Radiation Synthesis of Interpenetrating Polymer Networks Based on *N*-Vinyl Pyrrolidone – Acrylic Acid Copolymer and Gelatin. I. Swelling, Morphology, and Thermal Characterization for Biomedical Applications

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ABSTRACT: Interpenetrating polymer networks (IPNs) based on *N*-vinyl pyrrolidone (NVP) : gelatin (Ge), and a copolymer of NVP – acrylic acid (AA) : gelatin (Ge) were prepared using *N*-*N*′methylenebisacrylamide (BIS) (0.5, 1% w/w) and glutaraldehyde (GLU) (0.5% v/v) as crosslinkers, respectively, by gamma irradiation technique. GLU was incorporated after irradiation to crosslink the gelatin chains, whereas BIS was placed in the respective solutions before irradiation. Several samples were prepared by varying the composition of gelatin to NVP or by changing the ratio of NVP : AA in preparing IPNs. The swelling behavior of the hydrogels was investigated as a function of variable doses, crosslinker (BIS) concentration, copolymer composition (NVP : AA ratio) or Ge : NVP ratio and pH of the immersion medium (3, 7.4, and 11). As expected, the swelling ratio increased with increasing acrylic acid content and decreased with increasing BIS content. No definite trend in the swelling behavior was observed as a function of dose. The interpenetration of the polymeric chains was established by morphological and thermal characterization. Scanning electron microscopy of IPNs showed a hybrid of coral and honeycomb structures as compared with the crosslinked polymers based on Ge and NVP (G_x and PVP_x). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1456–1463, 2007

Key words: interpenetrating polymer network (IPN); crosslinking; gelatin; swelling behavior; gamma irradiation

INTRODUCTION

Hydrogels, i.e., polymeric 3D networks, have been a topic of extensive research because of their unique bulk and surface properties, such as a soft and rubbery nature that minimizes irritation to the surrounding tissues. Stimuli-sensitive hydrogels can respond to external stimuli like pH, temperature, etc., have low interfacial tension, and high water uptake, which in turn reduces protein adherence and as a result increases their biocompatibility.[1–3] Hydrogels have been widely used in biomedical fields such as pharmaceuticals, tissue engineering, biotechnology, etc. They cannot be used as long-term implants because of their low mechanical strength. However, interpenetrating polymer networks (IPNs) prepared by the combination of synthetic and natural polymers are expected to yield materials with better strength that can find applications as a wound-dressing material as well as in drug delivery systems.[4,5]

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The prime requirements of a wound-dressing material are superabsorbing capacity and elasticity, and for a drug delivery system bioabsorption or bioerosion, controlled drug release, and biocompatibility. Hence the aim of the present study was to synthesize IPNs based on *N*-vinyl pyrrolidone, gelatin, and acrylic acid. Poly(vinyl pyrrolidone) (PVP) is well known for its biocompatibility,[6–8] and hence finds application in pharmaceuticals, adhesives, washing additives, food additives, and cosmetics. It forms a complex with iodine and is sold under the trade name of Betadine as an antimicrobial gel. Recently, it has also been used as one of the components for making contact lenses because of its excellent wettability characteristics. Acrylic acid is used as mucoadhesive in ocular drug delivery and also in gastrointestinal tract[9–11] and drug delivery systems.[12,13]

The synthesis and characterization of IPN systems based on gelatin have been reported in the literature.[14–16] Gelatin is a biopolymer and is not found in nature, but it can be produced by acid or base hydrolysis of collagen. Gelatin is widely used for wound dressing and drug delivery because of its biocompatibility and biodegradability.[17–21] In comparison to other chemical crosslinking agents, glutaraldehyde is

the most widely used due to its high efficiency of collageneous material stabilization.[22,23]

Homopolymerization of NVP is difficult and needs a higher amount of crosslinker.[24,25] Gels prepared using a higher amount of crosslinker will be brittle and their degradation time will be higher. This problem can be eliminated by radiation polymerization of NVP. In the present study, polymerization of NVP in the presence of a low concentration of BIS (0.5, 1%) and gelatin was done using γ-irradiation at different doses. In the second step, gelatin was crosslinked to prepare IPNs. We anticipate that the synthesis of IPNs by gamma irradiation and the choice of monomers/polymers in various combinations will have a potential as a wound-dressing material as well as in drug delivery because of their inherent properties of superabsorption, degradation, and wettability. This article describes the synthesis and characterization of IPNs based on FDA-approved polymers.

EXPERIMENTAL

Materials

Gelatin-B (CDH, India), *N*-vinyl pyrrolidone (NVP) (Merck, India), acrylic acid (AA) (Lancaster, India), *N,N*methylenebisacrylamide (BIS, Germany), and glutaraldehyde (GLU) 25% solution (v/v) (S. D. Fine Chemical, India) were used as received.

