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SEMI-INTERPENETRATING POLYMER NETWORK HYDROGELS BASED ON CHITOSAN AND POLY(ACRYLIC ACID)

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Abstract

New semi-interpenetrating polymeric network (IPN) hydrogels based on chitosan and poly(acrylic acid), crosslinked with glutaraldehyde, were prepared by free radical polymerization method. IPN hydrogels were synthesized by simultaneous polymerization/crosslinking of acrylic acid monomer in the presence of chitosan and crosslinker. The structure and surface morphology of the IPN hydrogels were characterized by FTIR and SEM, respectively. Variation in composition of the IPN was achieved by varying the concentration of crosslinker. In addition, these semi-IPNs were characterized for their pH-sensitive behaviour by equilibrium swelling studies. From these preliminary evaluations, it is possible to conclude that these IPN materials have potential applications in the biomedical field. Finally, the swelling kinetics of the synthesized composite with various particle sizes was preliminarily investigated.

1. Introduction

The preparation and properties of interpenetrating polymer networks (IPNs) have received considerable interest in recent years due to their widespread applications such as ion exchange resins, high impact

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plastics, adhesives, vibration dumping materials, and high temperature alloys. A search of past literature reveals that the field of IPN was laid down by Millar in 1960 [7]. Since then a number of IPNs based on homo and copolymers have been synthesized, followed by multicomponent IPN systems [2, 6, 10, 14-16].

Interpenetrating polymer networks (IPNs) are described as an intimate combination of two (or more) crosslinked polymers [13]. The tight entanglement of these networks ensures a good interpenetration of the two components and a good dimensional stability. Moreover, one can observe an improved combination of the properties of its components.

Polymeric hydrogels in the form of interpenetrating polymer networks (IPNs) are able to absorb large amounts of water without dissolving. They have been proposed for many biomedical applications due to their good biocompatibility and water permeation properties [1]. Polymeric hydrogels are promising candidates for various applications due to the hydrophilic nature and mechanical properties of polymeric hydrogels [3-5].

Chitosan, a natural poly(aminosaccharide), is non-toxic and easily bioadsorbable. This biopolymer is a weak base with an intrinsic pK_a of 6.5 and with gel forming ability at low pH. In acidic solutions, the amine groups of a crosslinked chitosan are protonated and form a cationic hydrogel and result in swelling of the hydrogel network. For several years, chitosan has been largely evaluated as a potential vehicle for drugs administered orally. The development of hydrogel matrices incorporated with chitosan for oral drug delivery is still a virgin area of study. In the current study, we investigate the synthesis and properties of an IPN hydrogel from poly(acrylic acid) and chitosan backbones by using glutaraldehyde.

2. Experimental

2.1. Materials

Chitosan was obtained from Aldrich, Milwaukee, WI, USA and used without further purification. Glutaraldehyde (GA, from Merck) and ammonium persulphate (APS, from Fluka) were of analytical grade and used without further purification. Acrylic acid (AA, Merck) was used after vacuum distillation. Double distilled water was used for the hydrogel preparation and swelling measurements.

2.2. Preparation of hydrogel

In general, 0.50g of chitosan was dissolved in 30mL of distillated degassed 1wt% acetic acid solution, and then 1.50g of poly(acrylic acid) was added to the chitosan solution and it was stirred to achieve a homogeneous solution. The reactor was placed in a water bath preset at 60°C. Desired volume of the glutaraldehyde solution was added to the mixture. The crosslinking reaction was allowed to proceed for 1h. The hydrogel was neutralized with NaOH solution (1N) to pH 7. Ethanol (300ml) was added to the gelled product while stirring. After complete dewatering for 24h, the hardened semi-IPN hydrogel product were filtered, washed with fresh methanol and dried at 50°C.

2.3. Swelling behaviour of hydrogels

The swelling ratios and swelling kinetics of hydrogel samples were measured gravimetrically. Weights of swollen hydrogels were obtained after being wiped off the excess water on the surfaces with moistened filter paper. The average value of three measurements from three parallel specimens in the same hydrogel was taken for each sample.

