or hydrophobic components. The hydrophilic nature of the selected materials used to fabricate the structure makes it possible for hydrogels to incorporate water (Laftah et al. 2011). A controlled use of hydrophobic components can thus be used in the manufacturing steps to tailor binding/incorporation of water into the hydrogel structure. The crosslinking of the materials contained in the hydrogel prevents its polymeric structure from dissolving. When such a material is placed in a fluid, swelling is observed, which can cause the final structural geometry to be much larger than the original size (Akhtar et al. 2016).

   Water is the main component in a hydrogel, this allows it to perform several functions and interact with internal or external stimuli. The physical properties of the material depend on how water is retained on the surface and within the material. Water can exhibit different characteristics due to the existence of different states in the hydrogel. Thus, different melting points of water can be observed. Free water melts at 0 °C (Liu and Yao 2001). Secondary water melts at a lower temperature and bound water does not freeze. The relative amounts of water that are maintained in the various states can vary significantly as the swelling extent of the hydrogel structure varies (Quinn et al. 1988).

### 7.2.1 The Critical Gel and the Gel Point

The critical gel also called the incipient gel, is the material at the gel point. The gel point marks the transition point where the starting material changes from a fluid (often viscoelastic liquid) into a viscoelastic solid (Winter 1987). Thus, the gel point marks the beginning of the formation of crosslinked networks in the material, i.e. the gel point is an intermediate state between the liquid and solid states. This is also the critical point in the reaction of the material as it undergoes the phase transition. It is widely considered that at the gel point, the molecular weight (Mw) of the
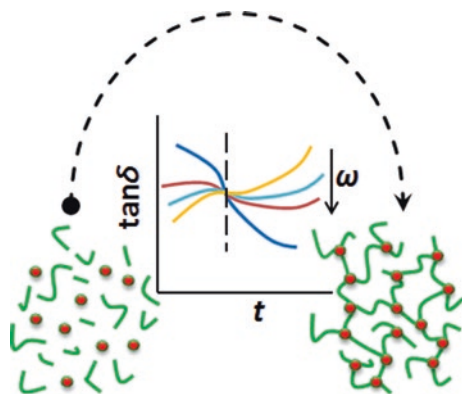
system begins to diverge (Magami and Williams 2018). Therefore, this provides a window through which the molecular flexibility of the formed network clusters can be observed and defined (Chiou et al. 1996). Figure 7.1 shows a rheological inter-section point where the convergence and subsequent divergence of tanδ is observed during the creation of typical hydrogel materials. This intersection point represents the rheological gel point of the material. The time (during creation or synthesis) corresponding to the intersection point is the gel time.

The critical state of the gel also marks the stage at which the mechanical proper-ties of the hydrogel are formed. Thus, at this stage, the material is characterized by properties such as fractal dimensions, mesh size, relaxation exponent and stiffness (Magami and Williams 2019). The relaxation exponent describes the critical micro-structure of the gel and provides an understanding of the dynamics of the macromo-lecular chains and crosslinks that are formed (or begin to be formed) at the gel point. This can be calculated using Eq. 7.1. The stiffness of the critical gel, given in Eq. 7.2, describes how 'soft' or 'hard', in viscoelastic representation, is the critical gel (Chiou et al. 1996). The fractal dimension of the critical gel, given in Eq. 7.3, describes how open/closed or branched the clusters of networks are formed. The value of the fractal dimensions ranges between one and three, which describes the types of sparse/open and dense network, respectively. Therefore, this defines the spatial distribution of macromolecules and crosslinks in the material (Muthukumar 1989).

$$\tan\delta = \tan\left(n\pi/2\right) \tag{7.1}$$

$$G'(\omega) = ST\left(1-n\right)\cos\left(n\pi/2\right)w^{n} \tag{7.2}$$

$$n = d\left(d+2-2D_{f}\right)/2\left(d+2-D_{f}\right) \tag{7.3}$$

where: $d$ is the space-dimension of the material, $D_{f}$ is the fractal dimension, $G'$ is storage modulus, $n$ is the relaxation exponent, $S$ provides the stiffness value, $T$ is the gamma function and $\omega$ is the oscillation frequency. For hydrogels, the value of $d$ is considered to be 3.

### 7.2.2  Microstructure

In addition to the micromechanical properties of the functional hydrogel, which defines the polymer backbone, the characteristics of the liquid component surrounding the network are also critical. The degree of linking up of the macromolecular chains in the hydrogel also defines their microstructure. A polymer network, in which both ends of the polymer chains are connected as crosslinks, with all the crosslinks connected to the polymer network, is an ideal end-linked polymer network and has the highest strength (Patel et al. 1992). The presence of defects in the polymer network, such as loops and dangling ends, reduces the strength of the gel and makes it softer.

The microstructure of the polymer backbone also influences the gel response in the application of a stress/force. The polymer chains are reorganized when a stress is applied, and by removing the stress, the polymer tends to return to its original form (Borzacchiello and Ambrosio 2009). The relaxation time depends on the crosslinking density/Mw/structure of the polymer matrix, as well as the viscosity of the liquid component present. However, not all hydrogels when deformed fully recover their original state. Despite this, the materials act as viscoelastic solids dissipating a certain amount of the energy (Llorente and Mark 1979).

The microstructure can also be described from the point of view of how the pores/clusters are interconnected in the hydrogel. The physical dimensions of the network clusters can dictate the opportunities or limitations that the hydrogel can possess when considered for different applications. Physical restrictions on the hydrogel microstructure can affect the distribution, migration and movement of incorporated molecules (Nair 2016). When spatial arrangements in the microstructure can hinder the subsequent loading of releasable molecules, studies have shown that the hydrogel microstructure can often be designed with a sacrificial component which can allow a defined microstructure. This sacrificial component can then be removed by processes such as targeted enzymatic degradation. The removal of the sacrificial material then improves the porosity of the microstructure and paves the way for the loading of desirable materials (Namba et al. 2009).

## 7.3  Crosslinking in Functional Hydrogels

The design of hydrogels can be achieved using chemical or physical crosslinking, or a combination of both approaches. In the first, chemical crosslinks are formed when the side functional groups of the polymer chains react with the functional groups in the crosslinking agent to form the strong covalent bonds (Hennink and van Nostrum 2012). This ensures the chemical stability and mechanical strength of the formed hydrogels. However, the physical crosslinking physical is the result from the association of adjacent polymer chains through relatively weak forces, such as hydrogen (H) bonds, van der Waals forces and physical entanglements or electrostatic

attractions (Singhal and Gupta 2016). The crosslinking in hydrogels may arise from formulations containing predominantly hydrophilic components or those containing a significant proportion of hydrophobic components.

Hydrogel materials can be assembled from predominantly hydrophobic starting materials such as hydrophobically modified chitosan (Cs) biopolymers (Valencia et al. 2019). When this is reacted with dodecyl groups, in the presence of a β-glycerophosphate disodium salt, a hydrogel material can be observed. Through this preparation procedure, it has been shown that the extents of the reactions and the properties of the crosslinked hydrogel, such as the size of the pores, could be tailored by a combination of hydrophilic and hydrophobic starting materials (Dashtimoghadam et al. 2014). This approach can also be used to create a balance of covalent and non-covalent forces that are required for specific gelation processes. In some cases, the starting material must be modified in order to adapt the hydrogel synthesis. For example, Cs is a very hydrophilic material. This hydrophilicity often needs to be modified using functionalization techniques, such as grafting the biopolymer with several side chains *via* Schiff-base reactions with salicylaldehyde or dodecyl aldehyde materials, followed by reductive amination procedures (Abdulganiyu et al. 2017). Figure 7.2 provides an illustration of a range of molecular interactions that are involved in the gelation of a Cs, hydrophobically modified Cs chains, β-glycerophosphate groups, in a thermoresponsive material. In this, the ionic forces can be seen at play, in addition to the chemical crosslinkers which are formed through functional group interactions.
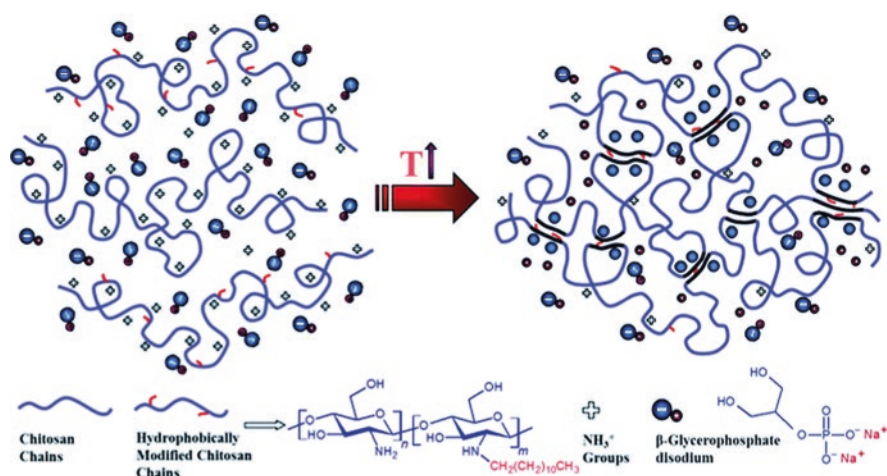


