

OPTIMIZATION OF THE SYNTHESIS OF ACRYLAMIDE HYDROGEL BY γ -RAY IRRADIATION

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Abstract Hydrogels have been synthesized from 10%, 20%, 30%, 40%, 50% and 60% aqueous solutions of acrylamide monomer by gamma radiation employing doses in the range of 0.2–30 kGy from a Co-60 source. The effect of solution concentration, γ -ray dose, pH and time was studied in order to observe the optimizing conditions in the characterization of hydrogels. Gel fraction increases with dose for all concentrations indicating hundred-percentage conversion of gel at doses $\geq$ 5 kGy for homogenous solutions in the range of 20%–50% concentration. On the other hand, 10% solution provides conversion less than 86% even at 30 kGy, whereas 60% monomer makes an inhomogeneous solution which still gives about 100% gel fraction. Swelling of hydrogels under water with respect to time varies with both the doses and concentrations due to the change of crosslinking density in the gels. The maximum volume change of hydrogels during swelling and water desorption mainly occurs within 24 h. Swelling is also enhanced with the rise of pH due to change of ionic content of the solvent. Considering the amount of gel fraction and the properties of hydrogel, the samples prepared from 20% solution at 5 kGy show better results. Moreover, the effect of bacteria on hydrogel was found to be nil, suggesting a prohibition of growth of microorganism in it.

Keywords Hydrogel, Acrylamide, γ -radiation, Swelling, Microorganism

INTRODUCTION

A hydrogel is a crosslinked polymer having three-dimensional network structure that absorbs water and swells to a definite shape^[1]. Swelling in water is an inherent property of a hydrogel, which imbibes water from the hydrophilic interaction between the network and the water molecules^[2]. The hydrophilic character of the gel was derived from the polar groups attached to the backbone of network molecules^[3].

The most important and interesting property of a hydrogel is the equilibrium degree of swelling that involves its volume change. This change occurring by solvent sorption with respect to time is strongly responsive to different factors such as environmental temperature, pH, ionic strength, mechanical stress and so on. The fast response time for a hydrogel to reach equilibrium is the key to its successful use in many applications. Thus hydrogels have attracted much attention for their potential applications in drug delivery devices, artificial muscles, chemical separation systems, sensors and actuators^[4, 5].

Though various techniques are adopted in preparing hydrogels the radiation cross-linking method has advantages over others, especially with respect to a clean environment and higher production rate^[6]. Many researches have been performed on synthesis and characterization of acrylamide hydrogel and its derivatives^[7–11]. However, specific work focusing on optimizing synthesis and characterization conditions of acrylamide hydrogels has not been done based on gamma dose, concentrations and pH of solvents and the time of swelling. The present work was aimed at finding the optimal values of these parameters for the preparation and characterization of acrylamide hydrogels.

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Received February 10, 2003, Revised March 14, 2003, Accepted March 21, 2003

EXPERIMENTAL

Sample Preparation

Acrylamide monomer of purity 99.5% was purchased from LOBA, Chemic, Bombay, India and used without any further purification for hydrogel synthesis. Aqueous acrylamide solutions having 10%, 20%, 30%, 40%, 50% and 60% concentrations (W/W) were well blended by stirring with a magnetic stirrer. The prepared monomer solutions were irradiated at doses of 0.2, 0.4, 0.6, 0.8, 1.0, 5.0, 10.0, 15.0, 20.0, 25.0 and 30.0 kGy from a Co-60 gamma source and kept 24 h for the completion of reaction. The irradiated samples became solid after radiation-induced polymerization except those of 10% concentrations exposed to 0.2 to 1.0 kGy. The solid samples were then subjected to water solubility test to confirm that they were in gel state. Then various physical properties of each sample were measured.

Thermal Measurement

To compare the thermal properties of monomer and hydrogel, thermal measurement was performed using a differential scanning calorimeter (DSC). The samples were placed in aluminum pans and sealed, and were then introduced into the heating cell of the DSC (Model- DSC-50, Shimadzu, Japan). Of two heating cells in the chamber, one was used for the reference material and the other one for the authentic sample. The reference material in DSC measurement is generally an empty but sealed pan. The heating process was performed from room temperature up to 400°C at a heating rate of 10 K/min. During the measurement, a continuous flow of inert gas (nitrogen) was maintained inside the chamber. Thereafter, the data were analyzed and assessed with the appropriate software.

