

EFFECT OF GAMMA RAYS IN THE PREPARATION OF POLYMER AND HYDROGEL FROM ACRYLAMIDE MONOMER

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Abstract The formation of polymer and hydrogel from aqueous solutions having 20, 30 and 40% concentrations of acrylamide monomer by γ -ray irradiation processing in the dose range 0.06–30 kGy using a Co-60 source and their characterization have been observed. Polymer conversion and gel fraction are found to depend on radiation doses. Polymer conversion increases with the increase of dose, depending on the solution concentration, where maximum conversion is achieved at 0.18, 0.16 and 0.10 kGy for 20%, 30% and 40% concentrations, respectively. On the other hand, gel fraction increases with dose from the gel point (0.12 kGy) for all concentrations, where 100% conversion of gel occurs at doses ≥ 5 kGy. Tensile strength, viscosity and molecular weight (M_w) of polymer samples increase with both the dose and the concentration, showing a high value of M_w up to $\approx 10^8$. Swelling of hydrogels under water with respect to time varies due to the variation of cross-linking density formed in the gels and the maximum swelling mainly occurs within 24 h. A remarkable change of surface morphology reveals characteristic features of monomer, polymer and hydrogel films.

Key words Polymer, Hydrogel, γ -Radiation, Cross-linking, Swelling

INTRODUCTION

Polyacrylamide possesses versatile applications among water-soluble polymers because of its tendency to change the rheological properties of many water-based products and is gaining prominence due to very stringent environmental regulations^[1, 2]. Similarly, acrylamide hydrogels have been suggested for use in drug delivery devices, artificial muscles, separation of chemical systems, sensors, artificial corneas, eye capillary drains, plastic surgery and biomaterials^[3–5]. Hydrogels are cross-linked polymers that swell to an equilibrium volume and preserve their shape. Their insolubility and stability of shape are due to the presence of a three dimensional network^[6, 7].

The synthesis of polymer and hydrogel from acrylamide monomer at moderate temperature by the method of free radical polymerization in solutions, emulsions and suspensions requires free radical initiators^[8–10]. On the other hand, ionizing radiation processing offers unique advantages for preparing polymer and hydrogels from vinyl monomer without the addition of any chemical substances^[9, 11, 12].

Much of the research has been done in the synthesis of polyacrylamide from aqueous solutions in the presence of different chemical atmospheres^[8–10, 13, 14] but all these are different from ours in that a clean technology has been followed in this investigation, where the solutions have been prepared in single-distilled water and irradiated by γ -rays to observe the effect of radiation dose on physical behavior of the products.

EXPERIMENTAL

Preparation and Irradiation of Saturated and Unsaturated Acrylamide Solutions

Synthesis grade acrylamide ($\text{CH}_2=\text{CHCONH}_2$) monomer (99.5% pure) was purchased from LOBA, Chemic,

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Bombay, India and used without any additional purification. A series of solutions with 20%, 30% and 40% concentrations (W/W) of monomer were saturated with gaseous argon purified from O_2 at a flow rate of 100 mL/min. Another series of solutions having 20%, 30% and 40% concentrations of monomer not saturated with argon were also prepared. All of the prepared monomer solutions were irradiated by γ -rays from a Co-60 source.

Saturated solutions along with 20% unsaturated ones were exposed to doses of 0.06, 0.08, 0.09, 0.10, 0.12, 0.14, 0.15, 0.16 and 0.18 kGy at a dose rate of 1 kGy/h, whereas all unsaturated solutions were irradiated at higher doses 0.2, 0.4, 0.6, 0.8, 1.0, 5.0, 10.0, 15.0, 20.0, 25.0 and 30 kGy and kept for 24 h for completion of the polymerization reaction. Then different physico-chemical properties of the prepared samples were evaluated.

Evaluation of Solubility, Polymer Conversion and Gel Fraction of Irradiated Samples

Polyacrylamide is dissolved in water, whereas acrylamide hydrogel swells. When irradiated samples were immersed under water and stirred for a while, different solubility characters were observed. Irradiated products prepared in the range 0.06–0.18, 0.06–0.16 and 0.06–0.14 kGy corresponding to 20%, 30% and 40% solutions were almost completely dissolved in water. The solubility of the samples decreases after the above-mentioned ranges of dose and disappears at 5 kGy. These differences primarily provide a rough idea to distinguish the irradiated samples as polymer and gel. Further investigation followed on from this result.