**Fig. 7.2** Interactions involved in the formation of a chitosan-based hydrogel. Reproduced with permission from Dashtimoghadam et al. (2014)

### 7.3.1   Covalently Crosslinked Hydrogels

Hydrogels, when crosslinked by covalent bonds are obtained materials with improved mechanical properties. Due to the strength of covenant crosslinks, the relative movement of macromolecular chains is limited or impeded in the gels. In contrast, hydrogel networks formed from physical interactions are more dynamic. This is because molecular diffusion is very possible in physically crosslinked hydrogels. In the design of hydrogels with target mechanical strength, therefore, care must be taken to ensure that the flexibility, rigidity and stiffness of the final hydrogel is controlled. This can be done using a balanced or near-balanced stoichiometry of reactant species. In covalently crosslinked hydrogels, the growing macromolecular chains arising from the reaction of monomers, dimers, oligomers, polymers and crosslinkers are reacted covalently, which leads to the formation of an interconnected micro-molecular structure (Magami 2020). Figure 7.3 depicts covalent reactions, crosslinking and branching in a hydrogel formulated using monomeric acrylic acid (AA) and crosslinkable *N*,*N'*-methylenebisacrylamide. All these reactions/interactions lead to the creation of a 3D material.

### 7.3.2   Ionically Crosslinked Hydrogels

Functional hydrogels can be manufactured when metal cations are incorporated into suitable polymerization matrices (Koohi et al. 2011). This leads to the formation of 3D network clusters which arise due to the chelation of the macromolecular chains by the incorporated metal ion(s) (Higham et al. 2014). An important factor to be considered in the ionic crosslinking of hydrogels is the solubility of the chosen metal specie (Magami and Williams 2019b). Effective crosslinking in aqueous systems can be achieved using cationic species including $Ca^{2+}$, $Mg^{2+}$, $Cu^{3+}$ and $Fe^{3+}$ (Bai et al. 2011a). The reactivity of the starting material can be dictated by the type of metal salt chosen. A limitation often associated with the preparation of ionically crosslinked hydrogels is the solubility of some of the metal salts (Ma and Elisseeff 2005). Metal oxides and metal hydroxides often have limited solubility in water-based hydrogels, due to the chemistry of their dissociation and their tendency to precipitate. Recent studies have shown that it is possible to calculate the solubility of metal hydroxides, oxide-hydroxides and oxides as a function of the equilibrium pH of the solutions, while considering the formation of several anionic and cationic species of metal ions (Scholz and Kahlert 2015). This can serve as a guide in the selection of starting metal-based compounds when formulating hydrogels. When the metal-based compound has undesirable hydrolysis tendencies, the Pechini process is often considered (Pechini 1967). This process allows the formation of metal-polymer bonds during *in situ* polymerization of suitable polymeric systems. With this technique, coatings, complexes, fibers, films and gels of transitions metals and non-transition metals can be synthesized (Dimesso 2018).
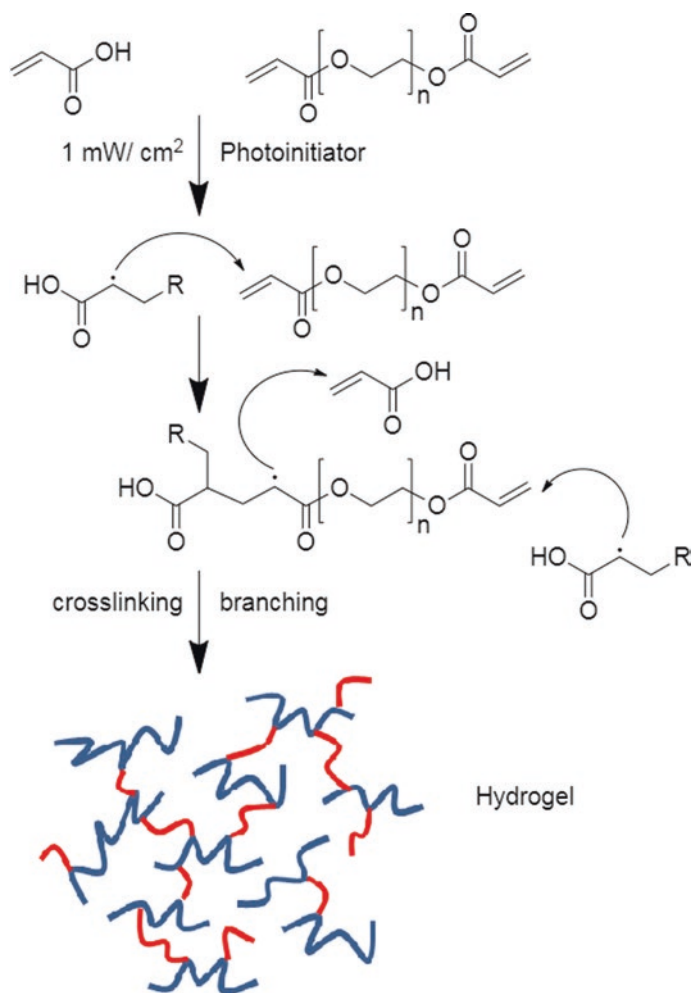
**Fig. 7.3** Reactions involved during the polymerization and crosslinking reaction between AA and *N,N′*-methylenebisacrylamide. Reproduced with permission from Magami and Williams (2019a)

## 7.3.3 Entanglement in Hydrogels

Hydrogel networks can be formed through the physical entanglement of macromolecular chains. The entanglement in polymers and gels is often described in a too simplified manner, because the dynamics of entangled polymers require an approach where the macromolecular movement and relaxation of chains must be obtained in real space at different length and time scales (Abadi et al. 2018). One way to differentiate entangled bonds in hydrogels from covalently maintained networks is the

stress relaxation in the former. Stress relaxation can occur in entangled hydrogels due to relatively weaker forces holding the network together. When the material is strained, the generated stress is dissipated over time, i.e. the stress relaxation in entangled hydrogels is produced through a reptation mechanism, where a strain applied causes macromolecular chains to diffuse and glide pass each other in 'tubes' created by neighboring chains (Wyss 2016).

The entanglement in hydrogels can offer the advantage of producing materials *in situ*. In stimulus-sensitive hydrogels, in typical biomedical applications, entanglement chains can form as a response to changes in the environment, such as temperature (Zarrintaj et al. 2019). Entangled hydrogels can offer ease of degradation. This may be particularly important for *in vivo* applications where subsequent biodegradability is an essential characteristic/requirement (Khan et al. 2015).

