

Full Length Research Paper

Effect of acrylic acid on the properties of polyvinylpyrrolidone hydrogel prepared by the application of gamma radiation

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Hydrogels based on polyvinylpyrrolidone (PVP) networks grafted with acrylic acid (AAc) was prepared by using γ -rays from a Co-60 source at room temperature. The parameters like effect of radiation dose and concentration of AAc were studied. The properties such as gel content, swelling behavior and thermal stability were also evaluated. The result indicated that gel content of hydrogel increased with increased radiation dose and it reached a maximum value at 25 kGy radiation dose. Gel content also increased with increased concentration of AAc in the feed solution. Moreover, swelling ratio decreased with increased radiation dose, but increased with increased concentration of AAc. Water absorption of hydrogel increased from ~1400 to ~3800% for the range of AAc concentration 0 to 1.5% at 25 kGy. It was also observed that the melting temperature of hydrogel depended on concentration of AAc. The fourier transform infra-red (FTIR) spectroscopy investigation of hydrogel was carried out. The prepared hydrogel was applied to adsorb dye from aqueous medium.

Key words: Hydrogel, polyvinylpyrrolidone, acrylic acid, swelling behavior, gel content.

INTRODUCTION

Hydrogels are cross-linked polymeric structures that are capable of imbibing and keeping large amount of water. The water sorption of hydrogel includes the processes of hydration due to the presence of hydrophilic groups such as -OH, -COOH, -CONH₂, -CONH, -SO₃H, etc (Karadag et al., 2005; Park and Nho, 2004). Cross-linking of hydrophilic polymers/monomers can carry out the synthesis of hydrogel and cross-linking can be done either by chemical method or by radiation method. In radiation processing technology initiator, catalyst and cross-linker are not required because ionizing radiation is highly energetic (Jabbari and Nozari, 2000). The radiation

processing technique has many advantages like easy process control, simultaneous cross-linking of polymer to hydrogel formation and sterility of the product, and the technology is environment friendly since it leaves no residue or pollutant in the environment (Rosiak and Ulanski, 1999; Fei et al., 2000). The radiation induced hydrogel with or without cross-linker is much durable with respect to chemically prepared hydrogel (Saraydin et al., 2004).

Hydrogels are becoming increasingly attractive to researchers because of their application in controlled drug delivery, biosensors, artificial muscles, chemical valves, contact lenses, cell cultivation substrates, photo-responsive gels and in other fields (El-sherif and El-Masry, 2008; Rosso et al., 2003; Gombotz and Hoffman, 1986). Polyvinylpyrrolidone (PVP) hydrogel has excellent transparency and biocompatibility. PVP is used as a main component in temporary skin covers or wound dressings (Yaung and Kwel, 1998; Dafader et al., 2005). Blends of

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Abbreviations: PVP, Polyvinylpyrrolidone; AAc, acrylic acid; MB, methylene blue, CMC, carboxy methyl cellulose.

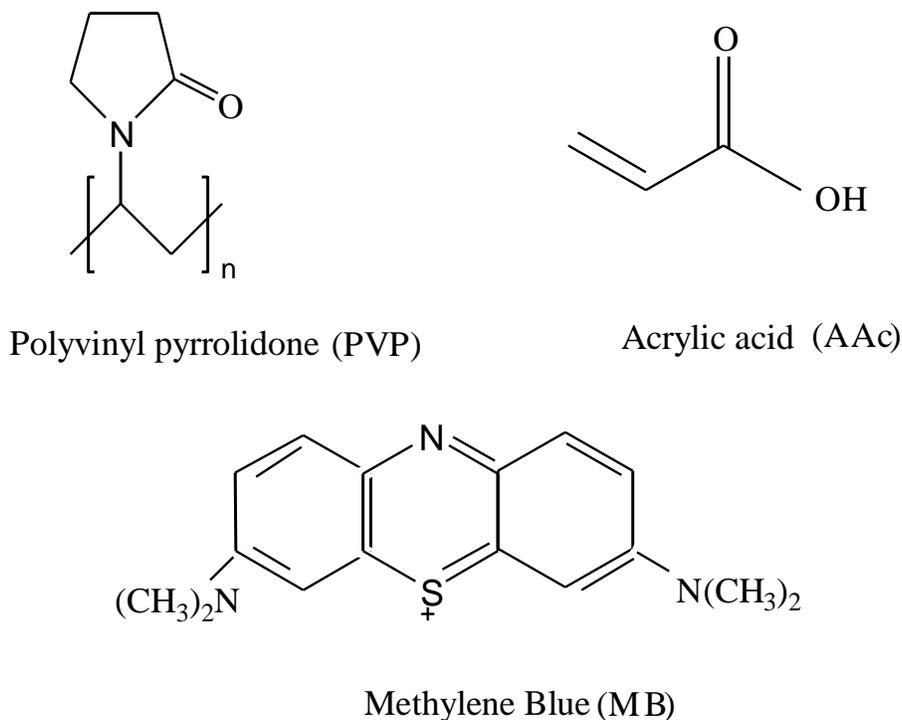


Figure 1. The chemical structures of PVP, AAc and MB.

synthetic polymer and natural polymer represent a new class of hydrogel materials. Hydrogels of synthetic/natural polymer blend materials such as PVP/cellulose diacetate, PVP/chitosan, PVP/agar/polyethyleneglycol (PEG), polyvinyl alcohol (PVA)/starch, PVA/chitosan, polyethylene oxide (PEO)/chitosan and poly(*N*-isopropyl acrylamide)/alginate, exhibit improved properties that are different from original polymers (Jinghua et al., 1997; Zhai et al., 2002; Jing et al., 2001; Khoo et al., 2003; Ju et al., 2001).

