



Study Of Water Absorption And Self-Healing Behavior Of Carboxymethyl Cellulose/ Poly (Acrylamide-Co-Vinyl Imidazole) Ph-Sensitive Hydrogel

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Abstract

In this work, acrylamide (AAM) and vinyl imidazole (VI) were co-polymerized in the presence of carboxymethyl cellulose (CMC) which resulted solid hydrogel electrolyte (SHE) with fair self-healing property. The hydrogel electrolyte exhibited pH-dependent swelling behavior with percent equilibrium swelling (PES) of 5170, 1892 and 5163 in the swelling media of pH 1.0, 6.8 and 13.0 respectively. In addition, the kinetic swelling was best interpreted by the Power function model, revealing a chain relaxation-controlled water uptake at pH 1.0 and 13.0. The SHE showed an excellent self-healing property which was confirmed by “LED glowing” experiment. As compared to its original elongation of 200 %, the self-healed hydrogel exhibited an elongation of 157 %, thus showing restoration tendency.

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Keywords: Solid hydrogel electrolyte, hydrogel, self-healing.

1. INTRODUCTION

A fairly high-water content, flexibility, adhesiveness are the basic requirements for use of hydrogels in biomedical field such as in tissue engineering [1, 2]. On the other hand, using these hydrogels as storage energy devices requires a high conductivity, flexibility and fair mechanical strength. However, development of a hydrogel with the above-mentioned properties still remains a challenge. The reason is that fairly high-water content usually results in a brittle polymer matrix. Similarly, a fairly high movement of polymeric segments is required for self-healing property, but this automatically reduces the mechanical strength [3, 4]. Therefore, in order to have a hydrogel with all such desired properties, a proper selection of monomers and polymers is required so that the polymer formed has an appropriate combination of hydrophilicity, bonding strength, presence of protonated /deprotonated groups and mutual entanglements of polymer chains.

Hydrogels with self-healing properties have been a focus of attention for material scientists. It is due to a wide range of their applications in wearable flexible devices, [5,6] electronic skin, [7,8] biomedicine, [9,10] tissue engineering, [1,2] cell therapy, wound dressing, [11-14] etc. There are a number of approaches that have been employed to fabricate self-healing hydrogels. These include hydrogen bonding, host-guest recognition, electrostatic interactions, hydrophobic associations, metal-ligand coordination, dynamic covalent bonds etc. [15-19].

In this way, the proposed solid hydrogel electrolyte (SHE) system has excellent self-healing and adhesive properties with fair flexibility and electrical conductivity. In addition, presence of ionizable moieties provides a conducting property to the gel that can be further enhanced by addition of electrolytes during the preparation of HER. To the best of our knowledge, a hydrogel system, consisting of CMC and copolymer poly (AAm-co-VI), with only H-bonding interactions as a cross linker is not reported till date.

2. EXPERIMENTAL

2.1 Materials

Vinyl monomers Acrylamide (AAM) and Vinyl imidazole (VI) were purchased from Hi-Media Chemicals, Mumbai, India. Monomer AAm was re-crystallized in methanol to remove the inhibitor. Carboxymethyl cellulose (CMC), initiator potassium per sulfate (KPS) and other salts were also purchased from Hi Media Chemicals and used as received. The double distilled water was used throughout the investigations.

2.2 Preparation of solid hydrogel electrolyte (SHE)

The SHE was prepared by carrying out free radical co-polymerization of monomer AAm and VI in the presence of dissolved CMC. A pre-determined quantity of monomers AAm and VI was mixed into a definite volume of CMC solution, followed by addition of glycerol (if required) and initiator KPS. The pre-polymerization mixture was poured into plastic rectangular molds and kept in an electric oven (Teamster, India) at 40° C for 1 h. Finally, the films were taken out carefully and placed in Polyethylene bags for further use. In all, four samples were prepared with different compositions.

2.3 Measurement of water absorption behavior

A pre-weighed small piece of the sample SHE-I was placed in swelling medium of definite pH and its mass was measured at definite time intervals till the attainment of equilibrium. The percent swelling (PS) was calculated using the following expression:

$$PS = \frac{W_t - W_o}{W_o} \times 100 \quad (1)$$

Where, W_o is the initial dry mass and W_t is the mass of the sample in swollen state at time 't'.

In order to study effect of pH of the swelling media on water absorption behavior of hydrogels, buffer solutions of different pH were prepared and the pre-weighed piece of sample SHE-I was equilibrated for a period of 48 h to allow the samples to attain equilibrium swelling (PES).

2.4 Self-healing studies

2.4.1 "LED glow experiment"

Two terminals of a 5-volt battery were connected to a LED bulb which started to glow. Now, a strip of hydrogel sample SHE-I was introduced in the electric circuit. The LED bulb continued to glow. Now the hydrogel was cut into two parts using a sharp blade. Due to break in the electrical circuit the LED bulb blew off. Now, the cut pieces of hydrogel sample were brought in contact for five min. As a result of healing of gel, the LED bulb again started to glow.