Evaluation of Gel Fraction

All irradiated samples (approximately 1 g) were subjected to 24 h extraction with hot distilled water. The extracted samples were dried in an air oven at 100°C and then in a vacuum oven at 70°C to constant weight (W_1) after which the weights of them were measured. The percentage of gel fraction was evaluated gravimetrically as: gel fraction (%) = $(W_1/W_2) \times 100$, where W_2 = weight of monomer in 1 g irradiated sample.

Measurement of the Degree of Swelling

A small amount of gel from each sample was cut and dried at first in a normal oven at 100°C and then in a vacuum oven at 70°C to constant weight. The dried gel samples were placed in distilled water (pH = 7) and then taken out to weigh them at 4 h intervals for the first 24 h and then at 12 h intervals up to 168 h. Degree of swelling was estimated as W_3/W_4 , where, W_4 = dry weight and W_3 = wet weight (at particular time). Swelling of the sample was also studied in other solvents of pH = 3 and 10 and then the results were compared. Buffer solutions of pH = 3 were prepared with glacial acetic acid and sodium hydroxide and pH = 10 was produced with ammonia and ammonium chloride.

Determination of Desorption

A known weight of each gel was placed in previously weighed Petri dishes and kept at 30°C and a relative humidity of 50%. Their weights were measured at 1 h intervals for first 5 h and then at 24 h intervals up to 240 h. Water desorption (%) of hydrogel was calculated by the formula: $(W_6 - W_7)/(W_6 - W_5) \times 100$, where, W_5 = weight of Petri dish, W_6 = weight of Petri dish plus hydrogel and W_7 = weight of Petri dish plus hydrogel at various times.

Measurement of Bacterial Action on Gel

Approximately 5 g of swelled gels prepared from 20% and 30% concentrations of using doses of 1 and 10 kGy in each cases was placed in measuring flasks and distilled water was added up to the mark of 100 mL and another flask containing only 100 mL of distilled water was taken separately. All of them were sterilized by using autoclave at 121°C under 15 pound pressure for 15 min. Sterilized gel containing water and sterilized distilled water were used as the experimental and reference materials, respectively. The experimental samples were incubated with pathogenic bacterium (*Staphylococcus aureus*) in a concentration of 10^6 cfu (colony forming unit)/mL under aseptic conditions using a laminar flow cabinet. Both experimental and reference samples were then incubated at 37°C for 48 h. The surviving organisms were then enumerated using solid plate agar medium

(Nutrient Agar, Hi-Media) following the standard plate count method.

RESULTS AND DISCUSSION

Thermal Properties of Hydrogel

Figures 1(a) and 1(b) shows the thermal transition of acrylamide monomer and hydrogel, respectively. The melting of monomer starts at 78°C, whereas several transition peaks, which commence at 215°C and 320°C are observed in the case of hydrogel. The original monomer film is very brittle, whereas the hydrogel is soft and strong, suggesting the hydrogel has a network structure through chemical and physical bonding of the molecules. During breaking of these bonds it may show several transition peaks.

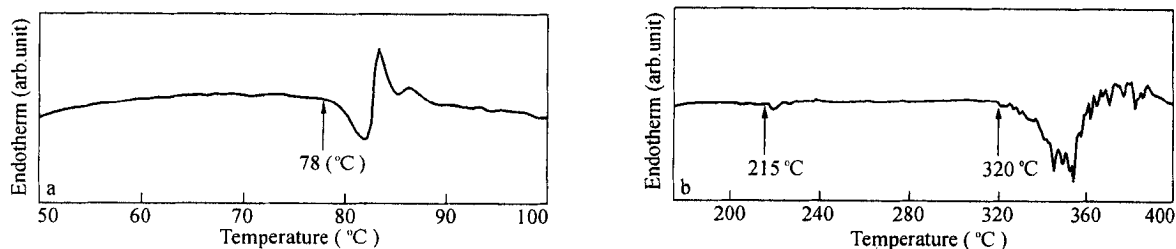


Fig. 1 (a) DSC thermogram of acrylamide monomer
(b) DSC thermogram of acrylamide hydrogel prepared by γ -ray irradiation