Dyes are complex organic compound used as color in textiles, leather, paper, plastic and other materials. Dye-mixed waste water from different industries pollutes the natural environment. They are firm and difficult to biodegrade; therefore dye in water is a major environmental problem. Today, more than 10000 dyes are in use. The common techniques for removal of dyes from industrial effluents include adsorption, coagulation, flocculation, oxidation, precipitation, ozonation, filtration and electrochemical processes etc. Polymeric hydrogels have excellent adsorption behaviors of dye. Hydrogels which are prepared by copolymerization with acidic monomers can interact with the cationic dye (Crini, 2005; Siddaramaiah et al., 2009).

In this study, we aimed at preparing hydrogel from aqueous solution of PVP with various concentration of acrylic acid by the application of γ -radiation. Acrylic acid was added to improve the properties of PVP hydrogel. The hydrogels were characterized in respect to gel content, swelling properties, melting point and fourier

transform infra-red (FTIR) spectrum. The possibility of dye adsorption from aqueous medium was investigated. Methylene blue (MB) was used as dye for adsorption by Polyvinylpyrrolidone/acrylic acid (PVP/AAc) blend hydrogels.

MATERIALS AND METHODS

PVP-k90 was obtained from Fluka AG, Switzerland, and acrylic acid from Fluka, Germany. The Methylene blue (MB), C.I number 52015, was obtained from Merck, Germany. Chemical formula of MB is C₁₆H₁₈CN₃S; molecular weight and λ_{\max} are 319.9 and 665 nm respectively. Distilled water was used as solvent. The chemical formula of main material used in this study is shown in Figure 1.

Preparation of hydrogels

An aqueous solution of PVP was prepared by dissolving in distilled water at 60°C for 1 h in a water bath. Various concentration of acrylic acid (0 to 1.5%) was added to PVP solution by stirring with a glass rod for homogeneous solution. The hot mixture was then cooled and poured into test tube, sealed and finally irradiated by γ -rays from Co-60 source with radiation doses of 10, 15, 20, 25, 30 and 35 kGy at the dose rate of 5 kGy/h. The hydrogels obtained in long cylindrical shape were cut into small pieces, dried in air and then under vacuum to constant weight.

Determination of gel content

The hydrogel samples dried to constant weight were immersed in distilled water for 24 h to remove sol fraction. Then they were taken out from the distilled water and dried to constant weight in an oven. The gel content was calculated as follows:

$$\text{Gel content (\%)} = \frac{W_1}{W_i} \times 100$$

Where, W_1 is the weight of dry gel after extraction in water and W_i is the initial weight of dry gel.

Determination of swelling ratio

The pre-weighed dry gel samples were immersed in distilled water for 24 h at room temperature. The swollen gels were then removed from distilled water and weighed after removing surface water with a soft tissue paper. The swelling ratio was calculated as follows:

$$\text{Swelling ratio} = \frac{W_2 - W_1}{W_1}$$

Where, W_2 is the weight of swelled gel and W_1 is the weight of dry gel.

Determination of water absorption

The pre-weighed dry gel samples were immersed in distilled water at room temperature (27°C) and periodically weighed after soaking the surface water by soft tissue paper. The water absorption was calculated as follows:

$$\text{Water absorption (\%)} = \frac{(W_t - W_1)}{W_1} \times 100$$

Where, W_t is the weight of swelled gel at time t and W_1 is the weight of dry gel.

Determination of thermal property

The melting temperature of dry hydrogel sample was measured using the thermo-mechanical analyzer (LINSEIS TMA, L-77, USA). The experiment was carried out in an inert atmosphere at the heating rate of 5°C/min. The dimension of the samples was 5 × 5 × 2 mm³.

Fourier transform infra-red spectroscopy (FTIR)

Infra-red spectra for AAC, PVP and PVP-AAC blend were recorded on a fourier transform infra-red spectrometer, model FTIR prestige-21, Shimadzu, Japan. The dry samples were ground with KBr and then pressed under high pressure to form transparent disks and the disks were placed in the sample holder for recording the spectrum.

