



Swelling and DC Conductivity Behaviour of Gelatin-Based Ferrogels

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Received: 14 May 2020 / Revised: 14 July 2020 / Accepted: 18 July 2020 / Published online: 25 July 2020
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Abstract

Gelatin-based systems have great potential in bio-medical applications. Here, we report the solvent uptake and DC conductivity of glutaraldehyde-crosslinked gelatin hydrogels and ferrogels. Both the parameters are found to depend on cross-linker (glutaraldehyde) and dopant (carbonyl iron) concentrations. Higher cross-linker proportions cause decrease in solvent uptake, equilibrium swelling ratio and DC conductivity. Solvent uptake is seen to increase while equilibrium swelling ratio and DC conductivity decrease with dopant concentration in the ferrogels. The solvent uptake and DC conductivity behaviour of the studied systems are explained on the basis of variations in pore size and polymer segmental mobility which, themselves, are functions of cross-linker and dopant concentrations. The diffusion process in the hydrogels and ferrogels obeys the second-order kinetic model.

Keywords Gelatin · Glutaraldehyde · Carbonyl iron · Swelling · DC conductivity

1 Introduction

In recent times, the design, synthesis and study of “smart materials” have attracted much scientific interest [1]. Smart materials can change their physical properties in a desirable manner in response to a specific stimulus/input. Temperature, pressure, added chemicals, electric and magnetic fields, hydrostatic pressure and nuclear radiations can act as stimuli while shape, viscosity and material stiffness could be the associated changeable physical properties. Smart materials are self-adaptable, self-sensing and possess “memory characteristics” and, therefore, have potential biomechanical applications in engineering, manufacturing and infrastructure systems. Magnetic hydrogels (i.e. ferrogels) are prime examples of wet and soft smart materials [2, 3]. Such hydrogels are composites comprising a soft gel matrix with a filler consisting of a magnetically-sensitive dopant [4, 5]. Ferrogels are mechanically soft, highly elastic and exhibit a strong magnetic response [6]. Their low elastic modulus leads to large deformations in response to even moderate

magnetic fields. The desired application can be obtained in a non-contact (remote), smooth and rapid manner by applying an appropriate magnetic field to the ferrogel [7, 8]. Such magnetically-sensitive hydrogels can be formed through physical or chemical cross-linking of polymer chains within a ferrofluid.

Targeted drug delivery and fabrication of artificial muscles are the two most promising applications of ferrogels [9]. In drug delivery-related applications, it is important to understand solvent uptake since drugs are generally incorporated as aqueous solutions. Swelling kinetics helps in understanding drug retention and release in polymer matrix-based sustained-release dosage formulations. This is because transport properties through gel systems depend on the amount of water present. Besides, it is necessary that artificial muscles closely mimic natural muscles. It is known that natural human muscles comprise proteins (about 20%) and multi-component aqueous solutions (about 80%) [10]. Natural muscles perform their functions through quick and reversible uni-directional contraction. They possess a special mechanism which transforms chemically-bound energy into mechanical work or locomotion. Since chemical-based actuation is undesirable in artificial muscles, the basic materials that are used for their fabrication should be provided with a suitable process for the generation of an internal mechanical stress. As electrically-driven actuators are promising candidates in this regard, it is necessary to understand electrical

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conductivity in ferrogels. This would lead to the design and fabrication of electrically-driven artificial muscles.

Gelatin is a commercially available, biodegradable and biocompatible biopolymer obtained from the partial decomposition of collagen [11]. Gelatin is non-toxic, possesses low immunogenicity and shows capacity for modification at the level of amino acids [12]. It has positively and negatively-charged amino acids on its polymeric backbone [13]. Its polyampholyte nature permits the formation of complexes with oppositely-charged polymers. Gelatin is widely used in food, pharmaceutical, medical and cosmetic applications [14]. It is used as a matrix for implants, device coatings, vaccine stabilizers, wound dressings, hard and soft capsules and in drug delivery systems. Gelatin-based polymer matrices possess high capacity for water absorption. Gelatin can be used to form physically as well as chemically cross-linked hydrogel systems. Gelatin forms homogeneous solutions in water or hydrogen bond-friendly solvents above 32 °C [11]. Such solutions form physically cross-linked hydrogels when cooled to room temperature. The physical hydrogels of gelatin have poor mechanical and chemical stability [15, 16]. Also, since gelatin is highly soluble in aqueous environments, appropriate chemical cross-linking agents need to be used in order to stabilize the hydrogel network and improve its thermal, mechanical and water-sensitive properties for long-term usage. Gelatin can be chemically cross-linked through its amino, carboxyl or hydroxyl groups [13, 17].

Earlier, gelatin has been used in the preparation of physically cross-linked ferrogels [18]. The samples were relatively short-lived and highly temperature-sensitive due to their physical cross-linking. This makes it necessary to introduce chemical cross-links in the gelatin ferrogel matrices so as to make them long-lasting. With this in mind, in the present study, we have synthesized chemically cross-linked gelatin-based ferrogels with glutaraldehyde (GA) as the cross-linker and micron-sized carbonyl iron as the magnetically-sensitive dopant. GA is a linear five-carbon di-aldehyde that is soluble in water, alcohol and organic solvents [13, 19]. It is inexpensive, easily available and rapidly forms cross-links when mixed with gelatin solutions [20–22]. GA is widely used as a cross-linking agent, in the fabrication of bio-prosthetic implants and tissues, and for enzyme immobilization [19]. In our samples, the gelatin content has been kept constant while GA and carbonyl iron concentrations have been varied. These variations cause structural modifications within the undoped and doped (i.e. ferrogel) samples. In order to explore the potential applications of the samples in drug delivery and artificial muscles, we have studied their solvent uptake and DC conductivity behaviour, with the aim of understanding the relationship with the structural changes. We have examined the two physical parameters viz. solvent uptake and DC conductivity as functions of cross-linker and dopant concentrations. The two parameters have been found

to be significantly dependent on the pore size and polymer segmental mobility. A judicious choice of cross-linker and/or dopant concentrations would, therefore, make it possible to develop suitable materials for optimal electric actuation in artificial muscles and for fine-tuned targeted drug delivery systems.