Effect of Doses and Concentrations on Gel Fraction

The amount of gel fraction (%) versus doses of hydrogels produced from different concentrations is presented in Fig. 2. Hydrogels are not produced at low concentrations (10%) with low doses (0.2–1 kGy). For all other concentrations, the gel fraction increases rapidly at doses lower than 5 kGy from which it becomes saturated. About 100% gel fraction is attained at doses ≥ 5 kGy for all solutions except that of 10% concentration, which shows the maximum value of gel fraction about 86 percent.

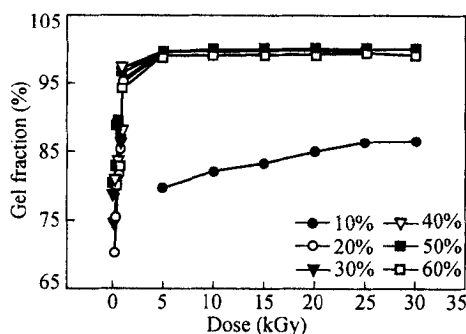


Fig. 2 Gel fraction of γ -ray irradiated hydrogels versus radiation dose for various concentrations

In principle, gel is synthesized by the same method as that used for the synthesis of linear polymers. Polymerization takes place when the solutions of monomer are irradiated by gamma rays. However, the limiting dose at which the production of gel begins is called the gel-point. Crosslinking of the molecules starts from the gel-point. If the doses are increased beyond it, the gel networks increase as evidenced by Fig. 2 and become saturated from 5 kGy.

In the case of 10% solution exposed to 0.2–1.0 kGy, the number of functional groups may be insufficient to achieve crosslinking. Though increasing doses are somewhat effective in enhancing crosslinking, they cannot make chemical reaction feasible among all surrounding molecules due to low concentration, whereas a 20%

solution can form gel even at lower doses. On the other hand, a 60% solution as an inhomogeneous solution ensures complete gel formation because of high monomer concentration. Considering the economic point of view, a 20% solution gives a high conversion to polymer network under the most favorable conditions. Generally, only hydrogels containing higher gel fraction have practical significance and hence the samples obtained from 10% solution are discarded for the evaluation of other physical properties.

Influence of Concentration, Dose, Time and pH on Swelling

Figure 3(a) shows the degree of swelling as a function of monomer concentration at various radiation doses. Swelling decreases with increasing concentrations up to 40% for all doses and then remains apparently unchanged. From the point of view of dose effect, hydrogels prepared at 20% concentration show the highest swelling and are thus considered as the superior samples. The change of swelling with dose at various times is shown in Fig. 3(b) for the hydrogels of 20% concentration. Swelling falls with doses up to 5 kGy and thereafter remains almost unchanged. Figure 4(a) indicates the variation of swelling with time of hydrogels prepared at a dose of 5 kGy. Swelling is virtually completed in 24 h after which it no longer depends on time. Figure 4(b) reveals the dependence of swelling on time and pH for the hydrogels prepared from a 20% solution at 5 kGy. From the results, it is evident that the solvent having pH = 10 provides comparatively higher swelling values than the others.

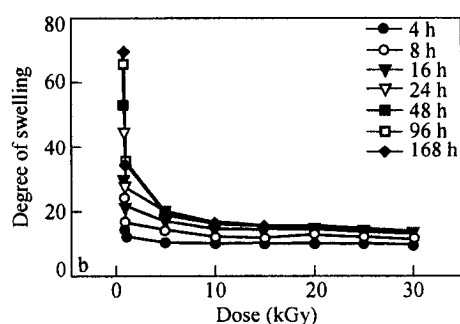
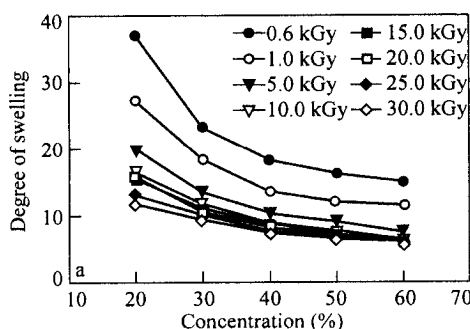