Preparation of interpenetrating polymer network by gamma radiation

IPNs based on gelatin/PVP or copolymers of PVP/AA were prepared by the gamma irradiation technique using BIS as a crosslinker for PVP or PVP : AA. Although crosslinking of gelatin by gamma irradiation has been reported in the literature,[26] in the present study leaching of gelatin was observed after irradiation, which was further confirmed by ninhydrin test. For stabilization of the gelatin inside the polymer chains, glutaraldehyde was employed as a crosslinker.

To study the effect of different parameters such as dose, composition, amount of crosslinker, and varying ratios of gelatin to PVP or PVP : AA copolymer, 45 samples were prepared by varying 1) dose (0.07, 0.14, 0.20, 0.25, 0.30, 0.40 Mrad); 2) mole percent of AA in NVP : AA copolymer; 3) amount of crosslinker (BIS); and 4) ratio of gelatin to PVP.

Procedure

For the preparation of hydrogels, gelatin (1 g) was dissolved in water (3 mL) by heating at 40°C followed by cooling to room temperature (30°C). BIS (0.005 or 0.01 g) was dissolved in NVP (1 g) or in a mixture of NVP : AA (1 g), then mixed with the gelatin solution. This reaction mixture was purged with nitrogen for 8–10 min to expel oxygen from the reaction mixture and then transferred into glass tubes (diameter 0.7 cm, length 15 cm). The glass tubes were then sealed with parafilm and placed in the gamma chamber. Polymerization was carried out at a maximum dose of 0.25 Mrad and minimum dose of 0.07 Mrad, at a dose rate of 18 rads/sec. After irradiation, samples were removed from the glass tubes and then immersed in glutaraldehyde (0.5% v/v) solution for 6 h. The samples thus obtained were washed thoroughly with distilled water for 1 week to remove the unreacted monomers/crosslinker. After washing, the samples were dried under vacuum at 37°C for 3–4 days. Homopolymers of NVP crosslinked with BIS and gelatin crosslinked with GLU were designated PVP_x and G_x, respectively. IPNs based on gelatin (crosslinked with GLU) and NVP (crosslinked with BIS) were designated GV. The numerical suffix represents the weight ratio of gelatin and NVP in the sample. For example, GV samples prepared by taking gelatin : NVP at ratios of 1 : 1, 1 : 2, 2 : 1 were designated GV, G_1V_2, and G_2V_1, respectively. The irradiation dose used for the preparation of samples is given in parenthesis; for example, GV prepared using doses of 0.07, 0.14, 0.20, and 0.25 Mrad were designated GV (0.07), GV (0.14), GV (0.20), and GV (0.25), respectively.

Similarly, IPNs based on gelatin and NVP : AA copolymer were prepared by taking 2.5/5/ or 7.5 mol% of AA in the initial feed and the samples were designated GVA followed by a numerical suffix, indicating mole percent of AA. For example, samples prepared using 2.5 and 7.5 mol% of AA, keeping the NVP-AA copolymer : gelatin at 1 : 1 were designated GVA-2.5 and GVA-7.5, respectively. The details of feed composition along with the sample designations are given in Tables I and II.

Characterization

Water uptake

Water uptake studies were carried out by immersing the crosslinked samples in a medium of varying pH, i.e., 7.4 (phosphate buffer) and 3, 11 (citrate-borate wide range buffer) at 37 ± 1°C. Swollen samples were then taken out at regular intervals; the surface water was removed by filter paper and weighed again. The percent water uptake was calculated using the equation:

$$\text{Percent water uptake} = \frac{W - W_0}{W_0} \times 100$$

where W is weight of the swollen sample and W_0 is the weight of the dried sample. The experiment was carried out until equilibrium was attained.

TABLE I
Details of Feed Composition and the Sample Designation for IPNs Based on Gelatin: NVP

Sample designation	NVP (g)	Gelatin (g)	BIS (g)	Gelatin : PVP
GV (0.07, 0.14, 0.20, 0.25, 0.30)[a]	1	1	0.005	1 : 1
GV (0.07, 0.14, 0.20, 0.25, 0.30)	1	1	0.01	1 : 1
G_1V_2 (0.25)	2	1	0.01	1 : 2
G_2V_1 (0.25)	1	2	0.01	2 : 1
G_x (0.25)	—	1	—	—
PVP_x (0.25)	1	—	0.01	—

[a] Represents the samples prepared using 0.5% w/w BIS crosslinker; numerals in parentheses represent the doses used for the preparation of samples.

Morphological characterization

For morphological characterization, hydrogels after swelling (equilibrium) in water were freeze-dried using a freeze drier (Christ, Germany, Alpha 1-2) at −52°C for 6 h. Transverse sections were cut from freeze-dried film samples using a cold knife. Samples were then viewed after sputter-coating (Pt-Au sputtering) using a scanning electron microscope DSM 289 (Gemini Electron Microscope, Zeiss, Germany) at 4 kV.