## 7.4   Composition of Functional Hydrogels

Functional hydrogels are assembled using a variety of starting materials, including crosslinking agents, initiators and monomers (Xu et al. 2018). A hydrogel, depending on the target application, may contain other components derived from materials such as drugs, inorganic salts, pharmaceutical agents and soil conditioners. Figure 7.4 shows the relationship between maintaining the hydrogel starting components.
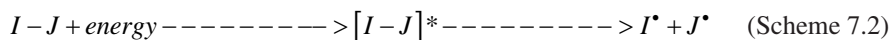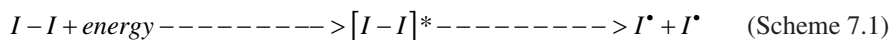
*Initiators:* the role of the initiator molecules is to initiate the polymerization/crosslinking reactions which will ultimately lead to the formation of the hydrogel. Three main mechanistic routes have been indicated by which molecules that absorb energy from light can generate free radicals or ions and potentially initiate a polymerization reaction. The first route is by homolytic dissociation of a bond of an

**Fig. 7.4** Illustration of key hydrogel starting materials in a typical polymerization set up. Reproduced with permission from Ahmed (2015)
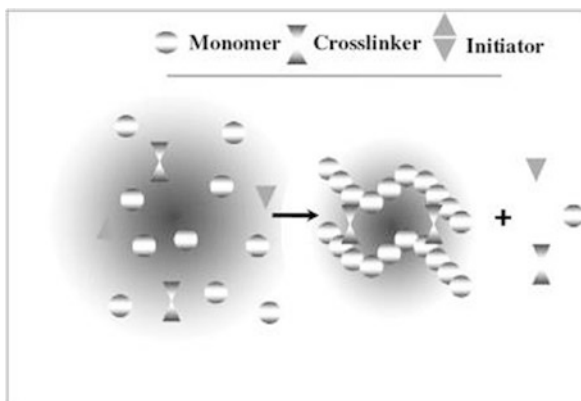
excited molecule in the absorption of photons (Gruber 1992). The example given in Scheme 7.1 involves a symmetric initiator molecule while the one given in Scheme 7.2 involves an asymmetric molecule.

$$I - I + energy \, - - - - - - - - > [I - I]* \, - - - - - - - - - > I^\bullet + I^\bullet \quad \text{(Scheme 7.1)}$$

$$I - J + energy \, - - - - - - - - > [I - J]* \, - - - - - - - - - > I^\bullet + J^\bullet \quad \text{(Scheme 7.2)}$$

The second pathway is by the transfer of energy, from a molecule that had absorbed light energy, (but not enough to cause dissociation of bonds) to another molecule (Yagci et al. 2010). In Scheme 7.3, M-M acts as the energy receptor molecule.

$$PS + energy \, - - - - - - - > [PS]* \, - - - - + (M - M)$$
$$- - - - - > M \, PS + M^\bullet \quad \text{(Scheme 7.3)}$$
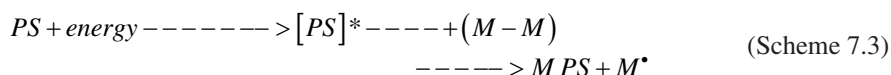
The third mechanism is by hydrogen abstraction from a hydrogen atom-donating molecule (McGinnes 1982). In Scheme 7.4, M-H acts as the hydrogen donor. This is shown in Scheme 7.4.

$$PS + energy \, - - - - - - - > [PS]* \, - - - - - + (M - H)$$
$$- - - - > PSH + M^\bullet \quad \text{(Scheme 7.4)}$$
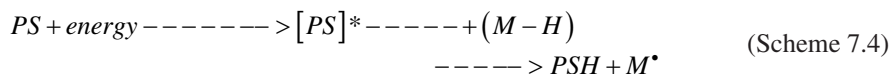
**Salts and Other Ionizable Species** in addition to the functions that salts can play at the start of polymerization reactions, they can also be incorporated into hydrogels in order to help determine how water is maintained in the microstructure of the hydrogel. The hydration enthalpy of ionizable species varies from one composition to another and governs the amount of water that can be maintained in the hydration sphere of the relevant ion. Thus, the appropriate salt(s) can be selected to tailor the target application. Figure 7.5 shows how water can interact with a range of anions and cations. The hydration enthalpy values of various anions and cations are given in Tables 7.1 and 7.2, respectively.
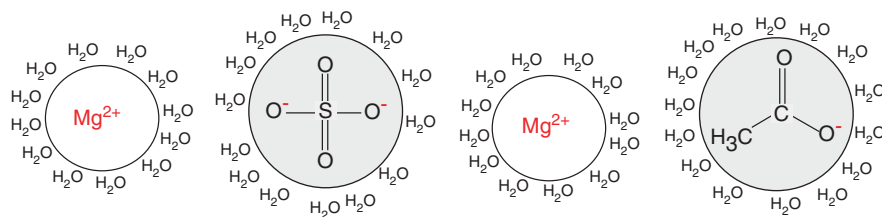


**Fig. 7.5** Illustration of the interaction that can exist between water and various ionic species in a functional hydrogel

**Table 7.1** Hydration enthalpy of a selection of cations

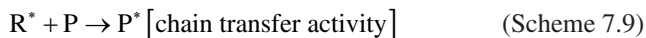| Ion | $H^+$ | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Zn^{2+}$ | $Fe^{2+}$ | $Sn^{2+}$ | $Al^{3+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\Delta H$ (kJ/mol) | -1130 | -444 | -361 | -307 | -2003 | -1657 | -2046 | -1946 | -1554 | -4446 |

**Table 7.2** Hydration enthalpy of a selection of anions

| Ion | $OH^-$ | $F^-$ | $Cl^-$ | $Br^-$ | $I^-$ | $NO_3^-$ | $CH_3COO^-$ |
|---|---|---|---|---|---|---|---|
| $\Delta H$ (KJ/mol) | -460 | -483 | -340 | -309 | -296 | -314 | -425 |

## 7.5 Routes for the Synthesis of Hydrogels

The synthesis of hydrogels can be achieved by a chain growth polymerization reaction, by a ring opening polymerization (ROP) reaction and by a step growth polymerization reaction. The most common method of polymerization by which hydrogels are produced is that of free-radical chain growth polymerization. This is mainly because of the unsaturated nature of monomers used in the typical hydrogel synthesis. The technique involves the use of free radicals from initiators that are generated by exposure to ultraviolet (UV) or gamma radiation and/or thermal initiators together with monomers and crosslinking agents. Free-radical polymerization reactions, carried out using UV and gamma irradiation, are known as radiation induced polymerization reactions.

The main steps involved in free-radical polymerization reactions are initiation, propagation, termination and chain transfer (Magami and Abdulganiyyu 2017). These are illustrated in Schemes 7.5, 7.6, 7.7, 7.8, 7.9.

$$PI + hv \rightarrow PI^* \left[ \text{initiation step} \right] \qquad \text{(Scheme 7.5)}$$

$$PI^* + M \rightarrow PI - M^* \left[ \text{chain propagation step} \right] \qquad \text{(Scheme 7.6)}$$

$$M^* + P \rightarrow P^* \left[ \text{chain propagation} \right] \qquad \text{(Scheme 7.7)}$$

$$M^* + P^* \rightarrow P \left[ \text{chain termination} \right] \qquad \text{(Scheme 7.8)}$$

$$R^* + P \rightarrow P^* \left[ \text{chain transfer activity} \right] \qquad \text{(Scheme 7.9)}$$
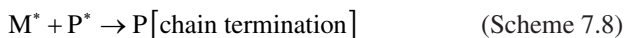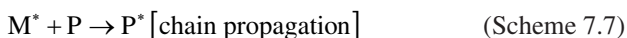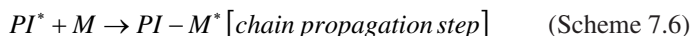
where * represents a free radical, *hv* denotes the energy of the incident radiation, *M* represents the monomer, *P* is the polymer chain, *PI* is the photoinitiator and *R\** is any free radical. Free radical polymerization of hydrogels, as is the case with other polymeric materials, is affected by several factors, including dissolved oxygen in the reaction mixture, as well as the type of crosslinker, photoinitiator and monomer, in addition to the concentration of these species. The oxygen inhibition of the reaction can take many forms, including the quenching of the excited states and the formation of a peroxyl radical. The formation of peroxyl radicals is a problem, since the radical cannot attack vinyl functional groups and maintain propagation (Ligon et al. 2014).

During the induction period, cleavage of the intramolecular bond is likely to occur. In the initiation stage, the generated radicals attack the monomer molecules (Matyjaszewski et al. 1998). Chain propagation and crosslinking are established and continue beyond the gel point. These processes lead to the formation of networks, macromolecular advancement and development, as well as the increase of viscoelastic properties. The crosslinking reaction and network branching continue until the network is fully formed. This is typically indicated when the elastic modulus has reached a plateau state.

## 7.6 Characteristics of Functional Hydrogels

Once the hydrogel has been produced, subsequent treatments and use require knowledge of the actual water content, the degree to which the polymerization has taken place, the number of crosslinks, the structure of the polymer network and the thermal properties and other characteristics of the hydrogel. Various analytical techniques have been used to answer questions related to the arrangement and location of the pendant groups, the degradation of the hydrogels, the degree of polymerization/crosslinking and conversion of monomers, the structure of the generated polymer and the thermal behavior.