2.4.2 Gel stretching experiment

A piece of hydrogel sample SHE-I of definite length was stretched and then brought back to its original length. Now, the hydrogel was cut into two pieces and the cut ends were put in contact for self-healing. After the gel was healed, it was again stretched and percent elongation was measured.

2.4.3 Construction of geometries/letters

A long piece of hydrogel sample SHE-I, in the form of a thick fiber, was cut into pieces and the cut ends were brought into contact for definite time period for self-healing, just to make different geometries.

3. RESULTS AND DISCUSSION

3.1 Water absorption studies

Results of water absorption kinetics of the sample SHE-I in the media of pH 1.0, 6.8 (distilled water) and pH 7.4 are shown in (Figure. 6 (a)). It can be seen that the hydrogel demonstrates a fast swelling in pH 1.0 while the kinetic water uptake profiles of the sample in distilled water and pH 7.4 run almost coinciding with each other. The higher water uptake in the swelling medium of pH 1.0 may probably be attributed to the

protonation of imidazole groups of VI which is a component of co-polymer. The positively charged imidazole groups repel each other, thus unfolding the polymer chains and letting more and more water to enter into the network. It was also observed that the hydrogel possessed fair shape stability, though no crosslinking agent has been used in preparation of SHE system. It appears that in the medium of pH 1.0, carboxymethyl groups and $-OH$ groups, present in CMC chains, may produce intermolecular H-bonding interactions among $-OH$ and CH_2COOH groups of CMC chains and intermolecular interactions between amide groups of AAm and hydroxyl, carboxymethyl groups of CMC. The percent equilibrium swelling (PES) in the medium of pH 1.0 was 5170 (i.e., almost 52 times swelling). The SHE with such high water content became very soft and slippery. Still it maintained its structural integrity. The dynamic water uptake profiles for distilled water and pH 7.4 medium were almost overlapped. The relatively much lower uptake could be attributed to the absence of protonated /ionized groups within the polymer matrix. This prevented the polymer chains from unfolding and therefore allowed limited water content within the SHE network. The kinetic data was interpreted in the terms of very well-known 'Power function' and 'Schott models (equations not shown). The linear plots, shown in Figure 1(b) and (c) respectively, were used to calculate respective parameters. All the parameters are given in Table-1. A close look at the Table-1, reveals that a high degree of regression is obtained for Power function model, thus indicating its suitability. However, the Schott model showed very poor regressions and, in addition, the experimental and theoretical values did not match. It is also noteworthy that swelling exponent 'n' is 0.738 for swelling of hydrogel in the medium of pH 1.0, thus supporting chain relaxation behavior of hydrogel.

The pH-dependent swelling behavior of the sample SHE-I was studied by observing variation in 'Percent Equilibrium Swelling' (PES) with pH of the swelling media, in the range of 1.0 to 13. The results, as shown in Figure. 1(d), reveal that a 'U' shaped profile is obtained, indicating a higher PES in the media of pH 1.0 (i.e., 5170) as well as 13.0 (i.e., 5163). The highest water uptake in the medium of pH 1.0 and 13.0 may be explained as follows: In pH 1.0, the imidazole groups get protonated and there occurs unfolding of chains. This allows a huge quantity of water molecules to enter into network. On the other hand, when pH of the swelling medium is 12.0, the highly alkaline medium induces hydrolysis of amide groups of constituents AAm of copolymer poly (AAm-co-VI) into carboxylic groups which get ionized to yield $-COO^-$ groups along the copolymeric chains.