2 Experimental

Gelatin and GA were procured from HiMedia Pvt. Ltd and Loba Chemie Pvt. Ltd, respectively. The carbonyl iron $[\text{Fe}(\text{CO})_5]$ powder was provided by ISP Technologies on complimentary basis. According to the supplier, the carbonyl iron had a density of 2.1 g/cc and a median particle diameter of 7.3 μm . All the chemicals were used without further purification.

2.1 Preparation of Samples

Two series of gelatin hydrogel samples were prepared with GA concentrations of 5 and 10 μL per mL of gelatin solution. Each series had five samples with carbonyl iron (dopant) concentrations of 0 (viz. the undoped/neat hydrogel), 10 mg/mL, 20 mg/mL, 30 mg/mL and 40 mg/mL.

Before the actual preparation of the samples, a 5 wt% solution of gelatin was made in double-distilled water by magnetic stirring for about 1 h at 50 °C. The solution was permitted to cool to room temperature for about 2 h. Required quantities of the solution were measured and poured into flat-bottom culture tubes. Appropriate amounts of carbonyl iron powder were carefully weighed and added to the gelatin solution in each culture tube. Each solution was stirred for about 1 min using a vortex mixer in order to ensure uniform distribution of the dopant. The appropriate amount of GA was added to the mixture (in order to ensure the desired proportion of the cross-linker) and vortex stirring was continued for about 5 min, at room temperature, until the formation of the ferrogels. A similar procedure was used for the preparation of the undoped hydrogels—though without the carbonyl iron powder—using a magnetic stirrer instead of a vortex mixer. Figure 1 is a photograph of the hydrogel (i.e. neat/undoped) and ferrogel (i.e. doped) samples.

2.2 Measurements

2.2.1 Swelling Tests

The swelling behaviour for each of the prepared samples was investigated using the gravimetric method. Prior to the investigation, portions of the samples were dried by exposure to the atmosphere for two days under ambient conditions. The



Fig. 1 Photograph of the undoped and doped hydrogels

initial mass of each dried sample was determined. The samples were immersed in excess double-distilled water at room temperature. The swollen samples were removed from the water after pre-set time intervals, wiped using filter paper so as to remove any adhering water and weighed immediately. The solvent uptake at a specific pre-set time was calculated using the formula,

$$\text{Swelling ratio} = \left(\frac{\text{mass}_{\text{final}} - \text{mass}_{\text{initial}}}{\text{mass}_{\text{initial}}} \right) \quad (1)$$

In Eq. 1, “swelling ratio” (in g/g) is defined as the grams of absorbed water per gram of the dry hydrogel; $\text{mass}_{\text{final}}$ is the mass of the swollen sample at time t (in min); $\text{mass}_{\text{initial}}$ is the mass of the dry hydrogel. The swollen samples were weighed after 30, 60, 90, 120, 150 and 180 min of immersion.

2.2.2 DC Conductivity

Due to the expected low conductivity nature of the samples, a two-probe resistivity set-up was used for the DC conductivity measurement. “Pellets” were created by capsizing each sample within a non-conducting cylindrical capsule with both ends open. It was ensured that the sample within the capsule did not contain fracture lines. The gel-loaded capsule was placed within the contact probes of a two-probe resistance measurement instrument which was indigenously designed, developed and manufactured by ADEC Embedded Technologies and Solutions Pvt. Ltd. The upper and lower faces of the gel-loaded capsule were placed in contact with the contact probes of the measuring instrument. A constant 2 V electrostatic potential difference was applied across the sample during the measurement. The circuit current (I) was measured at room temperature. Two standard dimension-measuring instruments viz. micrometer screw gauge and travelling microscope were used to quantify the length and diameter of the gel-loading capsule, respectively. The DC

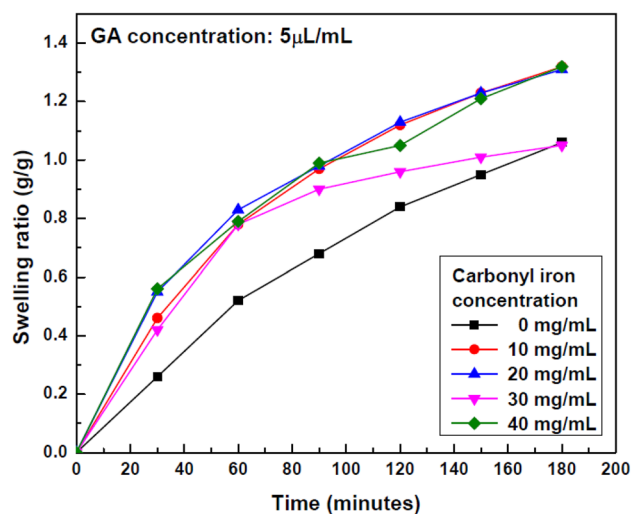


Fig. 2 Effect of time on swelling ratios of undoped and doped hydrogels with GA concentration 5 $\mu\text{L/mL}$ (the solid lines are only to guide the eye)

resistivity (ρ) value was calculated, for each sample, using the equation,

$$\rho = \frac{VA}{IL} \quad (2)$$

In Eq. 2, A is the cross-sectional area of the sample in CGS units; I is the measured current (in A) flowing through the sample; L is the length of the capsule measured in CGS units; $V = 2 \text{ V}$ is the potential difference applied across the sample. The DC conductivity was calculated as the reciprocal of the DC resistivity.