### 7.6.1 Swelling Characteristics

The swelling characteristics of hydrogels allow them to increase their volume up to several times their original size, by absorbing and accommodating liquid component into their microstructure (Mathur et al. 1998). The swelling of the hydrogel depends mainly on the degree of crosslinking in the gel, but also increases by the hydrophilicity of the polymer matrix. These two factors dictate the equilibrium swelling point (Hoffman 2012). A higher extent of crosslinking results in smaller pores and a lower equilibrium swelling point. This will be relevant to most hydrogel applications, since water will usually have a key role in the desired function. Therefore, the amount of water in the matrix is an integral property of the application. Swelling with ionic hydrogels such as those based on poly(acrylic acid) (PAA) and/or poly(acrylamide) is observed. The carboxylic acid moiety of PAA is ionized in an environment of increased pH, which increases swelling. The opposite is observed in poly(acrylamide)-based compositions, where the decrease in the pH increases the swelling properties (Brannon-Peppas and Peppas 1991).

The volume fraction of a swollen hydrogel is a measure of the water retention capacity of the hydrogel, i.e. the amount of water that the hydrogel can contain with maximum swelling. The volume fraction compares the volume of the non-swollen hydrogel with the volume of the swollen hydrogel (Lin and Metters 2006). It is, therefore, an inverse relationship of the equilibrium volume swelling ratio, given by Eq. 7.4. The volume fraction can be determined using Eq. 7.4.

$$V_f = \frac{V_u}{V_s} = \frac{1}{\left[1 + \frac{\rho_1}{\rho_2}(Q-1)\right]} \tag{7.4}$$

where $Q$ is the equilibrium mass swelling ratio, $V_f$ is the volume fraction, $V_s$ is the equilibrium swollen material, $V_u$ is the volume of the pre-swelled hydrogel, $\rho_1$ is the density of the underlining polymer material and $\rho_2$ is the density of the medium.

### 7.6.2 Optical Properties

Optical clarity and freedom from color are basic requirements for hydrogels that are prepared for use in double glazed units (Oh and Myungjin 2009). In many cases, the hydrogel material in the double-glazed assembly confers fire resistance property to the unit. The monomer and other precursors are carefully selected so that none absorb light in the visible region of the electromagnetic spectrum. In addition, materials that change color or lose their transparency in moderate temperature changes cannot be used in the synthesis stages.

In biomedical applications, the use of hydrogels in the (re)filling of lenses requires meeting strict refractive index requirements. It is known that in the natural lens, the refractive index gradually decreases from the center of the lens to the equator. When (re)filling of lenses is required across a natural lens, and a hydrogel with uniform refractive index is used, an undesirable optical aberration may arise (Ding et al. 2006). Therefore, this provides a challenge in the formulation and application of functional hydrogels for these applications. The transport of oxygen to the lens is critically important. The microporosity of many hydrogel matrices is suitable for this purpose, and thereby, allows enough diffusion of oxygen over the lens. A simple and fast method for the manufacture of contact lens is given as an illustration in Fig. 7.6.

### 7.6.3 Mechanical Properties

The mechanical properties of functional hydrogels are some of the key reasons for their varied applications. Hydrogels are often evaluated and described using terms such as compressive strength, fracture energies, fracture strains, tensile strength and toughness (Ma et al. 2016). Thus, an understanding of the mechanical properties of hydrogels is very important and provides information about their underlining structure and how such a structure is or may be paramount in a chosen application.

The tensile strength of hydrogels is tested when the material is subjected to a constant or varied force, under stress conditions. The corresponding response of the material is then defined by how it yields to the applied forces or by how it elongates
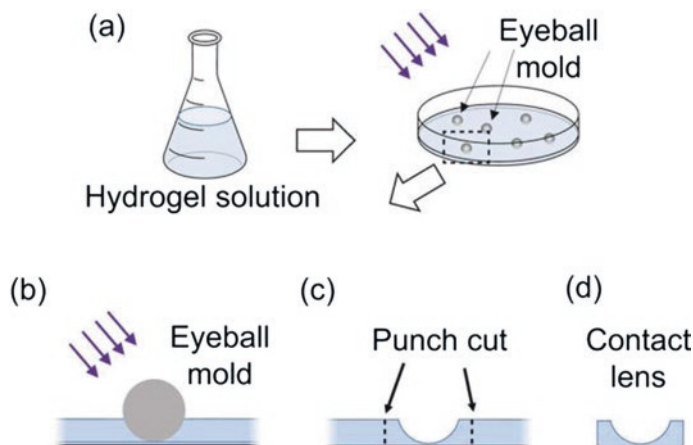
**Fig. 7.6** Schematic illustration of the manufacture of hydrogel contact lens, using Petri dish and steel balls as eyeball molds. Reproduced with permission from Childs et al. (2016)

or by how it deflects physically (Drury et al. 2004). The work required to cause these changes in the material is then estimated, having known its pre-test dimensions. Similar information is obtained from compression tests. However, in this case, the material is subjected to the applied forces under compression conditions (Stammen et al. 2001).

The mechanical properties of a hydrogel can be tuned by varying the composition and the amount of constituent starting materials. However, care must be taken during the synthesis to ensure that other essential properties, such as clarity, extent of swelling and porosity, are not compromised. Figure 7.7 shows that the composition of the starting materials in bio-ionic liquids conjugated with gelatin and methacryloyl/poly(ethylene glycol) diacrylate can be tailored during the visible light crosslinking reactions (Noshadi et al. 2017). In this sense, by increasing the final concentration of polymer, as well as the polymer/bio-ionic liquid ratio, the compressive moduli of the resulting hydrogels increased. This also shows that the increase in polymer concentration affects the elastic moduli of the various materials in similar extents, when the tests were conducted in tension mode. Clearly, in this example, the extents of the crosslinking reactions and network formation were improved as a result of the increase in the number of reactive polymer groups.

## 7.6.4   Stimulus Response

The stimuli-responsive nature of many hydrogels allows their applications in sensors and actuators. This paves the way for their applications in various technologies. There are many examples of electrical-signal-responsive, pH-responsive, solvent-sensitive and thermo-responsive hydrogels (Ahn et al. 2008; Zarrintaj et al. 2019).
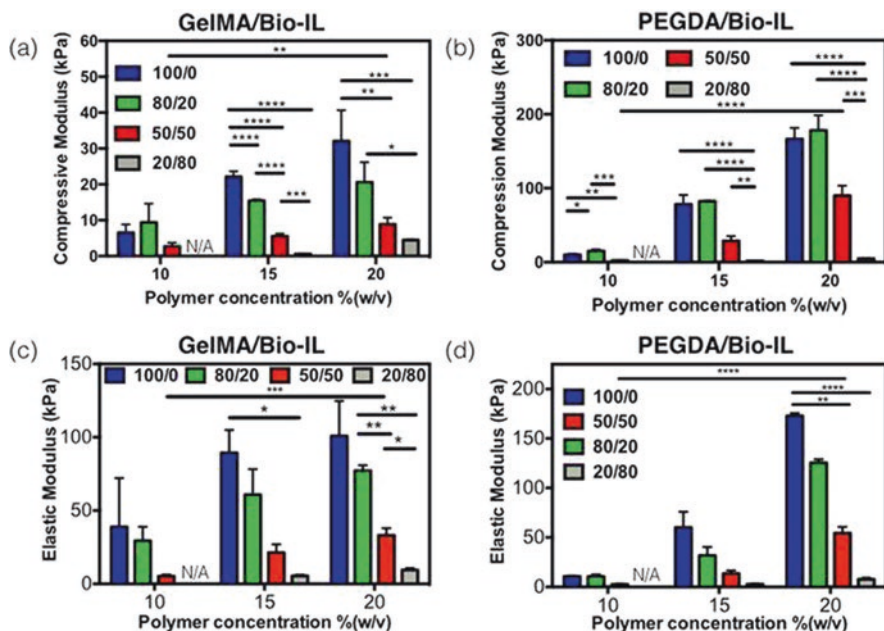
**Fig. 7.7** Compressive modulus of various hydrogel compositions depending on the polymer concentration. Reproduced with permission from Noshadi et al. (2017)

In all these cases, when the stimuli are applied or removed, changes in the hydrogel material occur. These changes are typically reversible and can lead to chemical, mechanical or physical alterations in the material. A temperature-induced phase change is used (below) to provide a general description of the stimuli-responsiveness in hydrogels.