For the measurement of polymer conversion, each of the polymer samples having a weight of about 8 g was poured into ethanol for extraction till 24 h. Furthermore, occasional stirring with a glass rod was performed with the changing of ethanol to remove unconverted monomer. The extracted samples were dried in an oven at 100°C to remove adhered water and thereafter dried again in a vacuum oven at 70°C to eliminate entrapped water. The drying and weighing procedures of the samples were repeated until constant weight. The conversion of monomer to polymer was calculated using the relation: conversion (%) = $(W_2/W_1) \times 100$, where, W_1 = weight of monomer and W_2 = weight of extracted sample after drying. Thereafter, the solutions of extracted samples in water were examined by UV-spectrophotometer (UV 1601, Shimadzu, Japan) at 199 nm that shows the presence or absence of monomer.

For the measurement of gel fraction, about 1 g of hydrogel samples was subjected to 24 h extraction with hot distilled water. The extracted samples were dried in air oven at 100°C and then in vacuum oven at 70°C after which the weight of them were measured. These weighing and drying processes were continued till constant weight (W_3) of each sample were reached. The percentage of gel fraction was evaluated gravimetrically as: Gel fraction (%) = $(W_3/W_4) \times 100$, where W_4 = Weight of monomer in 1 g hydrogel.

Determination of Gel Content in Polymer

To find the gel content, a known weight (W_5) of the polymer was placed in a stainless steel net and extracted with hot distilled water for a extended time (> 24 h). Then the undissolved part remaining in the stainless steel net packet was taken out and dried in an air oven at 100°C and then in a vacuum oven at 60°C to a constant weight (W_6). The gel content in the sample was calculated as follows: Gel content (%) = $(W_6/W_5) \times 100$.

Measurement of Tensile Strength

The tensile properties of polymer samples were measured by an Instron instrument (model 1011, England), interfaced to a personal computer. The polymer samples produced at different doses were dissolved in water and then poured on glass plates. Thereafter, they were air dried until films were produced. The films were cut into a dumbbell shape with a cutter (ASTM-D-1822-L). The ends of each film were clamped with grips of the testing machine separated at a gauge length of 30 cm and then pulled apart by a static load force. The measurement and the data collection were performed with appropriate software.

Determination of Viscosity and Molecular Weight

A cone type rotary viscometer (Visconic Model ED, Tokimec Inc., Japan) connected with a temperature controller (E-2000, TKI Sangyo Co. Ltd., Japan) was used for viscosity measurement. About 1 mL of a solution of polymer having a concentration (c) of 0.5 g/dm³ was prepared and placed in the viscometer cup that was maintained at $(25 \pm 0.5)^\circ\text{C}$ by means of thermostatic controller. The speed of rotation was kept at 0.5 r/min and

the value of viscosity was obtained from the recorder.

Since molecular weight (M_w) is empirically related to viscosity for linear polymers, therefore viscosities of the solvent and the solutions ($c = 0.5, 0.1$ and 0.02 g/dm^3) of irradiated samples having different doses up to 0.12 kGy were measured to evaluate M_w . Then, specific viscosity (η_{sp}) is estimated from the formula: $\eta_{sp} = (\eta - \eta_0)/\eta_0$, where η = viscosity of the solution of irradiated samples and η_0 = viscosity of the solvent. A straight line is obtained when η_{sp}/c is plotted versus c . The intersection of the straight line with the η_{sp}/c axis is a measure of the intrinsic viscosity (η_{in}). Finally, molecular weight was calculated by the relation: $\eta_{in} = 6.8 \times 10^{-4} M_n^{0.66[1]}$, where M_n is the molecular weight of the irradiated samples.

Measurement of the Degree of Swelling

A small amount of sample from hydrogels was cut and dried first in an oven at 100°C and then in a vacuum oven at 70°C till constant weight. The dried gel samples were dipped into the distilled water 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_8/W_7 , where W_7 = dry weight and W_8 = wet weight (at particular time).

Optical Microscopy

Surface morphology was observed by an optical microscope (Carton) connected to a video-TV system through a CCD (Model ET-88AP) camera. Five films prepared from the irradiated samples at different doses along with the monomer film were used in this study.