3 Results and Discussion

3.1 Swelling Tests

The swelling behaviour exhibited by the samples of the present study is shown in Figs. 2 and 3 as plots of swelling ratio versus time. In both Figures, the samples exhibit a rapid initial rise of the swelling ratios followed by a slower subsequent increase. This behaviour can be explained by the nature of the basic polymer network of the samples which has been formed by mixing gelatin and GA solutions. The mixing leads to the occurrence of a cross-linking reaction as shown in Fig. 4. The basic hydrogel framework of the samples may be modeled as a three-dimensional network of gelatin chains cross-linked by GA molecules. While GA molecules may combine with themselves, this will not affect the hydrogel network structure as the self-reacted molecules would be unavailable for cross-linking. Further, at very large GA concentrations, no significant increase of cross-links is

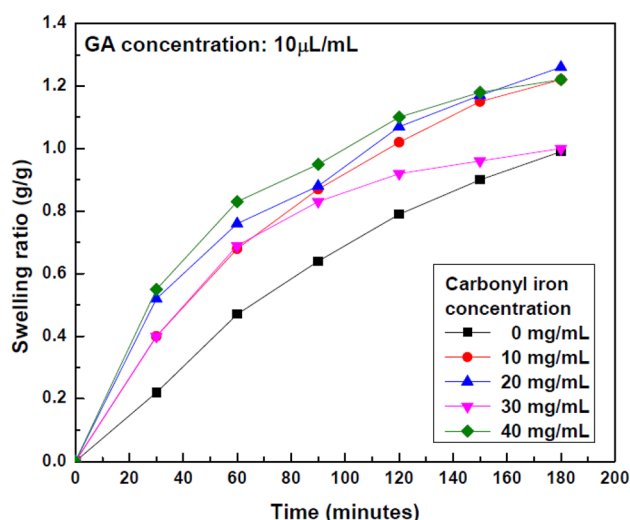
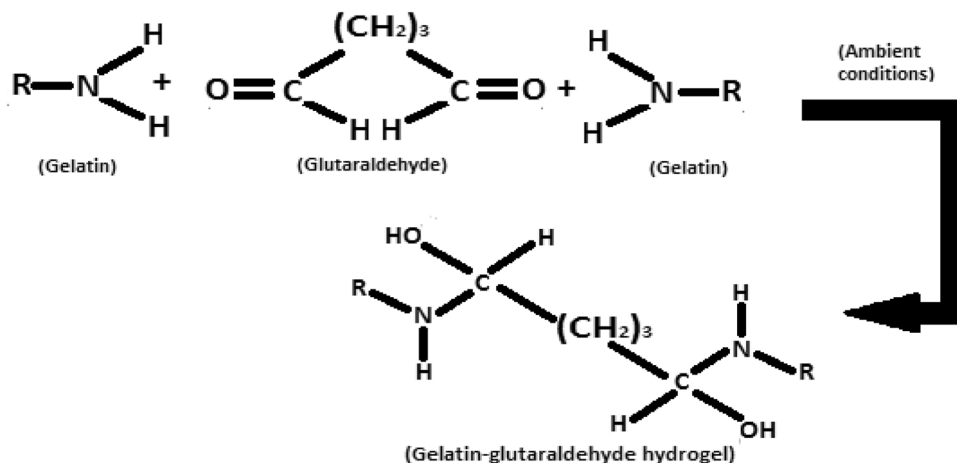


Fig. 3 Effect of time on swelling ratios of undoped and doped hydrogels with GA concentration 10 $\mu\text{L/mL}$ (the solid lines are only to guide the eye)

observed due to formation of pendant GA molecules [23]. Pore size would, therefore, be determined by the GA molecules which are available for cross-linking. The pores (voids) of the network are occupied by the solvent (water). The flexibility of polymer segments between adjacent GA cross-links permits them some degree of mobility within the solvent. This motion of the polymer segments occurs in co-ordination with other parts of the polymer chain. The increase of swelling ratios with sorption time, as observed in Figs. 2 and 3, is indicative of solvent uptake being a continuous process of transition from an unsolvated glassy or partially rubbery state to a relaxed rubbery one [24]. In general, the swelling behaviour of polymer hydrogel matrices is governed by osmotic pressure and viscoelastic forces. When first immersed in water, the high difference in osmotic pressures within and outside the dried hydrogel causes water

molecules to enter and diffuse into the network structure leading to rapid initial swelling. The swelling process causes gradual extension of the polymer segments between adjacent GA cross-links. With increasing water content inside the matrix, the difference in osmotic pressures within and outside the network decreases. For higher sorption times, though solvent uptake continues, the osmotic force is opposed by the viscoelastic force. The opposition balances the stretching of the network and prevents its complete deformation. The balance between the osmotic and elastic forces leads to a gradual approach towards an equilibrium value for the absorbed solvent leading to a slower increase in swelling ratio as a function of time, as observed for our samples. Swelling of polymer hydrogels involves three steps viz. (a) the diffusion of solvent molecules into the polymer network; (b) the relaxation of hydrated polymer chains; and, (c) network expansion into the surrounding aqueous solution [25]. When the swelling behaviour of the neat (undoped) samples of Figs. 2 and 3 is compared, it is noticed that the hydrogel with GA concentration 5 $\mu\text{L/mL}$ exhibits relatively higher solvent uptake. At this GA concentration, the number of cross-linker molecules is relatively lower leading to a smaller number of GA cross-links on each gelatin chain. The correlation length (i.e. the average distance between consecutive cross-links in the three-dimensional network), in this case, is larger and the cross-links are formed at relatively higher distances from one another. This phenomenon has been confirmed by Small Angle Neutron Scattering (SANS) measurements performed on gelatin-GA systems [20]. The average length of the gelatin chains between adjacent GA cross-links is also relatively greater for the samples with cross-linker concentration 5 $\mu\text{L/mL}$. The lower degree of cross-linking of the neat hydrogel with GA concentration 5 $\mu\text{L/mL}$ results in pores of relatively larger volume. The availability of more free space permits greater quantities of water to penetrate into the network yielding relatively-larger swelling ratios for the hydrogel with GA concentration

Fig. 4 The reaction of gelatin with glutaraldehyde



5 $\mu\text{L/mL}$. Further, the process of swelling causes increase in membrane free volume. It is known that lower cross-linker proportions lead to relatively higher membrane free volumes resulting in higher water sorption capacity [26]. In contrast, the higher cross-linker concentration in the hydrogel with GA concentration 10 $\mu\text{L/mL}$ reduces the membrane free volume and decreases free space within the network thereby lowering the swelling ratios.