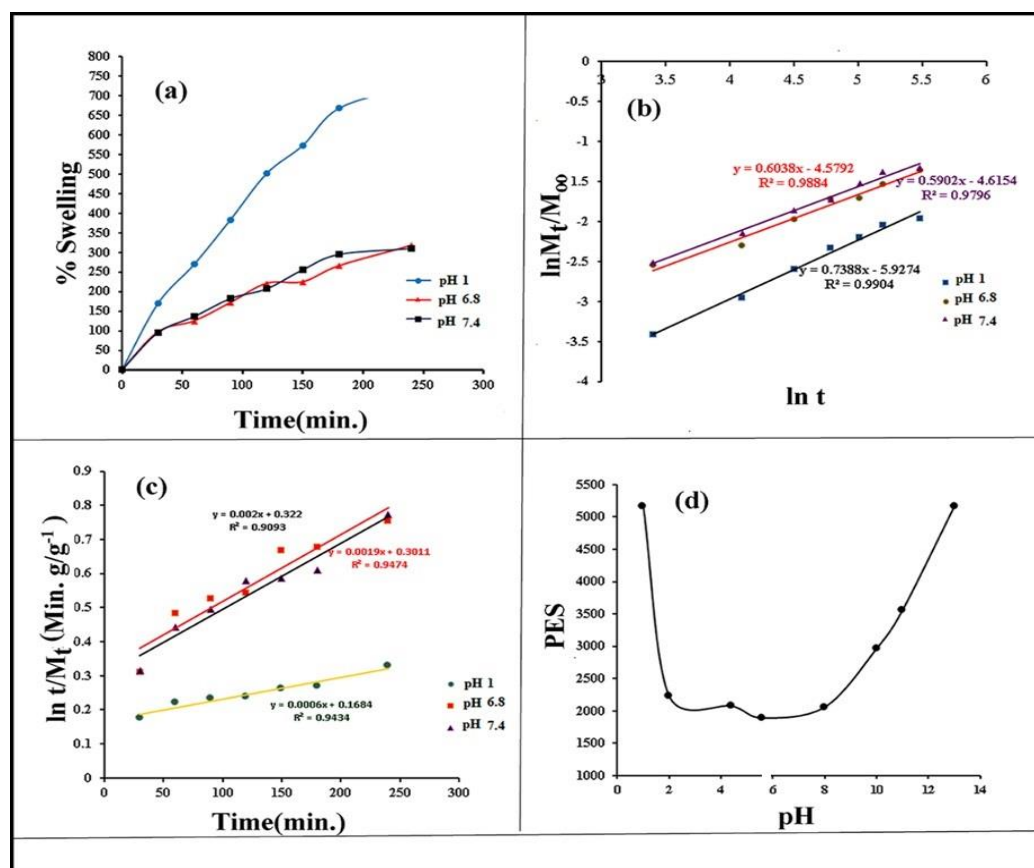


Figure 1: (a) Dynamic water uptake profile of sample SHE-I, (b) Power function, (c) Schott models for water uptake data and (d) pH-dependent equilibrium water uptake of sample SHE-I.

Hence, as a result of electrostatic repulsion, chains are unfolded and allow more and more water molecules to enter. In addition, ionized carboxymethyl groups also contribute to this unfolding. However, in the vicinity of neutral pH, i.e., 7.0, the polymer chains of CMC and poly (AAM-co-VI) are entangled with each other thus providing a folded network with H-bonding interactions, which act as physical crosslinks. Therefore, water absorption is restricted in this case. Finally, the PSE of 5163 in pH medium of 13.0 was attributable to the fact that in the strong alkaline medium, the acrylamide molecules, present within the co-polymer chains were hydrolyzed to yield $-\text{COOH}$ groups which were ionized to yield negatively charged carboxylate ions along the co-polymeric chains and thus induced chain relaxation process within the polymer matrix. This resulted in higher water uptake.

Table1. Parameters associated with kinetic models used to interpret the water uptake data for sample SHE-I at room temperature.

pH of the medium	Kinetic models						
	Power function model			Schott model			
	$k \times 10^3$	n	R^2	$k_2 \times 10^6$	$M_{\infty(\text{th.})} (\%)$	$M_{\infty(\text{exp.})} (\%)$	R^2
1.0	2.7	0.7388	0.9904	2.13	1666.6	5170.6	0.9434
6.8	9.9	0.5902	0.9796	12.42	500.5	1237.8	0.9093
7.4	10.3	0.6038	0.9884	11.98	526.2	1165.8	0.9474

3.2 Self-healing behavior

As mentioned earlier, presence of H-bonding interactions in a polymer matrix renders self-healing property to it. In this work, the self-healing behavior of the sample SHE-I was confirmed by ‘LED’ experiment. It can be seen (Figure. 2(a)) that initially, the intact SHE works as a connecting medium and allows the electric current to flow through and hence the LED bulb glows. However, when the SHE is cut into two pieces, the circuit is broken and therefore the LED blows off (Figure. 2B). Finally, when the two cut ends are brought into contact for five minutes, the hydrogel is self-healed and the continuity is again restored. This again maintains the flow of electricity, thus finally allowing the LED bulb to glow (Figure.2(c)). These results may be explained as follows: when the hydrogel is cut into two pieces, the H-bonding interactions are ruptured and the current supply is stopped. However, when the two ends are brought into contact, the imidazole, hydroxyl and amide groups are attached to each other again, thus making a continuous path for the flow of electric current. The re-formation of H-bonds across the interface of the terminals of cut ends is the major reason for self-healing of hydrogel electrolyte.