RESULTS AND DISCUSSION

Effect of Radiation Doses on Polymer Conversion and Gel Fraction

Conversion of monomer into polymer for different monomer concentrations plotted against radiation dose is shown in Fig. 1(a). The degree of conversion increases with radiation dose. For a low dose of 0.06 kGy , the conversions are about 66%, 82% and 89% at 20%, 30% and 40% saturated concentrations, respectively. Maximum conversion is reached at doses of $0.18, 0.16$ and 0.10 kGy corresponding to 20%, 30% and 40% saturated concentrations. At a dose of 0.10 kGy , conversion is approximately 100% for 40% solution and from 75% to 90% percent conversions are obtained for other saturated concentrations. The conversion is much lower in the case of 20% unsaturated solution than in that of 20% saturated solution at all doses. This result strongly indicates that the monomers undergo oxidative degradation at low doses while irradiated in the presence of dissolved oxygen and agrees with that observed by Collinson *et al.*^[15].

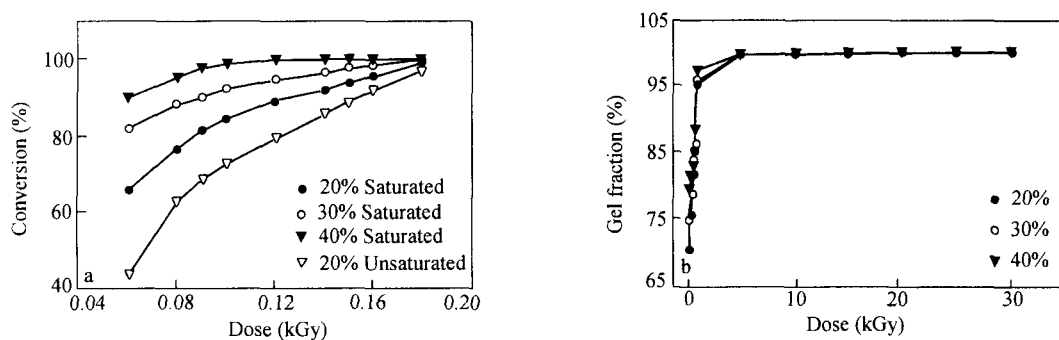


Fig. 1 Change of (a) degree of polymer conversion and (b) gel fraction with radiation doses for 20%, 30% and 40% saturated and unsaturated aqueous acrylamide monomer solutions

The gel fraction (%) versus dose of hydrogels produced from different concentrations is presented in Fig. 1(b). For all concentrations, the gel fraction increases rapidly at doses lower than 5 kGy after which it remains unchanged. About 100% gel fraction is attained at doses $\geq 5 \text{ kGy}$ for all solutions.

Gel Content in Polymer at Various Radiation Doses

The gel content represents the undissolved portion or an indication of cross-linking in the irradiated samples. Figure 2(a) shows the change of gel content with radiation dose. The gel content increases slowly with the solution concentration at doses > 0.12 kGy and rises more rapidly at doses > 0.14 kGy. No undissolved fraction indicating polymerization phenomenon is seen at doses from 0.08 to 0.10 kGy.

Effect of Radiation Dose on Tensile Strength

Figure 2(b) indicates the tensile strength (TS) as a function of radiation dose. TS increase with radiation doses and solution concentrations. Increasing the dose enhances polymer conversion and produces polymer with higher M_w . Some polymer molecules may be cross-linked at higher doses. Hence TS could increase depending both on M_w and polymer network. It is also found that the strength also depends on concentration.