In Fig. 2, the ferrogels (i.e. the hydrogels doped with carbonyl iron) are observed to exhibit higher swelling ratios in comparison with the neat hydrogel. The carbonyl iron dopant is the only additional component in the ferrogel samples. The higher swelling ratios of the ferrogels can be attributed to the presence of the dopant particles in the matrix. Though the dopant particles are not chemically bonded to the polymer network, their presence leads to a structural re-arrangement of the matrix. Small Angle Neutron Scattering (SANS) have shown ferrogels to have higher correlation length (ξ) values as compared to neat hydrogels (those data are being published separately). This entails longer chain lengths between successive cross-links and larger pore sizes within the ferrogels. As swelling rate is determined by the extent of porosity, ferrogels exhibit higher solvent uptake as seen in Fig. 2. Increase in dopant concentration to 20 mg/mL causes further increase in correlation length and enhancement in solvent uptake. It is noted that the swelling ratio for the ferrogel with dopant concentration 30 mg/mL is lower than for 20 mg/mL. Carbonyl iron particles exhibit sedimentation in aqueous gelatin solutions and tend to aggregate during gel formation [27, 28]. Consequently, at this dopant concentration (30 mg/mL), there are fewer newer (and, smaller) carbonyl iron sites created in the network while the existing dopant clusters increase in size. The higher amount of dopant in the matrix reduces the space available for occupation by the polymer chains and causes lower correlation length and smaller pore size, as also shown by SANS measurements. Further, the hindered flexibility of the chains enwrapped around the larger-sized clusters permits lesser solvent uptake leading to the observed lower swelling ratios of this sample. The ferrogel with dopant concentration 40 mg/mL, owing to further increase in dopant concentration, has newer smaller carbonyl iron sites in addition to the larger clusters. The flexibility of gelatin chains around the smaller dopant clusters is higher than those enwrapping the larger-sized ones. This increases pore sizes and enhances swelling ratio, as observed in Fig. 2.

From Fig. 3, it is observed that the undoped and doped hydrogels with GA concentration 10 $\mu\text{L/mL}$ show behaviour similar to that of samples with lower cross-linker proportions. This includes the observed decrease in solvent uptake for the ferrogels with dopant concentration of 30 mg/mL. The explanation for this behaviour is similar to that narrated above for gelatin hydrogels having GA concentration

of 5 $\mu\text{L/mL}$ (presented in Fig. 2). Comparison of Figs. 2 and 3 shows the swelling ratios to be lower for the ferrogel samples with GA concentration 10 $\mu\text{L/mL}$. The higher GA concentration within these samples lead to greater cross-link density. Consequently, the samples are more compact, possess smaller pore sizes and exhibit lower solvent uptake vis-à-vis the samples with cross-linker proportions of 5 $\mu\text{L/mL}$.

Schott's second-order kinetic model was applied to the entire swelling process, for all the samples of the present study, using the equation [29, 30]:

$$\frac{t}{S} = \frac{1}{k_2 S_{eq}^2} + \frac{t}{S_{eq}} \quad (3)$$

In Eq. 3, S_{eq} (in g/g) is the swelling ratio of the particular sample at equilibrium, S (in g/g) is the swelling ratio at a given time t (in minutes), k_2 (in min^{-1}) is the second-order swelling rate constant. The coefficient of determination (R^2) was used to evaluate the fitting of the experimental data with the model. The plots of t/S versus t are shown in Figs. 5 and 6 for the samples with GA concentrations of 5 and 10 $\mu\text{L/mL}$ respectively. The values of $S_{eq} = \frac{1}{\text{Slope}}$ and $k_2 = \frac{1}{\text{Intercept} \times S_{eq}^2}$ were calculated from the plots. The corresponding calculated values of S_{eq} , k_2 and R^2 are listed in Table 1 for both sets of samples.

In Figs. 5 and 6, it is observed that the fitting yielded straight lines while Table 1 shows that the linear correlation coefficient (R^2) has values in the range 0.974–0.997 confirming that the data were well-fitted by Schott's second-order kinetic model. Clearly, the model is suitable for describing the entire swelling behaviour of the samples of the present study. From Table 1, it is observed that the

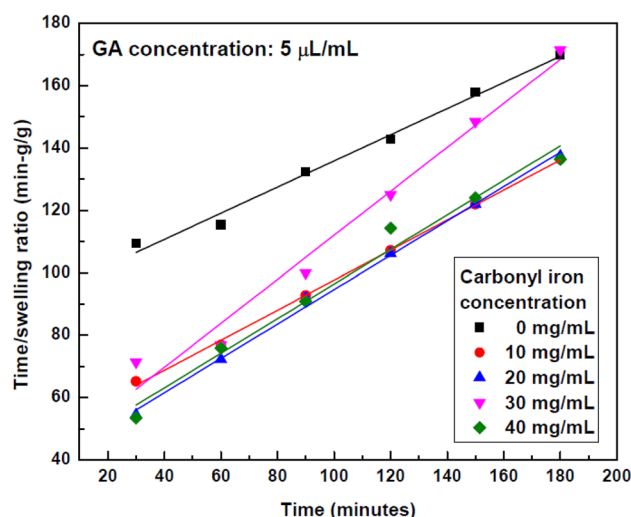


Fig. 5 Plots of t/S against t for hydrogel and ferrogel samples with glutaraldehyde concentration 5 $\mu\text{L/mL}$ and varying carbonyl iron proportions