Certain hydrogels may exhibit temperature dependent light transmittance. Figure 7.8 shows a temperature *vs* light transmittance relationship at 450 nm for an AA-based hydrogel, where the hydrogel exhibits a temperature dependent light transmittance. In this sense, the hydrophilic/hydrophobic nature of the polymer's backbone plays a central role, which leads to optical transitions where the hydrogel is seen as clear or as cloudy, depending on the prevalence of hydrophilic or hydrophobic interactions (Magami 2017). Below a certain temperature (the critical temperature), the hydrogel remains clear and transparent, suggesting that hydrophilic interactions, such as H-bonding between water and polar functional groups that are present in the matrix, such as –COOH and –C=O, are dominant. As the temperature changes (usually increased), these hydrophilic interactions are reduced, allowing any cation that may be present (such as $Ca^{2+}$, $Mg^{2+}$, $Al^{3+}$) to form a complex with the ionic macromolecules that are present (such as poly(carboxylate) ions). When such complexation occurs, the composition of the hydrogel becomes more hydrophobic in nature, which leads to precipitation or phase separation, resulting in cloudiness. In addition, Magami (2017) showed that when the concentration of
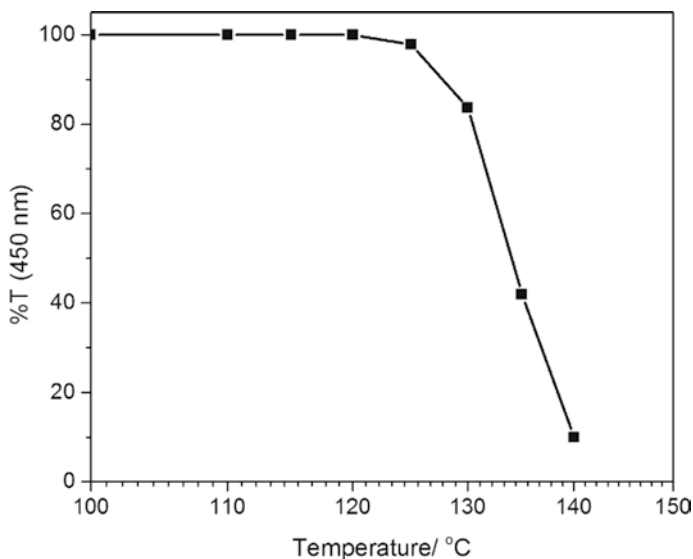
**Fig. 7.8**  Temperature *vs* light transmittance (showing 450 nm) of AA-based hydrogels. Reproduced with permission from Magami (2017)

β-acryloxypropionic acid is increased, the optical clarity of the hydrogel at the test temperature increases markedly, reaching a 100% light transmittance. Thus, the carboxyl groups in the hydrogel material can form strong H-bonds with water molecules in both ionized and protonated form. When strong enthalpic interactions occur in these hydrogels, the criterion of lower critical solution temperature (LCST) is met (Ruel-Gariépy and Leroux 2004; Shen et al. 2019).

The LCST phenomena in acrylate hydrogels can be dictated by varying a series of parameters such as ionic strength, pH, nature of anion and cation, and by copolymerizing with hydrophobic or hydrophilic (ionic, non-ionic) monomer. Thus, simple changes to the polymer backbone can significantly affect the degree to which the ionic interactions are formed, broken or sustained. The LCST of hydrogels can also be influenced by changing the polymer backbone through copolymerization. For example, 2-carboxyethyl acrylate (higher pKa value) can be copolymerized with AA to achieve hydrogels. The difference in pKa value between the two monomers is enough to affect the pH of the solution formulations. At elevated temperatures, the carboxyl groups of poly(carboxyethyl acrylate) (PCEA) would remain protonated, which would lead to a reduction in hydrophobic complexation by any ionic species that might be present, by maintaining their hydrophilic interactions with water molecules *via* H-bonding. Thus, intramolecular H-bonding and the intermolecular bonding between cations and carboxylate groups of either the PAA or the PCEA species that are attached to the polymer backbone play a role in the LCST phenomenon (Magami 2017).

## 7.7 Characterization Methods

There are several characterization techniques which are applicable to the characterization of functional hydrogels. Often, the choice of the characterization technique is influenced by the required application of the material. Typically, hydrogels are characterized in different stages: during synthesis and post-preparation. During synthesis, crosslinking, structure development and transparency can be monitored. It may be important, post-preparation, to differentiate the type of network that is characteristic of the test material. For example, a mechanical spectrum or viscoelastic spectrum from a test material could reveal whether it is simply a dense polymer or if it is composed of entangled network or chemical crosslinks.

### 7.7.1 Spectroscopic Analysis Methods

Spectroscopic analysis methods provide insight into the structure and composition of polymers, through the excitations of electrons or atom groups, when irradiated with a source of electromagnetic radiation. In addition, the spectroscopic analysis of residual materials in the hydrogel can be vital in understanding how they can affect performance properties. For example, the presence of residual initiator molecules/ fragments may affect the long-term stability and aging characteristics of the hydrogel material.

Generally, an infrared spectrophotometer is used to analyze the transmitted light after the molecules in a polymer sample have absorbed radiation in the infrared region of an electromagnetic spectrum. The radiation absorption by molecules in this region causes bending, stretching and molecular vibrations occurring at different frequencies that are unique to the nature of the bonds and atoms present (Stuart 2015). UV-visible spectroscopy has also been widely used to study the structure-performance properties of hydrogels. While this is typically relevant for optical applications of hydrogels, the technique has proven useful for obtaining the absorbance spectra of components of functional hydrogels (Hebeish et al. 2013). In this way, the conversion of reactive species in the hydrogels can be monitored and evaluated.

Raman spectroscopy is another technique that can be used to identify chemical bonds and subsequently analyze the composition of functional hydrogels (Pastorczak et al. 2009). A notable advantage that Raman spectroscopy has over other spectroscopic techniques is that Raman spectroscopy is not affected by water. This technique can thus be used to analyze hydrogels in their swollen form. Raman micro-spectroscopy can be used to evaluate differences in the 3D structure of

different hydrogels (Hwang and Lyubovitsky 2013). This can be valuable in assessing the effects of different formulations on the final hydrogel product.

## 7.7.2    Microscopic Analysis Methods

Microscopy can allow obtaining valuable information on hydrogel materials (Liao et al. 2008). These include pore sizes, porosity, network homogeneity or inhomogeneity. Figure 7.9 shows a microscopic image of a collagen hydrogel network. In this sense, an interconnected network mesh can be observed, as a representation of the crosslinked network in the material. To perform scanning electron microscopic (SEM) analysis in hydrogels, test samples are commonly immersed in water to swell. This is usually carried out at room temperature. After equilibrium swelling in water is achieved, the test samples are then dehydrated using the lyophilization technique. The cross-section of the samples is then coated with a thin layer of gold or platinum before making the measurements. Using an SEM instrument, an accelerating voltage (kV) of the electrons is then used. The voltage used depends on the topographic information sought. To obtain deeper information from the material, a higher energy of the accelerating electrons may be required. However, very high energy electrons penetrate deeper into the sample and decrease the yield of secondary electrons, thus lowering surface detail/resolution. In addition, the use of high energy electrons can cause damage to the test samples. This can be disadvantageous particularly when analyzing biological samples.

When SEM images are combined with X-ray diffraction (XRD) spectroscopy, the elements on the surface of the hydrogel can be mapped and evaluated (Bai et al.



**Fig. 7.9**  SEM of a collagen gel network, with a 5 μm scale bar. Reproduced with permission from Holder et al. (2018)
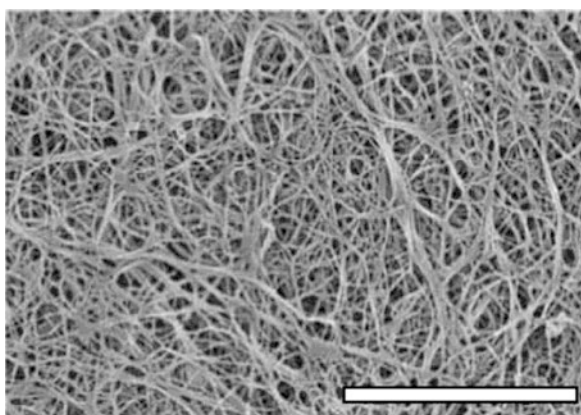
2011b). A map of the distribution of the various elements on the surface of the hydrogel can determine the distribution of materials, such as enzymes, pharmaceuticals and salts, in the hydrogel. When the mapping of high density elements is required, higher acceleration voltages may be preferred, in order to improve the X-ray performance (Niranjan et al. 2013).