Fig. 3 (a) Dependence of swelling on initial monomer concentrations
(b) Change of swelling with radiation dose

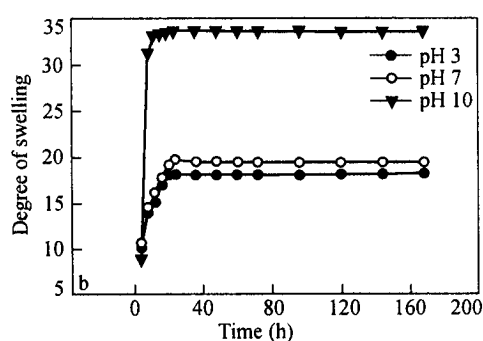
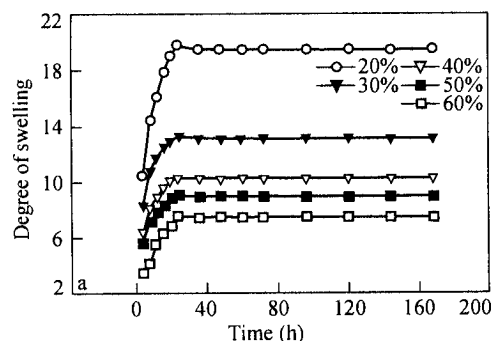


Fig. 4 (a) Variation of swelling with time
(b) Dependence of swelling on pH of swelling media

The change of swelling of hydrogels with the increase of dose could be explained as a consequence of the existing pressure involved between the polymer network (gel) and the solvent that tends to expand or shrink the gel. Generally, polymer solvent mixing represents the interaction of the polymer with the solvent as elucidated by the classical Flory-Huggins theory^[12] and more sophisticated theories, which account for specific interactions^[13]. When a hydrogel is immersed in water, it swells and the swollen equilibrated state results in a balance between

the osmotic driving forces that cause the water to enter into the gel. For the case of the same hydrogel with varying crosslinking density, the balance force no longer remains the same, causing a change of swelling values. In practice, the density of crosslinking in the hydrogel increases rapidly with increasing radiation dose, resulting in a rise of network elasticity contributions and these restrict the extensibility of polymer chains induced by swelling to counteract any tendency to under go dissolution^[14]. Thus, swelling decreases with the increase of networking. Besides, increasing solution concentrations also induces the gel to produce more crosslinking, which lowers the swelling.

It is an inherent property of a hydrogel to increase swelling with time because of its hydrophilic character. Initially, gel swells rapidly due to its greater affinity to take up water and shows a sharp rise of the curve that eventually becomes saturated. The time frame within which the volume of gel changes is faster could have applications in many cases like drug delivery, separation processes and so on.

Moreover, acrylamide hydrogel becomes a polyelectrolyte when it is partially hydrolyzed and its existing ionizable groups are also sensitive to external pH. The number of ionized groups within the gel changes on changing the pH. A gel increases its swelling degree in response to external pH change, which increases ionization; reducing ionization in pH causes the gel to shrink. Kinoshita *et al.* suggested that hydrogels containing weakly acidic functional groups show a tendency of swelling with respect to the increase of pH of the medium^[15]. All these explanations are in accord with the results obtained by us, and thus pH = 10 shows higher ionization among the other three pHs assuring higher swelling.

Dependence of Dose and Time on Desorption

Water is released with time from the gel if it is kept under ambient or heating condition. The relations between water desorption and time are shown in Fig. 5(a). It was found that water loss mainly occurs within 24 h, indicating an abrupt increase of water desorption which then slowly rises up to 48 h and ultimately becomes constant for all concentrations. In addition, water desorption is the same for the first 5 h for all concentrations and then varies according to the concentrations. Desorption dose not change with dose as can clearly be seen in Fig. 5(b).

An understanding of water desorption is of practical importance in that the time frame within which the water is removed from the gel is evident under ambient conditions and in end uses.