Determination of dye adsorption

The dry gel sample was immersed in aqueous solution of dye at room temperature (27°C) and periodically the residual concentration of dye in the feed solution was determined spectrophotometrically (UV-2401PC, Shimadzu, Japan). The amount of dye adsorption per unit mass of hydrogel was evaluated by using

the following equation:

$$Q_e = \frac{(C_0 - C_e) \times V}{W}$$

Where, Q_e is the amount of dye adsorbed per unit dry mass of hydrogel (mg/g), C_0 and C_e are the concentration of dye in the initial solution and aqueous phase after treatment with gel sample of certain period respectively (mg/L), V is the volume of aqueous phase in liter (L) and W is the weight of dry gel (g).

RESULTS AND DISCUSSION

Figure 2 shows the gel content of PVP/AAC blend hydrogels with different radiation dose and varying concentrations of AAC in feed solution. Result indicates that the gel content of blend hydrogels increased with increased radiation dose and reaches a maximum value at the radiation dose of 25 kGy. After this radiation dose (25 kGy), the increasing trend of gel content did not vary significantly. The gel content of blend hydrogel also increased with increased amount of AAC in PVP/AAC blend. It varied from ~96 to ~99% for increased concentration of AAC (0.0 to 1.5%) at the radiation dose of 25 kGy. When aqueous solution of PVP/AAC was exposed to irradiate with gamma rays, free radicals were generated on PVP and AAC. Random reactions of these radicals led to formation of cross-link, graft copolymer and homopolymer of AAC. When two radicals of neighboring chains come close, their combination leads to cross-link of macromolecules. At higher concentration of polymer the free radicals come closer than lower concentration of polymer and that tends to form more cross-links. In the present investigation, the concentration of polymers increased with increased amount of AAC in PVP/AAC mixture, and this may be the cause of increased gel content of PVP/AAC blend hydrogel.

Furthermore, the swelling ratio indicates the extent of cross-linking of a polymer. With increased cross-linked density in a polymer, swelling ratio decreased due to reduced vacant space of cross-linking network for free solvent to enter into it. Figure 3 shows the effect of radiation dose and concentration of AAC on swelling ratio of PVP/AAC blend hydrogel. It was found that the values of the swelling ratio reduced from ~33.66 to ~11.26 without AAC, ~62.25 to ~16.07 with 0.5% AAC, ~86.95 to ~18.05 with 1.0% AAC and ~104.75 to ~21.12 with 1.5% AAC in PVP/AAC mixture for the increased radiation dose from 10 to 35 kGy. This result was due to increased cross-linked density with increase in radiation dose. The swelling ratio of hydrogel increases with increased concentration of AAC in mixture of PVP/AAC. It increased from ~14 to ~27 for increased concentration of AAC (0 to 1.5%) at the radiation dose of 25 kGy. This may be due to the addition of AAC in PVP/AAC mixture that increases the number of hydrophilic groups in produced hydrogel.

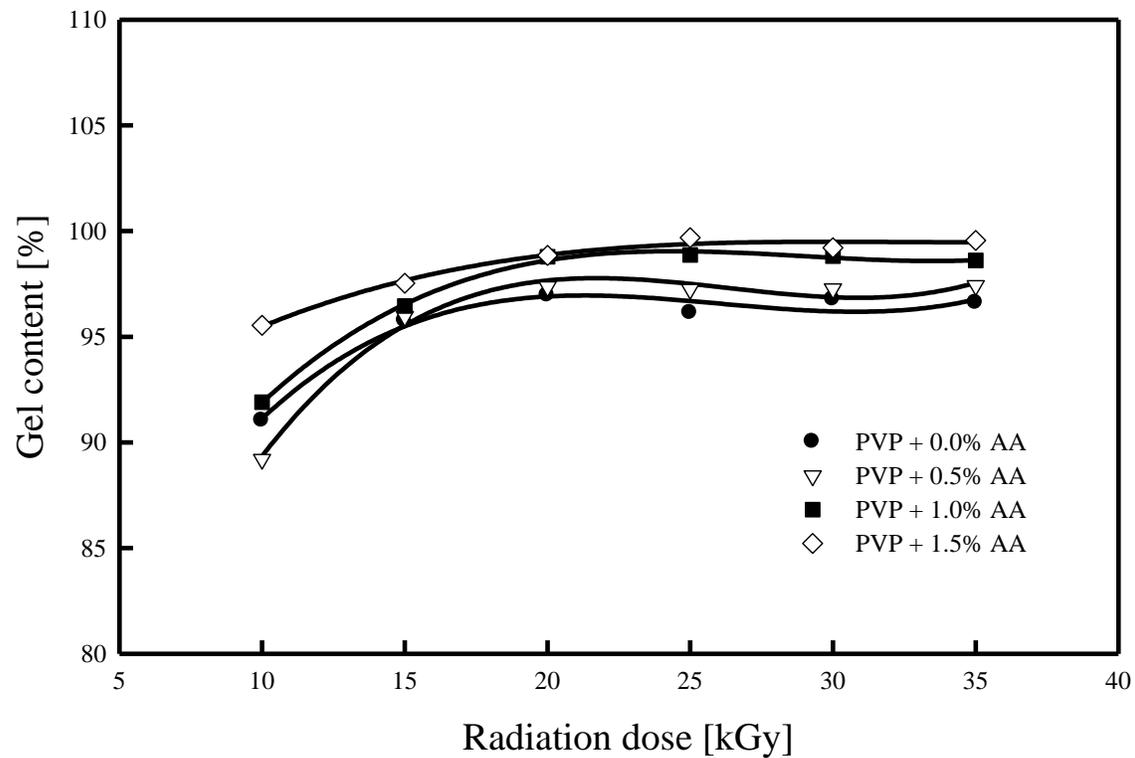


Figure 2. Effect of radiation dose and concentration of AAc on gel content of PVP/AAc blend hydrogel. PVP, Polyvinylpyrrolidone; AAc, acrylic acid.