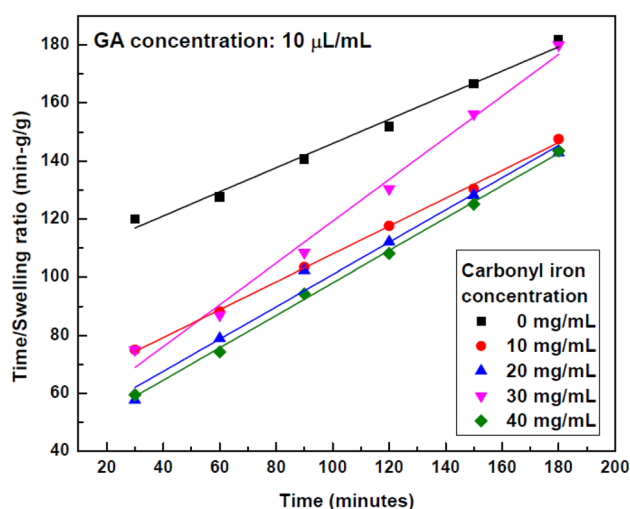


Fig. 6 Plot of t/S against t for hydrogel and ferrogels samples with glutaraldehyde concentration $10 \mu\text{L/mL}$ and varying carbonyl iron proportions

value of k_2 decreases upon increase of cross-linker concentration. This is indicative of the polymer network becoming more compact with increase in cross-link density thereby causing a higher degree of difficulty for solvent penetration into the matrix. The ferrogels show higher values of k_2 as compared to the corresponding (neat) hydrogels. This indicates greater ease of solvent penetration into ferrogels vis-à-vis hydrogels which may be attributed to the presence of carbonyl iron particles within the matrices. The ferrogels with GA concentration $10 \mu\text{L/mL}$ have relatively lower k_2 values. Cross-linking density, therefore, also plays a role in solvent uptake in the ferrogels. For both sets of samples, the ferrogels exhibit lower S_{eq} values pointing to lesser maximum solvent absorption and retention abilities. The presence of carbonyl iron particles in the matrices seems to lessen the volume available

for the expansion of gelatin segments between adjacent cross-links. Higher GA concentration also reduces the values of S_{eq} in the hydrogel and ferrogel samples. The relative closeness of the cross-links, in this case, reduces the length of the gelatin segments which inhibits their ability for stretching when solvent (water) enters the pores of the matrix. These findings are of immense importance for the design and fabrication of gelatin ferrogel-based drug delivery systems as it increases the possibility of well-tuned incorporation, uptake, retention and controlled release of drugs.

The suitability of second-order kinetic model for the solvent uptake of our samples indicates that the rate of swelling is directly proportional to two factors viz., (a) the relative amount of unrealized uptake of swelling medium i.e. the fractional amount of swelling capacity still available; and, (b) the internal specific boundary area A_{int} which encloses the sites that have not interacted with water but will be hydrated and get swollen in due course of time [29]. A_{int} is the specific boundary area separating the un-hydrated sites capable of swelling from areas that are already hydrated and swollen and from crystalline regions that never swell. A_{int} may be also described as the sum of the surface areas encapsulating the swellable sites in a given volume and is directly proportional to the percent unrealized swelling capacity. Initially, A_{int} has a large value owing to the high availability of un-hydrated sites. The expansion of the network due to progressive swelling increases the stress on the cross-links that hold the network together. The stressed cross-links resist further swelling and slow down the rate of swelling in direct proportion to the relative swelling capacity. As sorption time increases, the percent unused swelling capacity diminishes leading to decrease in the value of A_{int} . Taken together, the two factors cause retardation in the swelling, as observed in Figs. 2 and 3, and asymptotically lead to the attainment of an equilibrium value of swelling.

Table 1 Second-order swelling kinetic model parameters of the doped and undoped gelatin hydrogels having GA concentrations of 5 and $10 \mu\text{L/mL}$

Carbonyl iron concentration (in mg/mL)	GA concentration: $5 \mu\text{L/mL}$			GA concentration: $10 \mu\text{L/mL}$		
	Equilibrium swelling ratio S_{eq} (in g/g)	Second-order swelling rate constant k_2 (in min^{-1})	Coefficient of determination R^2	Equilibrium swelling ratio S_{eq} (in g/g)	Second-order swelling rate constant k_2 (in min^{-1})	Coefficient of determination R^2
0 (undoped)	2.39	1.87×10^{-3}	0.9885	2.38	1.66×10^{-3}	0.9881
10	2.08	4.67×10^{-3}	0.9987	2.08	3.83×10^{-3}	0.9984
20	1.82	7.64×10^{-3}	0.9969	1.80	6.81×10^{-3}	0.9815
30	1.42	11.94×10^{-3}	0.9748	1.39	10.91×10^{-3}	0.9872
40	1.81	7.47×10^{-3}	0.9785	1.79	7.40×10^{-3}	0.9979

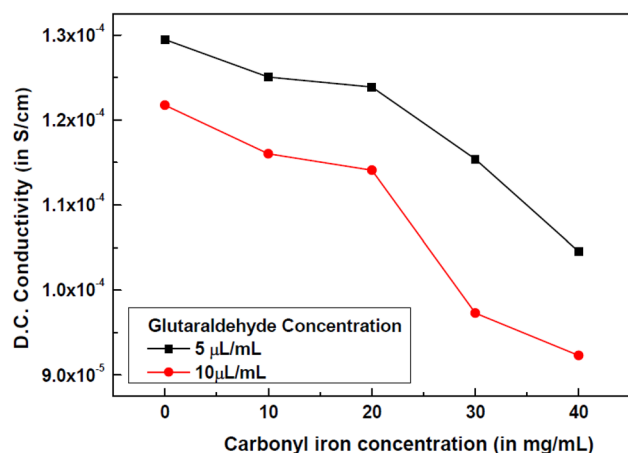


Fig. 7 DC conductivity of the hydrogel and ferrogel samples with varying GA concentrations (the solid lines are only to guide the eye)

3.2 DC Conductivity Studies

Tables 2 and 3 show the measured DC resistivity and its transformed conductivity for the samples having GA concentration 5 $\mu\text{L/mL}$ and 10 $\mu\text{L/mL}$, respectively. The reasonably high resistivity and low conductivity values shown by the samples are consistent with their low current-conducting behaviour. Figure 7 is a graphical representation of the DC conductivity values of the samples.