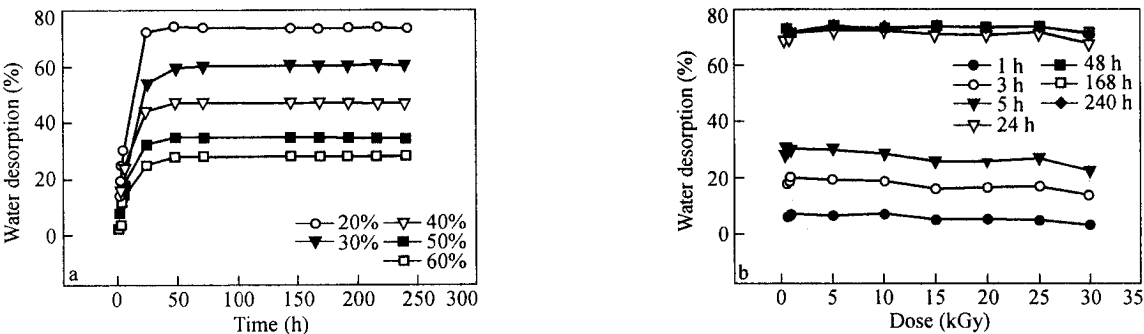


Fig. 5 (a) Change of water desorption with time
(b) Relation between water desorption and radiation dose

Action of Microorganism on Gel

The action of microorganisms on gels produced from 20% and 30% solutions at 1 and 10 kGy is depicted in Figs. 6(a) and 6(b), respectively. It is observed that the count rate is the same in both distilled water and gel containing water. In fact, pathogenic bacteria are responsible for wound infection through toxin production, food poisoning and so on. The gel can generally be used for the treatment of wounds. It was proved from our experimental result that the gel and the bacteria have no interaction between each other though antibiotic agents used during gel preparation may have some inhibiting actions for controlling the pathogenic bacteria.

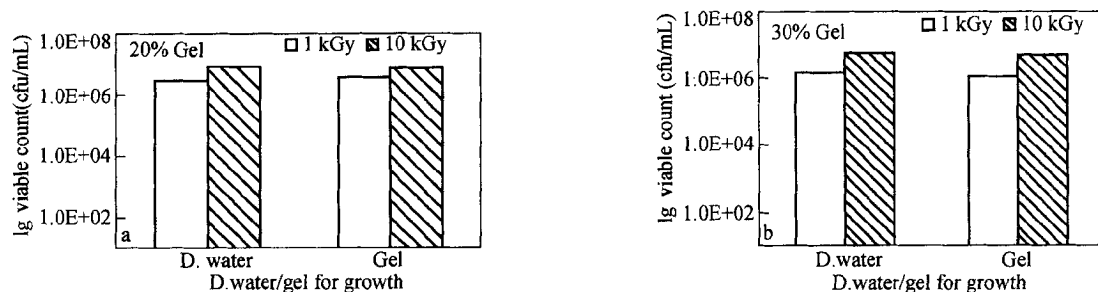


Fig. 6 Action of pathogenic bacteria on gel for (a) 20% and (b) 30% concentrations
D. water: distilled water

CONCLUSIONS

Synthesis of acrylamide hydrogels from aqueous solutions using γ -ray irradiation has been performed and the effect of solution concentration, γ -ray dose, pH and time has been observed in the characterization of the gels. Gel fraction increases with doses for all concentrations and nearly hundred-percentage conversion of gel is attained at 5 kGy for homogenous solutions in the range of 20%–50% concentration. On the one hand, total gel fraction not greater than 86 percent is obtained even at higher doses (30 kGy) for the solution of 10% concentration. On the other hand, the solution of 60% concentration is not homogeneous though it gives about 100 percent gel fraction. Thus, there is a limiting concentration above which the solution is not homogeneous and the below which higher doses are needed for the preparation of expected gel. Swelling varies with both the doses and the concentrations due to the change of crosslinking density in the hydrogels. The maximum volume change of hydrogels during swelling occurs within 24 h. Similarly, water desorption increases sharply depending on time up to 24 h. Swelling increases with the rise of pH of the solvent because of changing ionic contents. The effect of bacteria on hydrogel was not found. Considering the amount of gel fraction and the properties, the hydrogels prepared from 20% solution at 5 kGy shows better results.

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