### 7.7.3 Methods of Rheological Analysis

Hydrogels belong to the group of viscoelastic polymers. They may also exhibit some degree of elasticity in their swollen state, along with limited flow properties (Liu et al. 2015). This elastic behavior of the hydrogels depends not only on the water content but also on the type of polymerization that has taken place in the formation of the polymer networks, the cross-link density and the presence of any impurities. However, this degree of elasticity, translated as a degree of swelling, can be affected by a number of factors, such as the crosslinking density, the polymerization conditions and the presence of comonomers or insoluble inorganic species (Vural et al. 2010). An increase in the degree of swelling of hydrogel inversely affects the mechanical and flow properties of the composition.

The viscoelastic properties of hydrogels are commonly evaluated by rheological measurements. In this context, test specimens are typically subjected to stress-strain conditions. The response of the specimens to the applied forces is often expressed using a series of parameters, including loss modulus (G''), phase angle ($\delta$), G' and tangent delta (Anseth et al. 1996). The G' describes the elastic behavior of the material, through its ability to conserve the energy applied. However, G'' describes the flow tendency of the material, through its ability to dissipate the applied energy. The
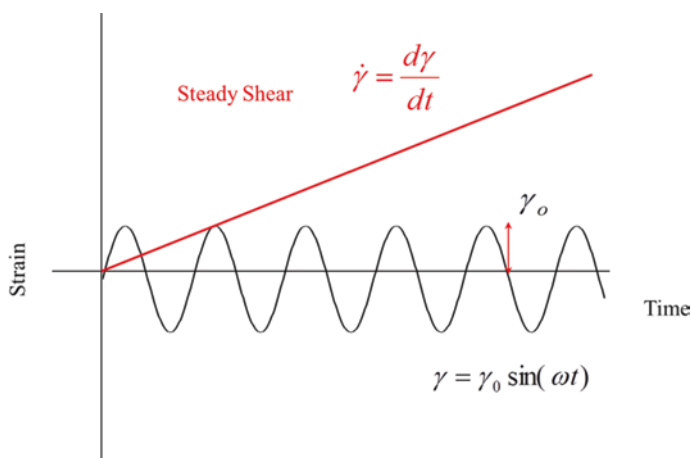


**Fig. 7.10** Small amplitude diagram, showing strain-time relationship

tangent delta combines the effects of the storage module and the loss module, in the same way that the $\delta$ does. In addition, these describe the in-phase or out-of-phase time relationship between the applied stress and the resulting strain, or vice-versa. The strain-time relationship is given in Fig. 7.10. In this sense, a small amplitude shear diagram is illustrated, where $t$ is the oscillation time and $\gamma_o$ is the strain amplitude. Constant shear is then given as the rate of change of strain over time. The applied sinusoidal strain and the generated stress are further described by the relationships given in Eqs. 7.5 and 7.6, where $\tau$ is the shear stress. The implications of the stress-strain relationship in hydrogels can be directly related to the effect of creep and the frequency response of the material (McKeen 2009).

$$\gamma = \gamma_o \sin(\omega t) \tag{7.5}$$

$$\tau = \tau_o \sin(\omega t + \delta) \tag{7.6}$$

### 7.7.4   Sol-Gel Transition and the Gel Point

Rheological methods are often used in determining the gel point of hydrogels, thus leading to an understanding of the sol-gel transition. Common techniques used for the gelation study of functional hydrogels are given in Table 7.3. The Chirp method and the multi-wave technique are more commonly used, compared to the other two techniques, when the gel point of the critical gel is identified. When the determination of the gel point becomes difficult, the stain approximation approach can be used as a complementary method. This monitors changes in strain during the gel synthesis and considers the point of sharp decline in strain as the gel point. The moduli crossover technique is a less accurate method of determining the gel point compared to the other techniques, especially when stoichiometric imbalance is a factor in the reaction. This technique considers the time corresponding to the crossover point of G' and G" during the synthesis steps (Magami and Williams 2019).

The multi-wave technique is highly accurate even where the relaxation exponent value is n < 0.5 or n > 0.5. It could be carried out using stress or strain time sweeps in a method considered as the Fourier transform mechanical spectroscopy (Hawkins et al. 2008). To maximize data quality, frequency ranges are carefully selected. These depend largely on the viscosity and reactivity of the test material, in addition to the mutation of the rheological data (Williams and Williams 1997). Sinewaves with different frequency values are shown in Fig. 7.11, with their combined image in Fig. 7.12. In the multi-wave techniques, a limitation may be the use of sinewaves with low frequency values. This is because the low frequencies correspond to long experimental times. This also means that the interval between observed data points is long to allow the material to change. Even at the gel point, the material typically experiences a characteristic stress relaxation. One way to ensure that the rheological data generated is significant/meaningful is to ensure that the mutation number

**Table 7.3** Typical methods used to establish the gel point of functional hydrogels

| Typical methods | Brief notes | Reference |
|---|---|---|
| Chirp(s) technique | $\omega$ increases or decreases over time. Quick acquisition of data compared to multi-wave technique. Time and frequency resolution are effectively achieved. Stress amplitude or strain amplitude of the individual frequencies do not require adding up. | Geri et al. (2018) |
| Multiwave rheometry | Fundamental and additional oscillation frequencies are required. These are kept constant while the material is subjected to controlled stress or strain at each frequency. Thus, cross-over of modules can be observed and compared as a function of frequency. | Jiao et al. (2012) |
| Strain decrease method | The point of intersection is controlled during the sharp decrease in strain. Method is less precise compared to Fourier transform methods, and therefore, is largely a complementary technique. | Bonino et al. (2011) |
| Moduli crossover technique | Relatively easy technique. Only valid for systems where the value of relaxation exponent n = 0.5. Data can be obtained from measurement at single frequency of oscillation. | Ishida and Allen (1996) |

criteria is met (Mours and Winter 1994). A mutation number value of <1 often indicates that rheological data points are collected within reasonable time intervals and that the test sample does not change significantly in the range of the data points.

As the structure develops in the possible gel and the crosslinks are formed, a crossover point is observed in the multi-wave plots of loss tangent delta (tan $\delta\Delta$) *vs* time. This crossover point is the gel point of the material, where the G' and the G" have the same variation of the power law with respect to the $\omega$. This is the so-called Winter-Chambon criteria (Chambon et al. 1986).

## 7.7.5   *Other Characterization Methods*

Thermal analysis techniques, such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) can be quite useful in the characterization of functional hydrogels (Thermal Analysis of Polymers 2009). In addition to the thermal stability that can be determined using TGA, the water bonding in the hydrogel network can be determined. Slightly bound water is easily lost during controlled heating, while tightly bound water is usually retained but is lost after excessive heating of the sample. On the other hand, DSC can be used to determine the influence of crosslinking on transition temperatures in hydrogels (Neto et al. 2005). However,
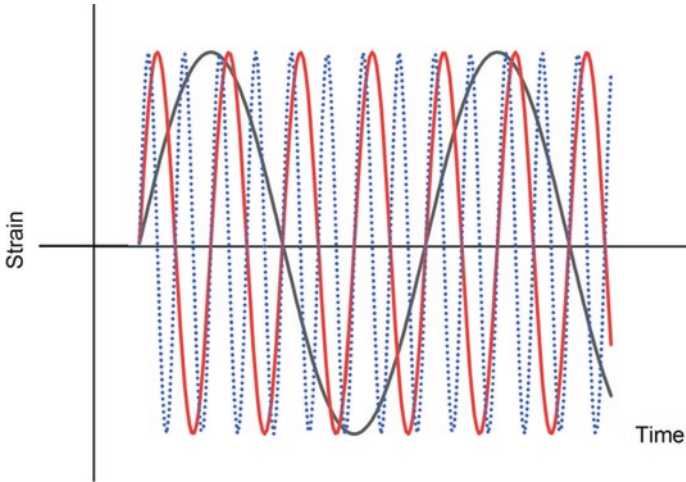
**Fig. 7.11** Sinewaves with different frequency values, having the same strain amplitude value



**Fig. 7.12** Sinewaves from Fig. 7.11 combined into a single wave screen
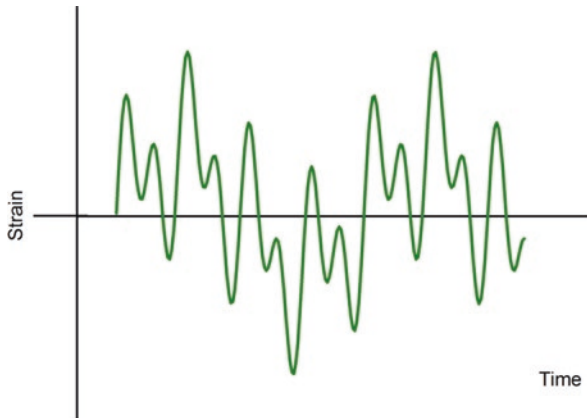
in highly crosslinked hydrogels, transition temperatures are very difficult to be observed. When the network of the hydrogel material is highly dense, it is unlikely, if not impossible, that despite heating of the material, stiff crosslinks and rigid network clusters impede mechanical movements (Wu and Freeman 2009).