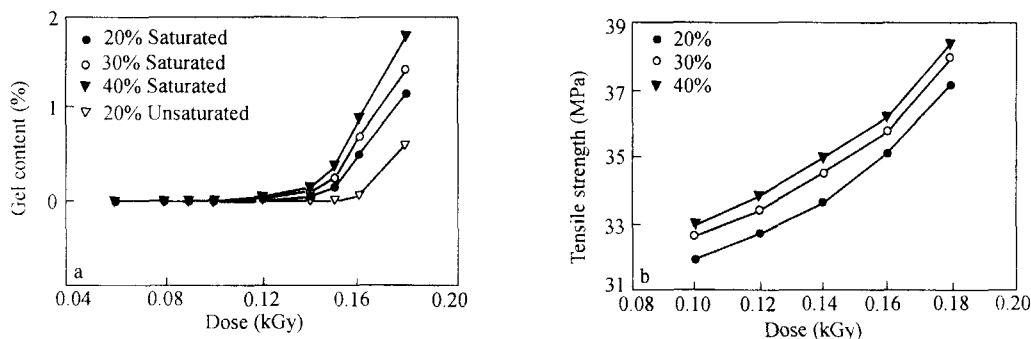


Fig. 2 Variation of (a) gel point and (b) tensile strength with respect to doses

Effect of Radiation Doses on Viscosity and M_w

The viscosity of polymer solutions increases with doses as shown in Fig. 3. This increase is somewhat enhanced from 0.14 to 0.18 kGy and shows the highest value at the later dose. The variation of viscosity on different concentrations is also clarified. It is evident that the viscosity increases with increasing concentration.

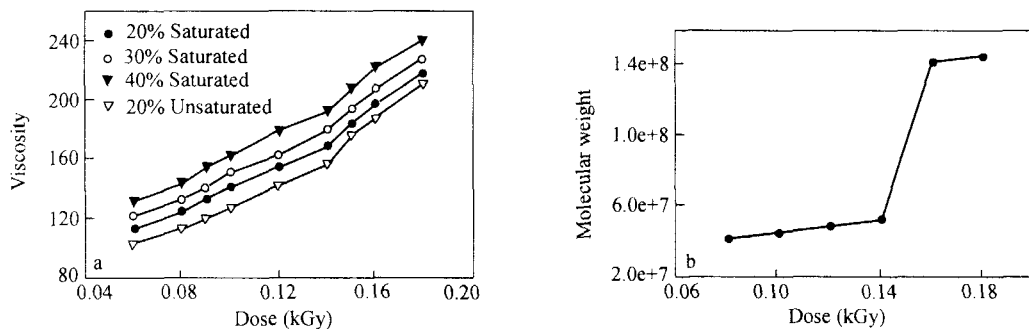


Fig. 3 (a) Viscosity (b) molecular weight as a function of dose for different concentrations

M_w of the polymer samples made from 20% concentration is calculated and is found to be $(4.16, 4.46 \text{ and } 4.88) \times 10^7$ for doses of 0.08, 0.10 and 0.12 kGy, respectively^[1, 12].

Dependence of Swelling on Doses

Figures 4(a) and (b) show the swelling as a function of dose at various times and concentrations, respectively. Swelling decreases with doses ≥ 5 kGy and thereafter remains almost unchanged at all times and concentrations. From the point of view of dose effect, hydrogels prepared at 20% concentration give the highest swelling and are thus considered as superior samples compared with others.

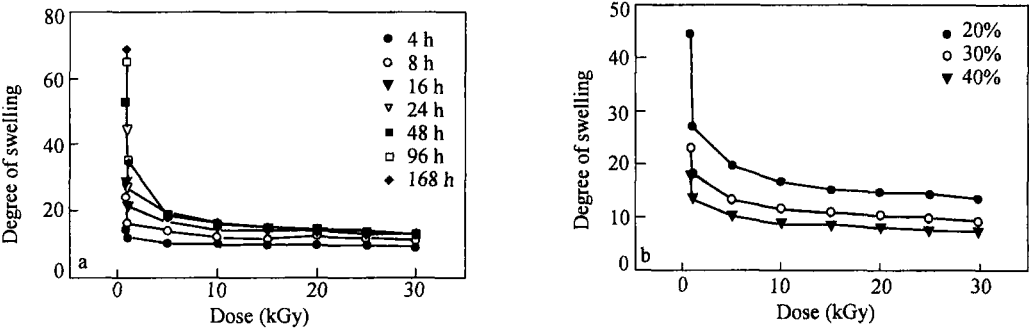


Fig. 4 Dependence of swelling on dose at various (a) times and (b) concentrations

The change of swelling of hydrogels with the increase of dose could be explained as a consequence of the existing pressure involved between the solvent and the polymer cross-linking that develops by γ -ray irradiation. When a hydrogel is immersed in water, it swells and the swollen equilibrated state results from a balance between the osmotic driving pressures that causes the water to enter into the polymer network. For the case of a hydrogel with varying cross-linking density, the balance force no longer remains the same, causing the change of swelling values.