In liquids and liquid-like substances (e.g. gels), electrical conduction occurs through the diffusion of charge carriers towards the oppositely-charged electrode upon the application of a potential difference. The conductivity path for charge diffusion is provided by the solvent contained within the pores of the three-dimensional polymer matrix. The structure of the polymer network, which is the solid phase of gels, plays a significant role in the diffusion process. For polymer gels, the motion of charge carriers through the solvent phase is dependent on internal viscosity rather than on bulk viscosity [31]. In general, transport properties are dependent on the concentration and velocities of the diffusing materials and on local viscosity [32]. In the case of electrical conductivity, the velocity of the diffusing material

Table 2 DC resistivity and conductivity values of the the gelatin hydrogels having GA concentration of 5 $\mu\text{L/mL}$

Carbonyl iron concentration (in mg/mL)	DC resistivity (in $\Omega\text{-cm}$)	DC conductivity (in S/cm)
0	7724.68	1.2946×10^{-4}
10	7996.74	1.2506×10^{-4}
20	8072.89	1.2387×10^{-4}
30	8665.34	1.1540×10^{-4}
40	9565.71	1.0454×10^{-4}

Table 3 DC resistivity and conductivity values of the the gelatin hydrogels having GA concentration of 10 $\mu\text{L/mL}$

Carbonyl iron concentration (in mg/mL)	DC resistivity (in $\Omega\text{-cm}$)	DC conductivity (in S/cm)
0	8213.56	1.2175×10^{-4}
10	8619.08	1.1602×10^{-4}
20	8765.91	1.1408×10^{-4}
30	10,279.13	0.9729×10^{-4}
40	10,834.87	0.9230×10^{-4}

depends on the applied electric field. For gels, the length of polymer segments between adjacent cross-links affects segmental mobility, leads to variations in internal (local) viscosity and significantly affects DC conductivity. Charge carriers jump between energetically-equivalent neighbouring sites aided by polymer conformation change due to segmental motion [31]. The resulting hopping process of the charge carriers constitutes the flow of current [33]. From Tables 2 and 3, the DC conductivity of samples with GA concentration 5 $\mu\text{L/mL}$ is seen to be higher than in those with 10 $\mu\text{L/mL}$. Owing to their lower GA concentration, the former series of samples have greater correlation lengths leading to adjacent cross-links being situated at relatively-larger distances. As a result, the matrices have greater solvent content, lower local viscosity and higher segmental mobility. The higher solvent content of these samples – which has also been shown by the swelling tests—provides a conductivity path with relatively-lower hindrance for the diffusion of charge carriers leading to the higher observed DC conductivity values in these samples.

In Tables 2 and 3, DC conductivity is observed to decrease when the carbonyl iron dopant is present in the matrix. The decrease occurs despite the higher correlation length (ξ) in ferrogels as compared to the corresponding neat hydrogel samples. Each ferrogel can be modeled as a network of gelatin chains cross-linked by GA and swollen with a ferrofluid comprising carbonyl iron particles dispersed in water. The mean diameter of the dopant particles (7.3 μm) is substantially higher than the correlation length of the ferrogels (50–90 $\text{\AA}$). The significant disparity in the dimensions permits the carbonyl iron particles to be modeled as large bodies surrounded by the dense mesh-like cross-linked gelatin network. Though not chemically bonded to the network, the enwrapping by the cross-linked gelatin chains prevents the dopant particles from diffusing through the solvent upon the application of a potential difference. Nevertheless, the presence of the dopant particles reduces the DC conductivity values of the ferrogel matrices. Within each series of samples, the neat hydrogel and the ferrogels possess the same polymer and cross-linker concentrations leading to similar cross-link density. Consequently, the number of

cross-links within the samples of a particular series is similar. The actual length of the gelatin chains between consecutive cross-links is the same within a particular series for the undoped and ferrogel samples though the correlation length of the latter is higher. The resulting higher tautness of the polymer segments in the ferrogels decreases their flexibility and restricts their motion. The consequent slowing of charge carriers through the solvent causes the observed decrease in DC conductivity. In the ferrogels with dopant concentration of 20 mg/mL, a further decrease in DC conductivity is observed despite their relatively higher correlation length values. Teixeira et al. have found carbonyl iron particles to coagulate during the formation of polyacrylamide ferrogels [27]. The cluster sizes of the coagulated particles were found to be higher within the gels as compared to un-enclosed ferrofluids. The carbonyl iron particles may be assumed to exhibit a similar behaviour in our doped samples. The increase in dopant concentration causes larger-sized clusters. The relatively-larger density of the dopant particles vis-à-vis the gelatin chains and GA cross-links leads to a smaller number density. The coagulation causes the restriction of dopant clusters to a lesser number of regions within the polymer matrix. The higher correlation length of the ferrogel samples with dopant concentration 20 mg/mL increases the tautness of the polymer segments between consecutive cross-links. The combination of the two factors further decreases polymer segmental mobility, reduces the diffusion of charge carriers and diminishes DC conductivity. A dopant concentration of 30 mg/mL is observed to cause a larger decrease in DC conductivity. This is despite the smaller correlation length of this sample that leads to the polymer segments possessing a smaller degree of tautness. The higher dopant concentration entails larger-sized coagulates constraining the cross-linked gelatin chains to occupy a smaller volume. The denser packing of the gelatin chains offsets the reduced tautness arising from the lower correlation length. The consequently higher local viscosity, combined with smaller pore size, reduces the diffusion of charge carriers leading to the observed diminished DC conductivity value. The higher correlation lengths when dopant concentration is 40 mg/mL leads to increased tautness of the polymer segments. Concomitantly, the higher dopant concentration leads to larger-sized clusters co-existing with newer/smaller ones and, thereby, causing the polymer chains between consecutive carbonyl iron particles to be more densely packed. The resulting increase in local viscosity hinders the diffusion of charge carriers and decreases DC conductivity.