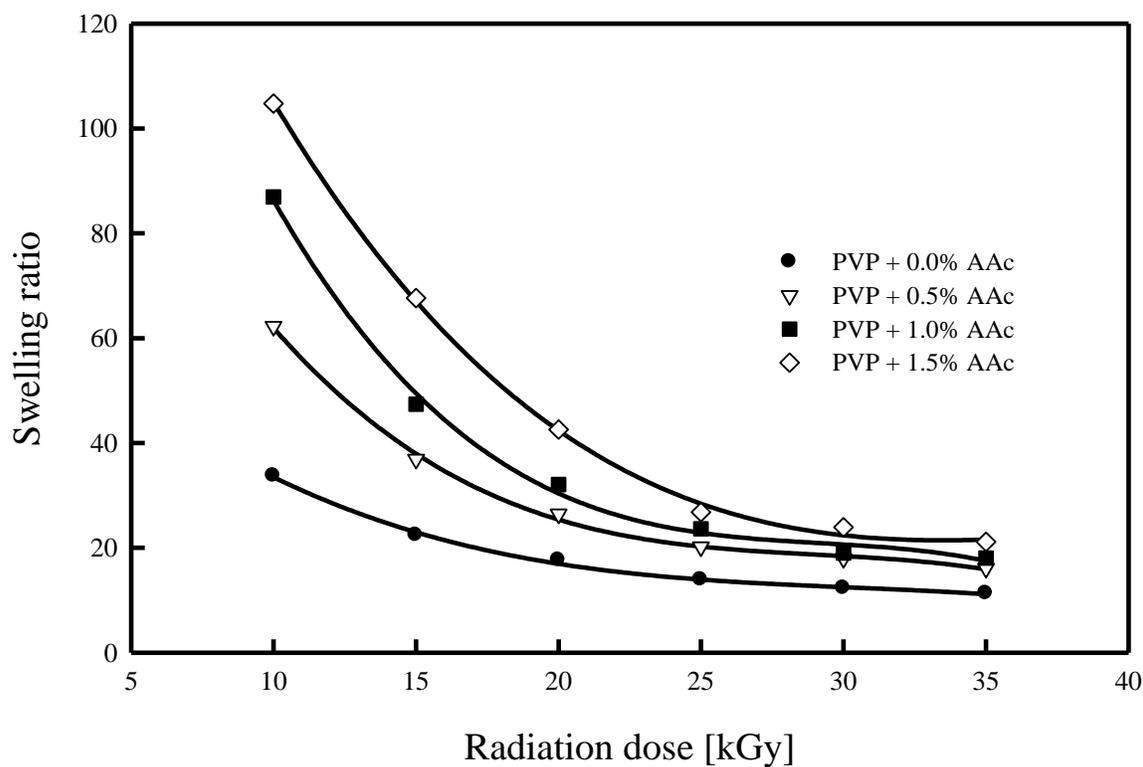


Figure 3. Effect of radiation dose and concentration of AAc on swelling ratio of PVP/AAc blend hydrogel. PVP, Polyvinylpyrrolidone; AAc, acrylic acid.