### 7.7.6  Practical Notes

1. If there is enough material, it is good practice to conduct the analysis of hydrogel samples in duplicate or triplicate. This can ensure confidence in that the statistical significance of the effects in structure-property relationship is determined.
2. It is not good practice to allow hydrogels to dry before lyophilizing them prior to microscopic evaluation. This can cause shrinkage in pore sizes.
3. Performing DSC experiments in a sealed pan can cause damage to the instrument, as pressure may build-up due to the water vapor formation as the heating temperature increases.
4. Moisture loss or moisture absorption can affect mechanical characterization data. Where relevant, tests should be performed in a controlled humidity environment.
5. Mutation in the test sample may occur during the rheological evaluation. Ensure that the mutation number values are << 1, thus meeting the so-called mutation number criteria.
6. If available and relevant, the use of an *in situ* rheological measurement is desirable. This can be critical for slightly crosslinked hydrogels or those with entangled network. The preparation of this type of hydrogels can be a challenge for obtaining the sample size that can match the test plate geometry. In addition, sample loading procedures may apply undesirable stress on the test material.
7. In the case of studying the gelation of low viscosity systems, the torque amplitudes in the first curing stages will be much lower than in the more conventional '100% solids' systems with the risk of a poor signal/noise ratio. This can affect the quality of the rheological data. It can, however, be overcome with a controlled stress instrument which has a magnetic bearing, which allows testing with lower torque amplitudes.
8. The cohesive nature of the hydrogel is increased by the high crosslink density.

## 7.8  Applications of Functional Hydrogels

The unique properties of hydrogels have made them useful in various fields of science and technology, including agriculture, architecture and biomedicine.

### 7.8.1  Healthcare and Biomedical Applications

In today's healthcare, functional hydrogels have been shown to be widely used due to their intrinsic properties. These include biocompatibility, biodegradability, flexibility, optical clarity, permeability, swelling ability, thermal stability and transparency. With this in mind, synthetic or natural polymers or blends are used (Rosiak

and Yoshii 1999). The use of hydrogels in tissue engineering can be achieved using a variety of strategies. Figure 7.13 shows a simplified process involved in the use of polymeric hydrogel scaffolds in tissue formation or tissue regeneration. Often, tissues are explanted from the subject and then preferentially infused, modified and engineered though *in vitro* techniques. These can then be implanted into the individual, thus exposing them to mechanical and molecular environments. When necessary, engineered scaffolds can be further developed in suitable bioreactors, in order to generate an artificial organ before implantation (Khan et al. 2015).

Soft contact lenses made from hydrogels have been synthesized so that the gel can deliver the necessary antibiotics to the eye and can also provide visual corrections (Kopecek 2009). Other biomedical applications of hydrogels include wound dressing for burns, supports for tissue engineering and biodegradable drug delivery systems capable of delivering anti-nausea/vomiting drugs, oral insulin and vitamins. The delivery of pharmaceutical products or the scaffolding application of hydrogels is largely determined by its network structure. Often, the hydrogels are required to be slightly crosslinked. This can thus lead to a greater tendency to swelling and less flexibility (Sun et al. 2011).

***Biocompatibility:*** hydrogels in biomedical applications in most cases are designed to be in contact with mammalian tissue. Therefore, this requires that they are biocompatible. When this is not achieved, cytotoxicity then arises. In many cases, it is the choice and the concentration of constituent materials in the hydrogel that determine whether they are biocompatible or not. Often, half maximal inhibitory concentration ($IC_{50}$) tests are designed and used to study the biocompatibility of hydrogels. $IC_{50}$ is thus used to measure the degree to which specific biological functions are effectively inhibited by the substance under investigation.

Hydrogels based on β-sheet peptides have now emerged widely for biomedical applications. Keeping this in view, the sequence design of the peptide material and the concentration of the peptide in the hydrogel are key factors in the material's
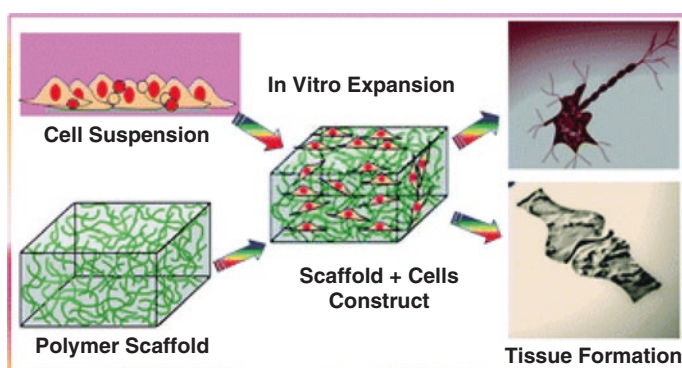


**Fig. 7.13** Illustration of the processes involved in the use of hydrogel scaffolds in tissue engineering. Reproduced with permission from Khan et al. (2015)

biocompatibility. It has recently been shown that functional hydrogels that are of peptide and inorganic compound hybrids can be successfully manufactured to possess great potential for tissue scaffolding engineering. For example, hydrogel networks can be formed successfully by combining graphene with selected peptide materials. In this context, Wychowaniec (2017) reported that cytotoxicity of the hybrid hydrogels were desirable and that the material possessed essential tissue injectability properties, in addition to being biocompatible. These hybrid hydrogels were proposed as a versatile platform for culturing cells in three-dimensions (Wychowaniec 2017).

*Biodegradability:* when functional hydrogels used in biomedical applications (e.g. as tissue scaffolds) are biodegradable, this ensures that their application is temporary in nature. Such biodegradable materials often continue to exist and fulfill their function until they are degraded and replaced by new biological tissues. Many biodegradable functional hydrogels are made from polymers that are themselves biodegradable. Typical examples include cellulose, Cs, collagen and poly(lactic acid) (PLA) (Gutiérrez 2017). Due to their biodegradability, the mechanical properties of hydrogels are degraded, which leads to a decrease in crosslinking, elasticity and stiffness over time. It is essential for these changes in the hydrogel occur at a rate equal or similar to the rate of formation of new tissues.

It has been shown that cellulose-based hydrogels are biodegradable, in addition to their biocompatibility. Among the list of biodegradable cellulose-based starting materials, carboxymethyl cellulose, hydroxyethyl cellulose and hydroxymethyl cellulose are widely used as monomers in hydrogel syntheses (Sarkar 1979). A challenge is to find a suitable biodegradable crosslinker for use during synthesis. Often, the salt molecules used in the preparations can act as chelating agents, leading to gelation and network formation. Another strategy is to use two or more cellulosic starting materials, with gelation achieved through physical entanglement of growing polymer chains. In line with this, hydrophobic interactions are key in the gelation process, which arise from the methoxy chains that are present in the growing cellulosic polymer chains. These interactions depend on temperature and occur faster when processing temperatures increase (Sannino et al. 2009).