In summary, our measurements indicate solvent uptake and DC conductivity to be dependent on the mesoscopic structure of the hydrogel and ferrogel samples which is a function of cross-linker and dopant concentrations. The two parameters can be used as tools for the description and understanding of matrix structure and in the design

of fine-tuned materials for potential applications e.g. drug delivery and electrically-driven soft actuators.

4 Conclusions

Two series of gelatin hydrogels and ferrogels, chemically cross-linked with glutaraldehyde (GA), were prepared. The solvent uptake and DC conductivity/resistivity of the ferrogels were measured in comparison with the corresponding neat hydrogels. The structural modifications caused by changes in cross-linker and dopant (carbonyl iron) concentrations affect the pore size of the samples leading to variations in the two parameters. Solvent uptake is found to be a continuous process until the gradual attainment of equilibrium and obeys the second-order-kinetic model. Higher cross-linker concentration leads to smaller correlation lengths, lesser swelling ratios and reduced DC conductivity. The presence of dopant particles causes increase in solvent uptake, and decrease in equilibrium swelling ratio and DC conductivity. Besides pore size, DC conductivity is also dependent on internal viscosity and polymer segmental mobility within the matrices.

Acknowledgements The authors express their gratitude to UGC-DAE-Consortium for Scientific Research, Mumbai Centre for funding this work through CRS-M-217. The supply of carbonyl iron powder by ISP Technologies, on complimentary basis, is gratefully acknowledged.

Funding This work is supported by UGC-DAE-Consortium for Scientific Research, Mumbai Centre through CRS-M-217.

Data Availability Not applicable.

Compliance with Ethical Standards

Conflict of interest The authors declare that there is no conflict of interest involved in this work.

References

1. S. Kamila, Introduction, classification and applications of smart materials: an overview. *Am. J. Appl. Sci.* **10**(8), 876–880 (2013). <https://doi.org/10.3844/ajassp.2013.765.880>
2. M. Zrinyi, Intelligent polymer gels controlled by magnetic fields. *Colloid Polym. Sci.* **278**, 98–103 (2000). <https://doi.org/10.1007/s003960050017>
3. Y. Osada, J.-P. Gong, Soft and wet materials: polymer gels. *Adv. Mater.* **10**(11), 827–838 (1998)
4. A. Sunaryono, E.G. Taufiq, A. Putra, I. Okazawa, N. Watanabe, S. Kojima, S. Ragmai, M. Soontaranon, S. Zainorr, Pratapa, Darminto, Small-angle X-ray scattering study on PVA/Fe₃O₄ magnetic hydrogels. *Nano* **11**(3), 0650827 (2016). <https://doi.org/10.1142/S1793292016500272>
5. R. Hernandez, G. Lopez, D. Lopez, M. Vlisquez, C. Mijangos, Magnetic characterization of polyvinyl alcohol ferrogels films.