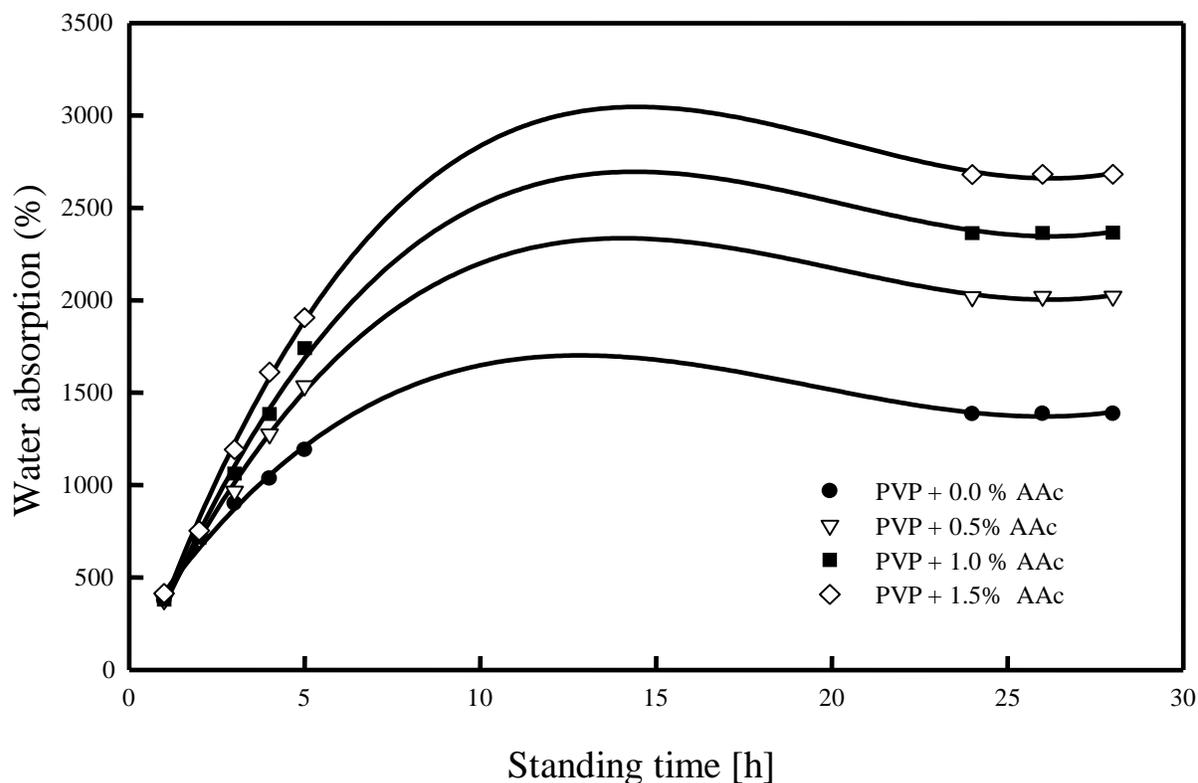


Figure 4. Effect of AAc concentration on water absorption of PVP/AAc blend hydrogel (radiation dose = 25 kGy). PVP, Polyvinylpyrrolidone; AAc, acrylic acid.

Swelling ratio of PVP hydrogel improves with addition of kappa-carrageenan (KC) due to the presence of $-\text{OSO}_3^-$ group in KC molecule (Dafader et al. 2005). It is also reported that the carboxy methyl cellulose (CMC) improves the swelling ratio of PVA/sago blend hydrogel due to the presence of the carboxyl group in the CMC molecule (Hashim et al., 2002). The present finding exhibited similar results to these reports.

Figure 4 illustrates the effect of AAc on water absorption of PVP/AAc blend hydrogel prepared at 25 kGy dose. Water absorption increased with increased standing time of blend hydrogel in water and attained a maximum value at 24 h. This maximum value of water absorption for hydrogel may be called equilibrium water absorption. The equilibrium water absorption of blend hydrogel increases from ~1386 to ~2681% as it increases AAc content from 0 to 1.5% in PVP/AAc. Moreover, when a dry hydrogel sample is brought in contact with water, water diffuses in the hydrogel and the hydrogel swells. Diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. The diffusion mechanism of water in the hydrogel has received considerable attention because of important application of hydrogel in biomedical, environment and agriculture field. The following equation is used to determine the nature of water diffusion into hydrogel (Peppas and Franson; 1983); $F = kt^n$; where, F is the

fractional uptake of water at time t, k is a constant incorporating characteristic of macromolecular network system and n is the diffusional exponent, which is indicative of transport mechanism. The aforementioned equation is valid for the first 60% of the fractional uptake. For cylindrical shapes, if n is in the range of 0.45 to 0.50, diffusion is Fickian, while $0.50 < n < 1.0$ indicates that diffusion is non-Fickian type.

Figure 5 shows $\ln F$ vs. $\ln t$ plot for radiation induced PVP/AAc blend hydrogels. The diffusion exponents (n) and k values were calculated from slopes and intercepts of the lines, respectively and are listed in Table 1, which showed that the number determining the type of diffusion (n) is over 0.50. Hence the diffusion of water into hydrogels was taken as a non-Fickian type. When diffusion type is non-Fickian behavior, the relaxation and diffusion time are of same order of magnitude. As the solvent diffuses into the hydrogel, rearrangement of the chains does not occur immediately. This behavior is generally explained as a consequence of very slow relaxation rate of copolymer hydrogels.