In practice, the density of cross-linking in a hydrogel increases rapidly with increasing radiation dose, resulting in a rise in network elasticity contributions. These restrict extensibility of the polymer chains induced by swelling to counter any tendency for dissolution. Thus, the swelling decreases with increasing network formation.

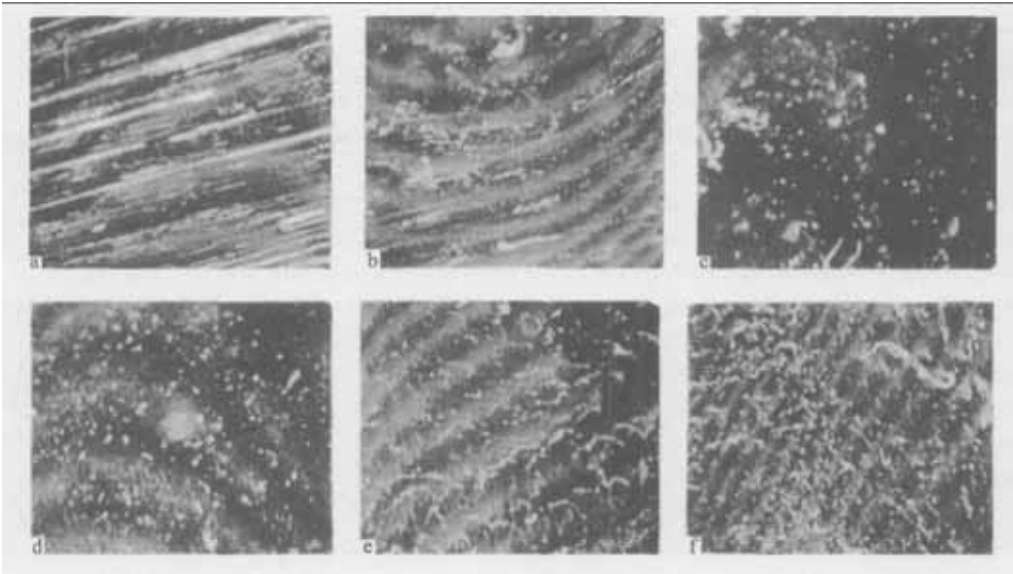


Fig. 5 Surface morphology of the films (a) monomer and the products prepared from 20% concentration at (b) 0.06, (c) 0.12, (d) 0.18, (e) 1.0 and (f) 10.0 kGy radiation doses

Radiation Intensity on Surface Morphology

Figures 5(a–f) show the photographs of monomer film and the films of the samples prepared at different doses as indicated. The surface of monomer film (Fig. 5a) contains striations and the number of striations decreases with the increase of dose as represented in Fig. 5(b), whereas Figs. 5(c) and 5(d) represent particle-like structures on the surface. At higher doses, polymers are formed from monomer for which the surface morphology changes. Further increase of dose affects the surface structure as shown in Figs. 5(e) and 5(f), which contain curvilinear or

cross-linked structures. This structure is supposed to have arisen due to hydrogel formation.

CONCLUSIONS

Polymer and hydrogels from 20%, 30% and 40% aqueous solutions of acrylamide monomer have been prepared by γ -ray irradiation processing in the dose range 0.06–30 kGy using a Co-60 source. Various properties of these products have been examined. Polymer conversion increases with increasing dose, depending on the solution concentration, where maximum conversion is achieved at 0.18, 0.16 and 0.10 kGy, corresponding to 20%, 30% and 40% concentrations, respectively. Moreover, it is found that dissolved oxygen in the solution inhibits polymerization reaction in the case of lower doses. Depending on the concentration, the gel point starts ≥ 0.12 kGy from where cross-linking mainly occurs among the molecules and thus the gel fraction increases. 100% Conversion of gel occurs at doses ≥ 5 kGy. Tensile strength, viscosity and M_w of polymer samples are found to rise with both the dose and the concentration, showing the value of $M_w \approx 10^8$. Swelling of hydrogels under water with time varies due to the variation of cross-linking density formed in the gels. Change of surface morphology of the samples clearly distinguishes the monomer, polymer and hydrogel samples.

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