The swelling ratios were measured by immersing hydrogel samples in water at each predetermined temperature for different time intervals. The weight of swollen sample was recorded at each immersion temperature with various immersion time intervals. The swelling ratio S was calculated as follows:

$$S = \frac{W_t - W_d}{W_d}. \tag{1}$$

For the equilibrium swelling ratio S_{eq}:

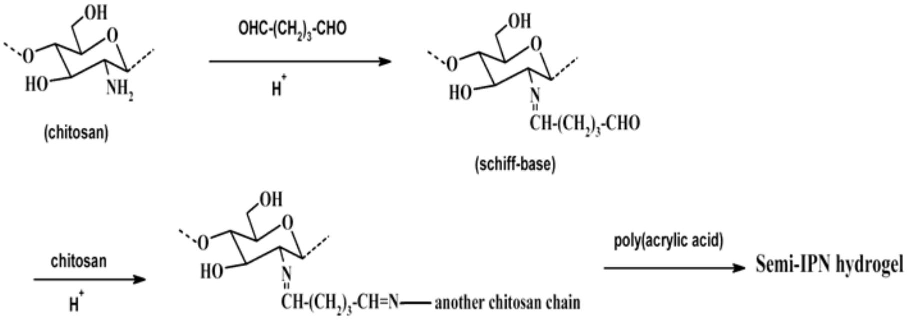
$$S_{eq} = \frac{W_e - W_d}{W_d}, \tag{2}$$

where W_t, W_e are the weights of swollen hydrogels at a time interval t or at equilibrium state under a given condition, respectively; W_d is the dry weight of the hydrogel.

3. Results and Discussion

3.1. Mechanism of hydrogel formation

The mechanism of crosslinking of chitosan via glutaraldehyde was illustrated in Scheme 1. At the first step, the schiff-base formation reaction takes place between amine groups of chitosan and glutaraldehyde. Then, aldehyde group in acidic medium is reacted with the amine group of other chitosan chain and the crosslinks formed result in the semi-IPN hydrogel in the presence of poly(acrylic acid).



Scheme 1. General mechanism for glutaraldehyde-crosslinking of chitosan to form the crosslinked part of the chitosan-based semi-IPN hydrogel.

For identification of the hydrogel, infrared spectroscopy was used. FTIR spectral analyses were carried out to confirm the chemical structure of chitosan-based semi-IPN. The FTIR spectra of pure chitosan and the semi-IPN hydrogel are shown in Figure 1. In Figure 1(a), a broad band at 3425cm^{-1} corresponds to the associated –OH stretching vibrations of the hydroxyl groups, and the peak at 1641 cm^{-1} corresponds to the N-H deformation bending of chitosan. In the spectrum of the hydrogel (Figure 1(b)), new peaks are appeared at 3206, 1647, and 1562 cm^{-1} that may be attributed to amide NH stretching, asymmetric, and symmetric amide NH bending, respectively [12].

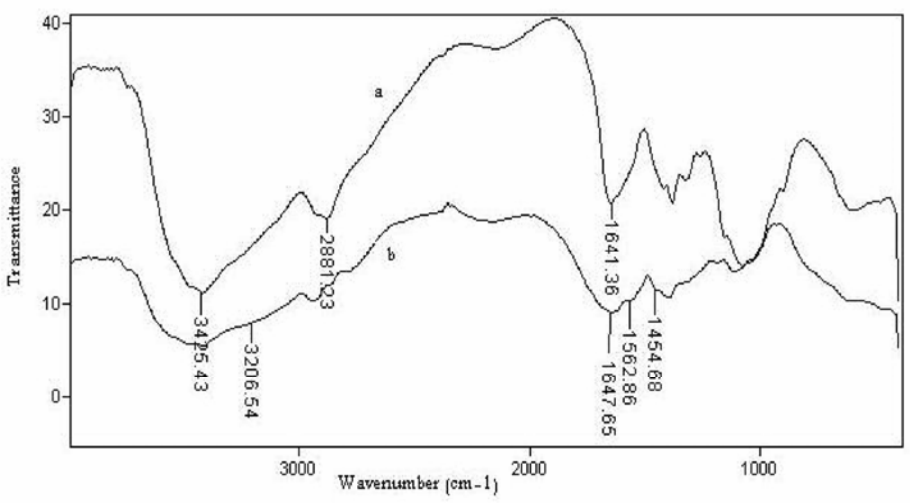


Figure 1. FTIR spectra of (a) chitosan and (b) chitosan-based semi-IPN hydrogel.