The melting point (T_m) of polymers may be defined as a transition from a crystalline or semi-crystalline phase to an amorphous phase. Two types of Brownian movement exhibit in a polymeric material: (a) the 'internal' or 'micro' Brownian movement (IBM), describing the segmental motion, and (b) the 'external' or 'macro' Brownian

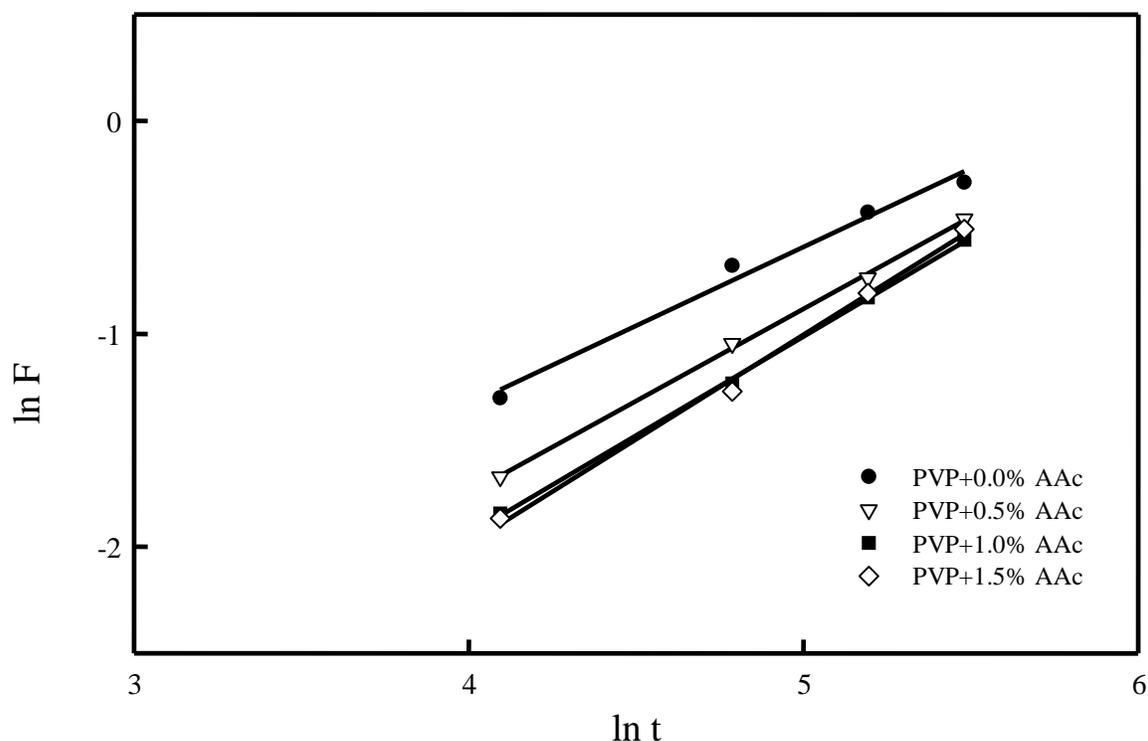


Figure 5. Plots of $\ln F$ vs. $\ln t$ for PVP/Ac blend hydrogel (radiation dose = 25 kGy). PVP, Polyvinylpyrrolidone; AAc, acrylic acid.

Table 1. The values of n and k for the hydrogels prepared at 25 kGy.

Hydrogel	$k \times 10^2$	n
PVP without AAc	1.373	0.7391
PVP with 0.5% AAc	0.549	0.8644
PVP with 1.0% AAc	0.349	0.9287
PVP with 1.5% AAc	0.269	0.9825

k , Constant incorporating characteristic of macromolecular network system; n , diffusional exponent.

movement (EBM), describing the molecular motion. With the increase of temperature, the IBM movement would be first activated, and only at a higher temperature, the EBM also come into play. At high temperatures, when both Brownian movements are activated, the individual polymer chains start moving apart and there will be flow of material instead of stress transfer. In addition, Figure 6 shows the effect of AAc on melting point (T_m) of PVP/Ac blend hydrogel prepared at the radiation of 25 kGy. It was found that T_m value of hydrogel increased with increased concentration of AAc in PVP/Ac mixture. T_m value increased from ~ 124.8 to $\sim 132.2^\circ\text{C}$ for the concentration of AAc from 0 to 1.5% at the radiation dose of 25 kGy. This result indicated that AAc may interact with PVP and improves thermal stability of PVP hydrogel.

The FTIR spectra of AAc, PVP and PVP/Ac blend prepared at 25 kGy radiation dose are shown in Figure 7. In the curve (a) for PAAc, the $-\text{CH}_2-$ stretching vibration was $\sim 2924\text{ cm}^{-1}$ and the band at $\sim 1267\text{ cm}^{-1}$ represents the C–C stretching vibration, whereas the band at $\sim 3687\text{ cm}^{-1}$ is assigned to the O–H stretching, band at $\sim 1647\text{ cm}^{-1}$ to the C=O stretching and band at $\sim 1161\text{ cm}^{-1}$ to the C–O stretching vibration of carboxylic group. In the curve (b) for PVP, the characteristic peak at $\sim 2945\text{ cm}^{-1}$ was due to the C–H stretching vibration of vinyl group, whereas $\sim 1650\text{ cm}^{-1}$ is assigned to the C=O stretching, and $\sim 1278\text{ cm}^{-1}$ to the C–N stretching vibration of pyrrole ring. While in curve (c) for PVP/Ac blends, the peak at $\sim 2963\text{ cm}^{-1}$ was ascribed for the C–H stretching vibration, $\sim 1284\text{ cm}^{-1}$ for the C–N stretching and the frequency of the carbonyl group of PVP shifts from 1650 to 1630 cm^{-1} due to the formation of hydrogen bonds to the carboxyl group. This result indicates that AAc interacts/entraps with PVP molecules.