In order to confirm whether the healed SHE also exhibits the same strength as the native one, a piece of hydrogel, 7 cm long, was stretched at its two ends. The percent elongation was almost 200 % as shown in (Figure. 2(d) and (e)). Now, the strip was cut into two pieces, which were joined together to start the healing process (Figure. 2(f)). After the gel was healed properly, the strip was again stretched at both the ends (Figure. 2 (g)). It was observed that the strip was elongated to 157 %, thus indicating that strength of hydrogel strip was restored to a great extent after healing through H-bonding interactions. The self-healing property of SHE was further demonstrated by cutting a long piece of hydrogel into small pieces and then joining them to make some geometries as shown in (Figure.2 (h)). It is also worth mentioning here that the geometries made had proper strength and they could not be deformed by external stress.

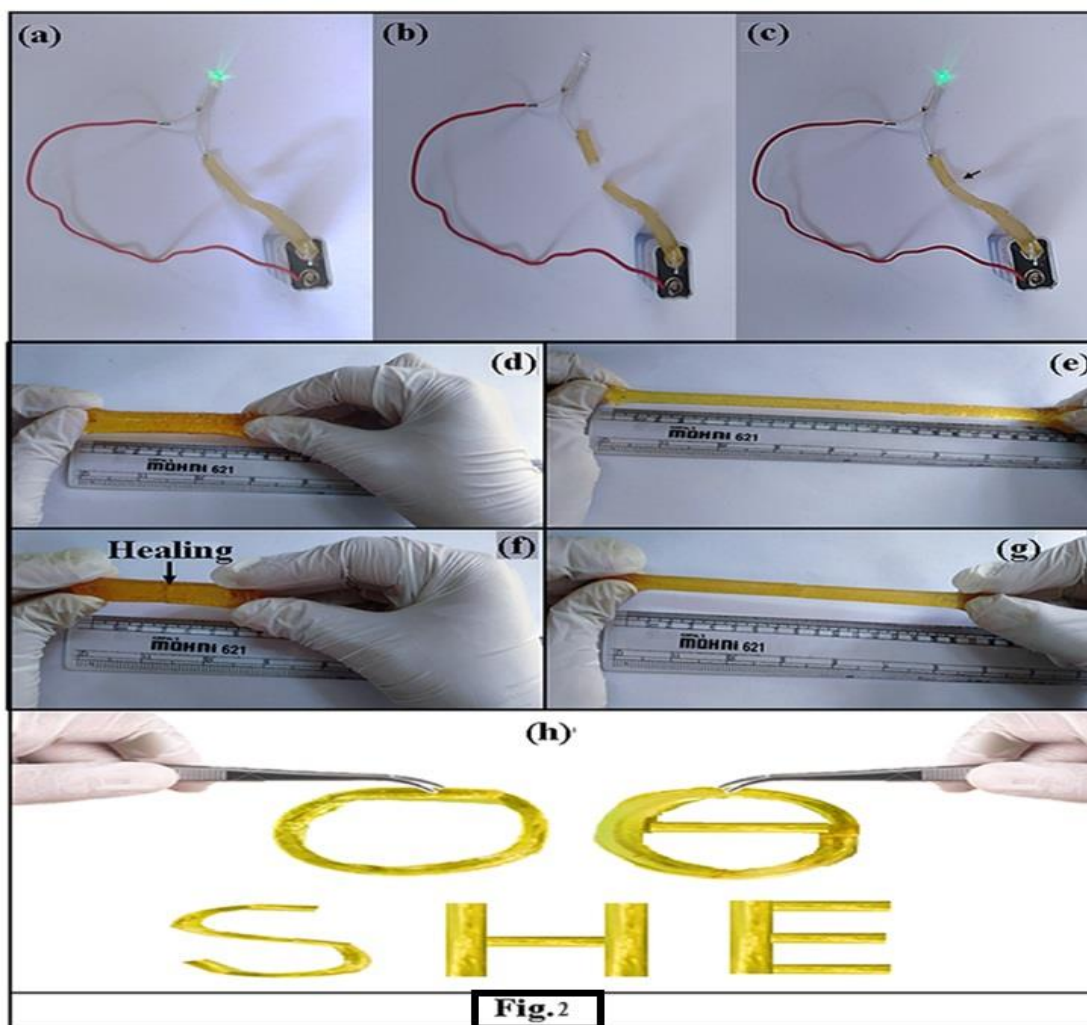


Figure 2: (a) SHE acts as a conductor and glows the LED bulb, (b) the gel is cut and the LED blows off, (c) LED glows again when two cut ends put together and gel is healed, (d) and (e) a 7 cm gel piece elongates to 200%, (f) gel is cut into two pieces and allowed to heal, (g) healed gel showing elongation of 157% and (h) some geometries fabricated using pieces of hydrogel.

4. CONCLUSION

Because of H-bonding interactions and mutual entanglements within CMC and poly (AAm-co-VI) macromolecular chains, the solid hydrogel electrolyte (SHE) possesses self-healing. The hydrogel exhibits pH-dependent swelling behavior, obtaining higher degree of swelling at lower as well as higher pH.

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