One of the most important properties that must be considered is hydrogel microstructure morphologies. Figure 2 shows the scanning electron microscope images of the hydrogel. This picture verifies that the synthesized polymer in this work have a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

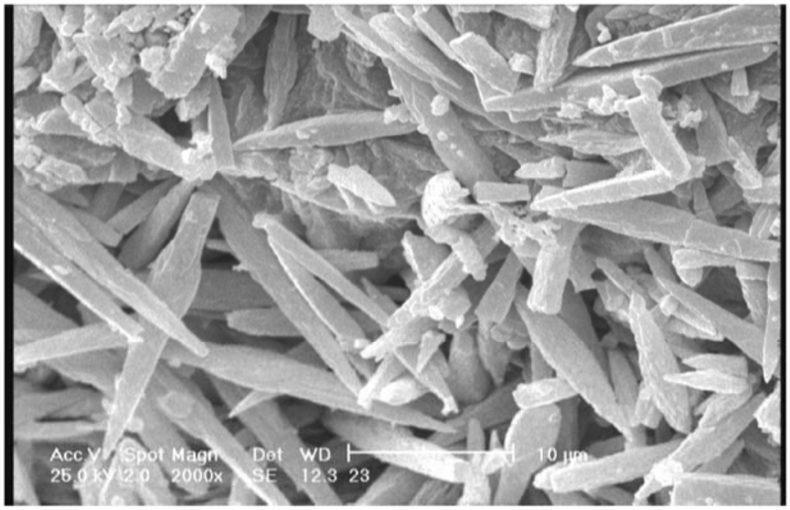


Figure 2. SEM photograph of the hydrogel. Surfaces were taken at a magnification of 2000X, and the scale bar is 10μm.

3.2. Effect of crosslinker concentration on swelling

The swelling ratio as a function of GA concentration was investigated (Figure 3). Crosslinks is necessary to form a superabsorbent in order to prevent dissolution of the hydrophilic polymer chains in an aqueous environment. As the concentration of GA was increased, the water absorbency of the superabsorbent composite was decreased. This is due to a decrease in the space between the copolymer chains as the crosslinker concentration is increased.

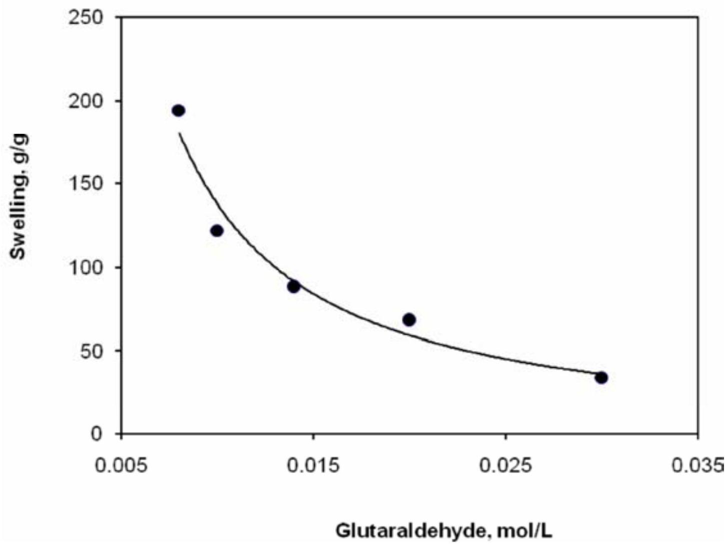


Figure 3. Effect of the crosslinker concentration on water absorbency of the semi-IPN.