Finally, Figure 8 shows the effect of standing time of hydrogel in dye solution and concentration of AAc in PVP/Ac blend hydrogel prepared at 25 kGy radiation dose on adsorption of dye. Adsorption of dye increased with increased standing period of PVP/Ac hydrogel in dye solution and attained maximum values at 30 h. As shown, PVP hydrogel without AAc adsorbs small amount of dye from aqueous solution. The imine groups of MB and carboxyl groups of hydrogel may form ionic complex.

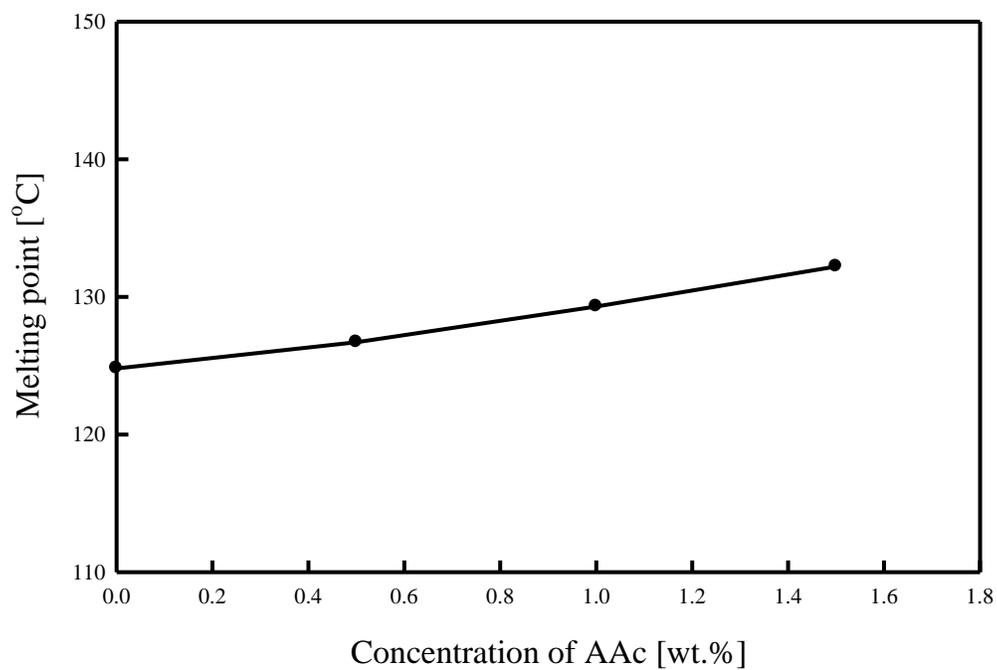


Figure 6. Effect of AAC on melting point of PVP/AAC blend hydrogel. PVP, Polyvinylpyrrolidone; AAC, acrylic acid.

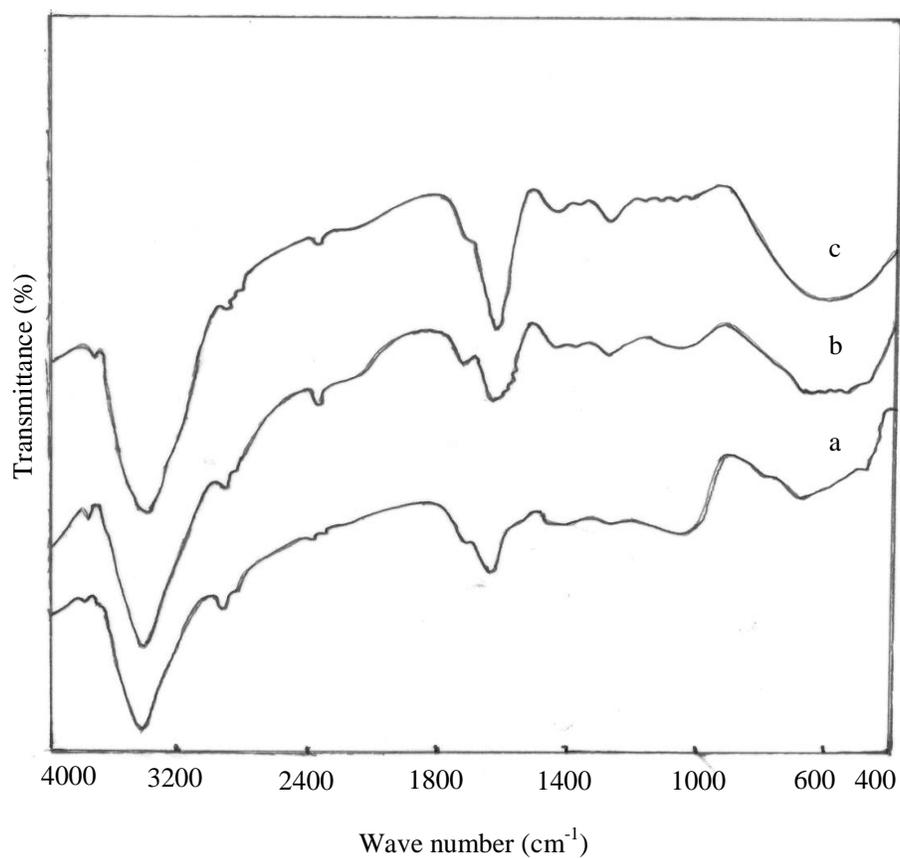


Figure 7. FTIR spectra on (a) AAC, (b) PVP and (c) PVP/AAC blend. PVP, Polyvinylpyrrolidone; AAC, acrylic acid.