- J. Mater. Res. **22**(8), 2211–2216 (2007). <https://doi.org/10.1557/jmr.2007.0298>
6. T.-Y. Liu, S.-H. Hu, K.-H. Liu, K.-M. Liu, S.-Y. Chen, Study on controlled drug permeation of magnetic-sensitive ferrogels: effect of Fe_3O_4 and PVA. *J. Controll. Release* **126**, 228–236 (2008). <https://doi.org/10.1016/j.jconrel.2007.12.006>
 7. T. Mitsumata, K. Ikeda, J.P. Gong, Y. Osada, D. Szabo, M. Zrinyi, Magnetism and compressive modulus of magnetic fluid containing gels. *J. Appl. Phys.* **85**(12), 8451–8455 (1999). <https://doi.org/10.1063/1.370626>
 8. P. Calvert, Gel sensors and actuators. *MRS Bull.* **33**(3), 207–212 (2008). <https://doi.org/10.1557/mrs2008.46>
 9. M. Babincova, D. Lesoczczynska, P. Sourivong, P. Cicimanec, P. Babinec, Superparamagnetic gel as a novel material for electro-magnetically induced hyperthermia. *J. Magn. Magn. Mater.* **225**, 109–112 (2001). [https://doi.org/10.1016/S0304-8853\(00\)01237-3](https://doi.org/10.1016/S0304-8853(00)01237-3)
 10. M. Zrinyi, D. Szabo, Muscular contraction mimicked by magnetic gels. *Int. J. Mod. Phys. B* **15**(6&7), 557–563 (2001). <https://doi.org/10.1142/S0217979201005015>
 11. J. Sharma, V.K. Aswal, P.S. Goyal, H.B. Bohidar, Small-angle neutron scattering studies of chemically cross-linked gelatin structures and gels. *Macromolecules* **34**, 5215–5220 (2001). <https://doi.org/10.1021/ma0022194>
 12. S. Yin, I. Ahmad, M.C.I.M. Amin, Synthesis of chemical cross-linked gelatin hydrogel reinforced with cellulose nanocrystals (CNC). *AIP Conf. Proc.* **1614**, 375–380 (2014). <https://doi.org/10.1063/1.4895226>
 13. S. Farris, J. Song, Q. Huang, Alternative reaction mechanism for the cross-linking of gelatin with glutaraldehyde. *J. Agric. Food Chem.* **58**, 998–1003 (2010). <https://doi.org/10.1021/9031603>
 14. M. Foox, M. Zilberman, Drug delivery from gelatin-based systems. *Expert Opin. Drug Deliv.* **12**(9), 1547–1563 (2015). <https://doi.org/10.1517/17425247.2015.1037272>
 15. J.F. Martucci, R.A. Ruseckaite, A. Vazquez, Creep of glutaraldehyde-crosslinked gelatin films. *Mater. Sci. Eng. A* **435**, 681–686 (2006). <https://doi.org/10.1016/j.msea.2006.07.097>
 16. A. Bigi, G. Cojazzi, S. Panzavolta, K. Rubini, N. Roveri, Mechanical and thermal properties of gelatin films at different degrees of glutaraldehyde crosslinking. *Biomaterials* **22**, 763–768 (2001). [https://doi.org/10.1016/S0021-9042\(00\)00236-2](https://doi.org/10.1016/S0021-9042(00)00236-2)
 17. H. Oikawa, H. Nakanishi, A light scattering study on gelatin gels chemically crosslinked in solution. *Polymer* **34**(16), 3358–3361 (1993). [https://doi.org/10.1016/0032-3238\(93\)90460-R](https://doi.org/10.1016/0032-3238(93)90460-R)
 18. M. Helminger, B. Wu, T. Kololmann, D. Benke, D. Schqahn, V. Pipich, D. Faivre, D. Zahn, H. Colfen, Synthesis and characterization of gelatin-based magnetic hydrogels. *Adv. Func. Mater.* **24**, 3187–3196 (2014). <https://doi.org/10.1002/adfm.201303547>
 19. I. Migneault, C. Dartiguenave, M.J. Bertrand, K.C. Waldron, Glutaraldehyde: behavior in aqueous solution, reaction with proteins, and application to enzyme crosslinking. *Biotechniques* **37**(5), 790–802 (2004). <https://doi.org/10.2144/04375RV01>
 20. J. Sharma, H.B. Bohidar, Gelatin-glutaraldehyde supramolecular structures studied by laser light scattering. *Eur. Polymer J.* **36**, 1409–1418 (2000). [https://doi.org/10.1016/S0014-3057\(99\)00206-2](https://doi.org/10.1016/S0014-3057(99)00206-2)
 21. Y. You, X. Sun, Q. Cui, B. Wang, J. Ma, The retention and drainage behavior of cross-linked gelatin with glutaraldehyde in a papermaking system. *BioResources* **11**(3), 6162–6173 (2016)
 22. N.A. Choudhury, S. Sampath, A.K. Shukla, Gelatin hydrogel electrolytes and their application to electrochemical supercapacitors. *J. Electrochem. Soc.* **155**(1), A74–A81 (2008). <https://doi.org/10.1149/1.2803501>
 23. L.H.H. Olde Damink, P.J. Dijkstra, M.J.A. Van Lyun, P.B. Van Wachem, P. Nieuwenhuis, J. Feijen, Glutaraldehyde as a crosslinking agent for collagen-based biomaterials. *J. Mater. Sci.* **6**, 460–472 (1995). <https://doi.org/10.1007/BF00123371>
 24. F. Ganji, S. Vashoghani-Farahanv, E. Vasheghani-Farahanv, Theoretical description of hydrogel swelling: a review. *Iran. Polym. J.* **19**(5), 375–398 (2010)
 25. J. Ostrowska-Czubenko, M. Gierszewska, M. Pierog, pH-responsive hydrogel membranes based on modified chitosan: water transport and kinetics of swelling. *J. Polym. Res.* **22**, 153 (2015). <https://doi.org/10.1007/s10965-015-0786-3>
 26. X. Lou, T.V. Chirila, Swelling behavior and mechanical properties of chemically cross-linked gelatin gels for biomedical use. *J. Biomater. Appl.* **14**, 184–191 (1999). <https://doi.org/10.1177/088532829901400204>
 27. A.V. Teixeira, I. Morfin, F. Ehrburger-Dolle, C. Rochas, P. Panina, P. Licinio, E. Gcissler, Structure and magnetic properties of dilute ferrofluids suspended in gels. *Compos. Sci. Technol.* **63**, 1105–1111 (2003). [https://doi.org/10.1016/S0266-3538\(03\)00031-9](https://doi.org/10.1016/S0266-3538(03)00031-9)
 28. N.M. Wereley, A. Chauduri, J.-H. Yoo, S. John, S. Kotha, K. Suggs, R. Radhakrishnan, B.J. Love, S. Sudarshan, Bidisperse magnetorheological fluids using Fe particles at nanometer and micron scale. *J. Intell. Mater. Syst. Struct.* **17**, 393–401 (2006). <https://doi.org/10.1177/1045389X06056953>
 29. H. Schott, Swelling kinetics of polymers. *J. Macromol. Sci. B* **31**(1), 1–9 (1992). <https://doi.org/10.1080/00222349208215453>
 30. H. Dai, S. Ou, Y. Huang, Z. Liu, H. Huang, (2017), Enhanced swelling and multiple-responsive properties of gelatin/sodium alginate hydrogels by the addition of carboxymethyl cellulose isolated from pineapple peel, *Cellulose*, <https://doi.org/10.1007/s10570-017-1557-6>
 31. N.A. Choudhury, A.K. Shukla, S. Sampath, S. Pitchumani, Cross-linked polymer hydrogel electrolytes for electrochemical capacitors. *J. Electrochem. Soc.* **153**(3), A614–A620 (2006). <https://doi.org/10.1149/1.2164810>
 32. S.S. Sekhon, Conductivity behaviour of polymer gel electrolytes: role of polymer. *Bull. Mater. Sci.* **26**(3), 321–328 (2003)
 33. H. Ochiai, Y. Fujing, Y. Tadokoro, I. Murakami, Polyelectrolyte behaviour of poly(vinyl alcohol) in aqueous borax solutions. *Polym. J.* **14**(5), 423–426 (1982). <https://doi.org/10.1295/polymj.14.423>

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