3.3. Equilibrium swelling at various pH solutions

In this series of experiments, equilibrium swelling for the synthesized hydrogels was measured in different buffer solutions with pHs ranged from 1.0 to 12.0 (Figure 4). According to Figure 4, the two sharp swelling capacity changes can be attributed to high repulsion of $-\mathrm{NH}_3^+$ groups in acidic media and $-\mathrm{COO}^-$ groups in basic media. However, at very acidic conditions $(\mathrm{pH} \leq 2)$, a screening effect of the counter ions, i.e., Cl^-, shields the charge of the ammonium cations and prevents an efficient repulsion. As a result, a remarkable decreasing in equilibrium swelling is observed (gel collapsing). Around pH 5, the carboxylic acid component comes in to action as well. Since the pK of the weak polyacid is about 6.4, its ionization occurring above this value, may favour enhanced absorbency. But under pH 6.4, at a certain pH range 4-6, the majority of the base and acid groups are as non-ionized forms, so hydrogen bonding between amine and carboxylic acid (and probable carboxamide groups) may lead to a kind of crosslinking followed by a decreased swelling. At higher pHs, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO^-) causes increasing in swelling. Again, a screening effect of the counter ions (Na^+) limits the swelling at pH 8-12.

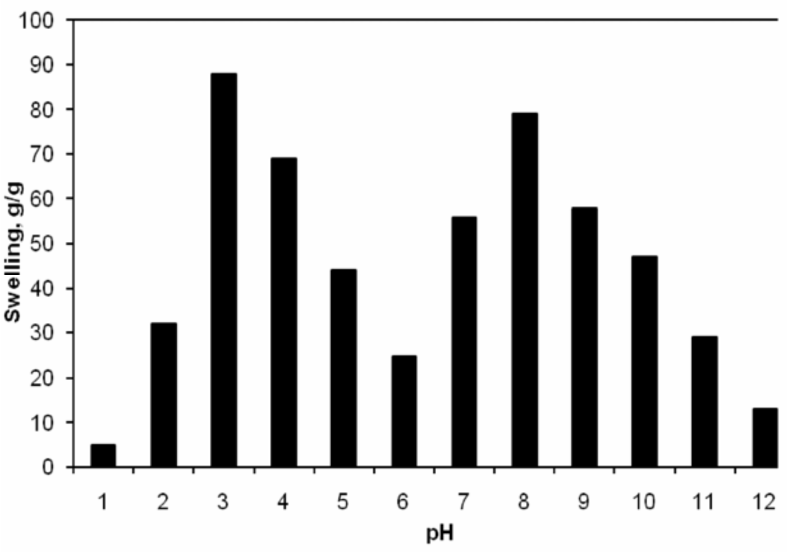


Figure 4. Effect of pH of buffer solutions on swelling capacity of semi-IPN hydrogel.

3.4. Swelling kinetics

A preliminary study was conducted on superabsorbent swelling kinetics. Figure 5 represents the dynamic swelling behaviour of the semi-IPN with various particle sizes in water. Initially, the rate of water uptake sharply increases and then begins to level off. The equilibrium swelling was achieved after 60 minutes. Power law behaviour is obvious from Figure 5. The data may be well fitted with a Voigt-based equation (Equation (3)) [8]:

$$S_t = S_e(1 - e^{-t/\tau}), \tag{3}$$

where $S_t(g/g)$ is swelling at time t, S_e is equilibrium swelling (power parameter, g/g), t is time (min) for swelling S_t, and τ (min) stand for the rate parameter. The rate parameters for superabsorbent are found to be 2.3, 3.1, and 4.2 min for superabsorbent with particle sizes of 100-250, 250-400, and 400-550μm, respectively. It is well-known that the swelling kinetics for the superabsorbent polymers is significantly influenced by particle size of the absorbents [9]. With a lower the particle size, a higher rate of water uptake is observed. An increase in the rate of absorption would be expected from the increase in surface area with decreasing particle size of composite.

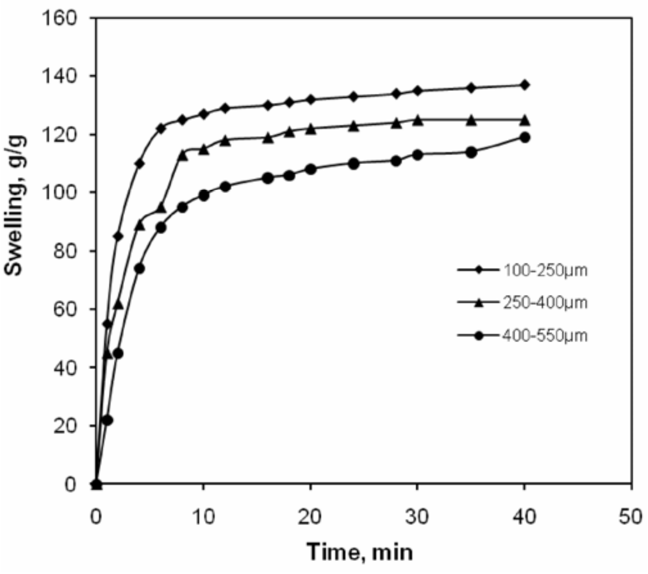


Figure 5. Representative swelling kinetics of a semi-IPN hydrogel with various particle sizes.