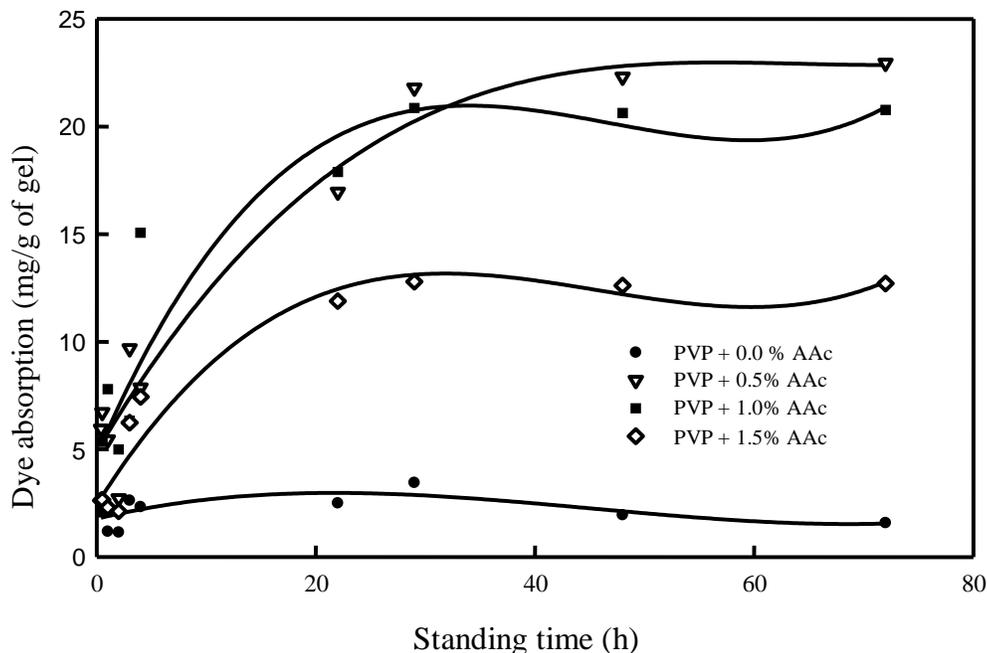


Figure 8. Effect of standing time and concentration of AAC of PVP/AAC blend hydrogel on dye adsorption. PVP, Polyvinylpyrrolidone; AAC, acrylic acid.

It was found that the amount of dye adsorption was ~23 mg/g of gel for 0.5% AAC, ~21 mg/g of gel for 1.0% AAC and ~13 mg/g of gel for 1.5% AAC in PVP/AAC blend gel. Since the highest gel content was obtained at 25 kGy radiation dose, the maximum cross-linking in the polymer chain was also obtained at the similar radiation dose and cross-linking density increases with increased AAC content in PVP/AAC blend. As a result, chain segment of polymer chain became shorter with increased cross-linked chain. The segment of PVP gel containing 0.5% AAC may be of better flexibility and more beneficial for the complex formation with dye than that of PVP hydrogel with 1 and 1.5% AAC. However, when most of the active functional sites in the adsorbent are occupied by dye molecules, the adsorbent may be unable to continually take additional dye molecules effectively. Although the functional carboxyl groups increased with increased AAC content in PVP/AAC hydrogel, the chain segments of the copolymer network cannot move freely toward dye molecules to form complexes as the flexibility of chain segments of the copolymer declines due to increased cross-linking.

Conclusion

Hydrogels were prepared from aqueous mixture of PVP and AAC by irradiation from Co-60 gamma source at room temperature. The gel fraction of hydrogel attained a maximum value at the radiation dose of 25 kGy. Swelling behaviors of hydrogel decreased with increased radiation dose, but gel fraction and swelling behaviors improved

with addition of AAC to the feed solution. Also, the diffusion mechanism of hydrogel was found to be non-Fickian type. The thermal stability of hydrogel improved with increased concentration of AAC. Furthermore, from FTIR spectrum, it is found that AAC interacts with PVP. The adsorption of MB was carried out with varying concentration of AAC in PVP/AAC hydrogel. The produced hydrogel adsorbs ~23 mg of dye/g of dry gel for 0.5% AAC in PVP/AAC mixture. As a result, PVP/AAC blend hydrogel may be useful in pharmacy, agriculture and environmental applications.

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