*Other safety aspects:* physically crosslinked hydrogels in particular are typically not considered for use in biological environments (e.g. in tissue scaffolding or visual correction applications), since the crosslinking in these materials is largely reversible, it is often difficult to control the nature and rate at which the entangled chains are unraveled (te Nijenhuis 2007). Examples of safety checks that are carried out in relation to the biomedical application of hydrogels are given in Table 7.5. The ways in which untangling of macromolecular chains in physically crosslinked hydrogels can be monitored include observing changes in their tendency to flow (increase) and assessing changes (loss or decrease) in viscoelasticity and other mechanical properties, due to application of stress or changes occuring in storage-influenced conditions, such as temperature. Thus, the degradation mechanisms of physically crosslinked hydrogels are largely uncontrollable.

**Table 7.4** Examples of biodegradable hydrogels used in tissue scaffolds

| Hydrogel | Function | Biodegradability | References |
|---|---|---|---|
| Dextran hydrogels | Wound healing | Largely influenced by the immobilization of vascular endothelial growth factors | Sun et al. (2011) |
| PLA-*b*-poly(ethylene glycol)-*b*-PLA end capped with acrylate groups | Tissue engineering cartilage | Biodegradability tailored by reaction and reactivity of the starting materials | Bryant and Anseth (2003) |

**Table 7.5** Examples of safety controls that are carried out in relation to the biomedical application of hydrogels

| Hydrogel | Application | Safety verification | Safety comment | References |
|---|---|---|---|---|
| Bukamid – poly(acrylamide) based hydrogel. | Management of conditions related to urinary incontinence. | Post-operative assessments, at 3 and 12 months, followed by specified annual checks. | Administered Bukamid was found to be durable, effective and safe. | Pai and Al-Singary (2015) |
| Bukamid – poly(acrylamide) based hydrogel. | Female stress management and stress-predominant mixed incontinence. | 24 months follow-up assessments. | There were no security problems after the evaluations. | Toozs-Hobson et al. (2012) |
| Raindrop corneal inlay. | Improvement of near vision in conditions related to emmetropic presbyopia. | 12 months of safety and efficacy checks. | Patients satisfied with the overview. Only a small effect on distance visual sharpness. | Garza et al. (2013) |

## 7.8.2 Fire Resistance Glazing Applications

Polymeric hydrogels have found applications in fire-resistant glazing assemblies. Usually, they are used as interlayers between glass sheets, in doors, partitions and windows. Their typical high-water content makes them suitable for these applications. When exposed to fire/flames, the hydrogel releases water in a controlled manner. In this way, the high specific heat capacity of water plays an advantage, by minimizing the increase in temperature on the glass surface. In this sense, the way in which water is bound to the internal structures of the hydrogel material is important. The water in hydrogels can thus be considered as strongly bound water or freely bound water. After exposure of the hydrogel at elevated temperatures, the latter is released first, followed by the former.

The composition of the hydrogel plays a very important role in the fire resistance application. The more hydrophilic the hydrogel backbone, the stronger would be the binding of the water molecules. In typical preparation procedures, water-solubilized

prepolymer formulations are created and then poured between the sealed double-glazing glass sheets. This formulation is then cured thermally or using UV light to give the resultant hydrogel. Specific examples are given Table 7.6. The properties of the fully formed hydrogel must be adequate so that they can be adhered to the glass and can withstand fire exposure for a specified period of time, thus providing the required insulating and fire resisting/retarding properties.

**The fire resistance mechanism:** char formation, free radical trapping, fuel dilution, heat absorption and thermal barrier are the key mechanisms through which intumescent fire-resistant compositions, including functional hydrogels. When a double-glazed unit, containing a formulation of hydrogels with dissolved salts, is exposed to flames and heat, water is released in a controlled manner once the first sheet of glass breaks through thermal shock. The dissolved salts then combined with the polymeric components of the gel to from an inorganic salt-carbonaceous composition that acts as an insulator, while adhering to the other glass sheet. This process of retarding fire is known as intumescence fire retardation. Fire tests are conducted in order to monitor the degree to which the hydrogel intumesce. This adds to the fire resistance monitoring of the structural components and the fire reaction of the flammable components in the material (Hull 2008). For fire resistant glass, the test panels are mounted onto a furnace in a vertical orientation. The furnace is then heated in a controlled manner so that it follows the temperature-time curve shown in Fig. 7.14. EN 1363–1 is a standard for testing fire resistance in materials intended for use in buildings. During the tests, the temperature on the fireless side of the glass (cold side) rises and is monitored using thermocouple thermometers. The pressure inside the furnace is also controlled. The inherent

**Table 7.6** Examples of functional hydrogels, monomer used in synthesis and curing method, relevant for the application of materials in fire-resistant glazing units

| Technologies | Monomer* (example) | Curing methods | References |
|---|---|---|---|
| Fire-resistant glazing unit comprising about 40–85% by weight of water. | AA | Thermal curing, with typical reaction temperatures between 35 ° C and 90 ° C. | Crook and Ali (2016) |
| Fire-resistant glazing unit consisting about 40–90% by weight of water. A gel stabilizing agent, such as a tin compound, is an essential part of the formulation. | AA | UV-induced polymerization, by using a photo-initiator such as 2-hydroxy-2-methyl-1-phenylpropane-1-one. | Oh and Myungjin (2009) |
| Fire-resistant glazing unit comprising about 70–90% by weight of water. | Acrylamide | Cured at room temperature based on the use of highly soluble persulfate initiators such as ammonium persulfate or peroxidosulfate. | Ortmans and Hassiepen (1989) |

*Other components are likely polymerizable and gel-forming
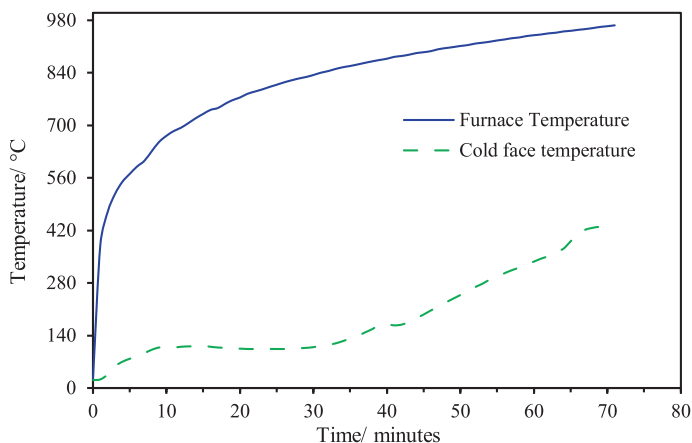
**Fig. 7.14** Temperature-time relationship during a fire test, showing a required furnace temperature curve and a hypothetical cold face temperature

fire-resistant property of the hydrogel ensures that the temperature on the cold side of the glass is significantly lower than in the furnace.

### 7.8.3   Personal Care/Hygiene Application

The ability of hydrogels to absorb large amount of water and retain this water in their microstructure is the reason they have found application for personal care and hygiene fields. A key application of acrylate hydrogels is the manufacture of nappies. By absorbing moisture in large quantities, they help the user to keep the dry skin, with such practice promoting comfort and hygiene. In addition, this practice helps prevent skin irritation and contamination. In order for such nappies to be suitable and fit for purpose and to be free from leakages, the design of the hydrogel network must be carefully considered. An ideal level of crosslinking must be achieved to allow the hydrogel material in the nappies to accommodate/retain desirable amounts of fluid. On the other hand, a balance of viscoelasticity (rigidity, softness, stiffness, etc.) is required to ensure that such nappies are comfortable for their users. With increasing awareness for the creation and use of environmentally friendly materials, the generation of biodegradable hydrogel-based healthcare products is becoming increasingly popular. One strategy is to use biodegradable starting materials during the manufacturing stages. For this, cellulose and its many derivatives have found application. This development is thus likely to result in a continuous decrease in the use of acrylate-based starting materials.

## 7.9 Remark Conclusions

A general description of the structure, composition, synthesis routes, properties and applications of functional hydrogels has been given in this chapter. The fundamental gel point of the critical gels was defined, and relevant gelation models were given, paying attention to the multi-wave mechanical technique. This technique provides a good basis for determining the properties of critical gels, such as network relaxation exponent, stiffness and fractal dimensions. Despite the availability or rigorous gelation models, the gelation of many hydrogels has not yet been tested or confirmed. Many reports on functional hydrogels refer to biomedical applications of such materials. Although inventions (patents) show the relevance of the use of functional hydrogels in fire-resistant applications, very little work has been reported through scientific journals. Despite this, it is expected that the outline given in this chapter provides a background of the science that supports the applications of hydrogels in fire-resistant applications.

**Conflicts of Interest** The author declares no conflict of interest.

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