We also analyzed the swelling kinetics in order to find out whether swelling follows first or second order kinetics. We adopted the procedure followed by Quintana et al. [11]. For the first order kinetics, rate of swelling at any time is proportional to the water content before the equilibrium absorbed water (W_∞) has been reached. The swelling can be expressed as Equation (4):

$$\frac{dW}{dt} = K(W_\infty - W), \tag{4}$$

where W is the water content of the superabsorbent at time t and K is a constant.

Upon integration of Equation (4) between the limits $t = 0$ to t and $W = 0$ to W, the following expression can be obtained:

$$Ln\frac{W_\infty}{W_\infty - W} = Kt. \tag{5}$$

If the swelling process of superabsorbent follows a first order kinetics, the plot of the variation of $\ln(W_\infty / W_\infty - W)$ as a function of time should give a straight line. But none of the swelling studies in water followed Equation (5).

Considering the second order kinetics, the swelling rate at any time may be expressed as Equation (6):

$$\frac{dW}{dt} = K(W_\infty - W)^2. \tag{6}$$

Integration Equation (6) with the limits $t = 0$ to t and $W = 0$ to W and after rearrangement, the following equation is obtained:

$$\frac{t}{W} = \frac{1}{K{W_\infty}^2} + \frac{1}{W_\infty}t. \tag{7}$$

According to this equation, the swelling data must fit a straight line with a slope of $1 / W_\infty$ and an ordinate of $1 / KW_\infty^2$. The variation of t / W against time is plotted in Figure 6. It was found that swelling data of superabsorbent in water gives straight lines. So, the swelling of the synthesized superabsorbent composites with various particle sizes obey second order kinetics.

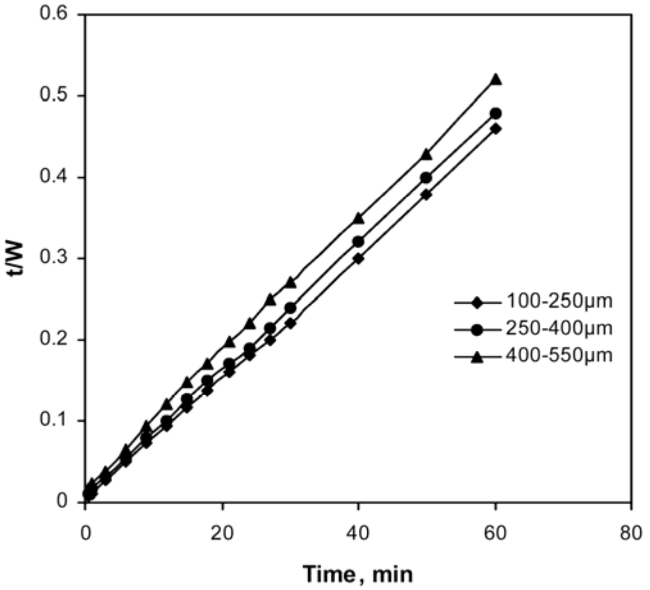


Figure 6. Plot t/W-time according to Equation (8) (second order kinetics) for semi-IPN hydrogel with various particle sizes.

4. Conclusion

In this paper, we prepared semi-IPN hydrogels composed of chitosan and poly(acrylic acid) by crosslinking with glutaraldehyde. The effect of the glutaraldehyde concentration showed that with increasing of this parameters, the water absorbency of the superabsorbent composite are decreased. The swelling of hydrogels in solutions with various pHs also exhibited a high sensitivity to pH. So, this hydrogel intelligently responding to pH may be considered as an excellent candidate to design novel drug delivery systems. In addition, according to the dynamic rate measurements, the swelling of the hydrogel composites showed a second order kinetics of swelling in water.

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