Thermal characterization

The thermal stability of IPN was investigated by recording TG/DTG traces in a nitrogen atmosphere using a TA 2100 thermal analyzer. Thermal stability was determined by recording TG/DTG traces in a nitrogen atmosphere over the temperature range of 20–800°C at a heating rate of 20°C/min using a sample size of 10 ± 5 mg.

The relative thermal stability of the samples was compared by recording the initial decomposition temperature (T_i), temperature of maximum rate of weight loss (T_{max}), and final decomposition temperature (T_f) and char yield at 800°C.

RESULTS AND DISCUSSION

The homopolymer of NVP prepared using redox initiator (APS and sodium metabisulphite) gave only viscous liquid at a low concentration of BIS (0.5 and 1% w/w). Solid samples were obtained at a higher concentration of BIS (~5% w/w) or in the presence of a small amount of AA. The reason for changing the polymerization route from redox initiation to gamma irradiation can be explained on the basis that at a higher percentage of BIS, nondegradable products would be obtained that cannot serve the purpose of simultaneous drug release and degradation *in vivo* studies. The difficulty in degradation of IPNs, based on AA and gelatin, has been extensively investigated in our laboratory and has been published.[27] It was also expected that the addition of a small amount of AA (2.5–7.5 moles) would be beneficial in drug uptake and release kinetics. Therefore, in the present study we prepared the samples with a gamma irradiation technique using 0.5 and 1% of BIS as crosslinker and NVP or NVP/AA as monomers. Rods having very good strength were obtained.

Water uptake

Water uptake of hydrogels is dependent on several factors, such as 1) immersion time; 2) pH of the immersion medium; 3) irradiation dose; 4) crosslink density; and 5) AA content. In the following, the effect of these factors on swelling characteristics is discussed.

Effect of immersion time

Figures 1 and 2(a–c) show the effect of immersion time on the percent water uptake in GV and GVA samples. In all the samples prepared using PVP and

TABLE II
Details of Feed Composition and the Sample Designation for IPNs Based on Gelatin : NVP-AA Copolymer

Sample designation	NVP (g)	Acrylic acid (g)	Gelatin (g)	BIS (g)	Gelatin : NVP-AA
GVA-2.5 (0.07, 0.14, 0.20, 0.25, 0.30)[a]	0.9836	0.0164	1	0.005	1 : 1
GVA-7.5 (0.07, 0.25, 0.30)	0.95	0.05	1	0.01	1 : 1
GA (0.07, 0.25, 0.30)	—	1	1	0.01	1 : 1
PVP-2.5 (0.25)	0.9836	0.0164	1	0.01	—

[a] Represents the samples prepared using 0.5% w/w BIS as crosslinker; numerals in parentheses represent the dose used for the preparation of samples.

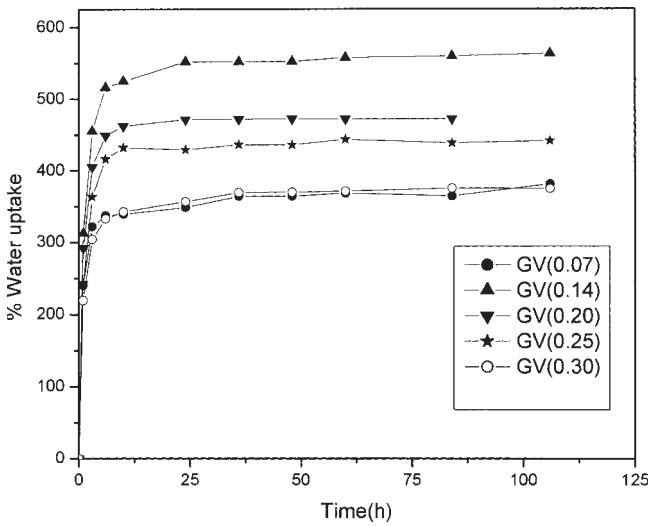

Figure 1 Effect of increases in dose on the swelling behavior of IPNs in phosphate buffer (pH 7.4).

gelatin (GV series), equilibrium water uptake (in phosphate buffer of pH 7.4, and citrate borate buffer of pH 3 and 11) was observed within 24 h, whereas in samples that were prepared using PVP/AA and gelatin (GVA series), a slow increase in water uptake was observed and equilibrium was attained after ~10 days. The differences in the swelling behavior between GV and GVA samples could be due to the loose and tight polymeric networks, respectively. In the GVA samples, intermolecular hydrogen bonding between –COOH of AA and $-NH_2$ of gelatin is expected, which might hinder the diffusion of water in the beginning due to the formation of a fine intermesh.

Effect of doses

The effect of doses on the percent water uptake in GV samples is shown in Figure 1. The swelling behavior in buffers of varying pH did not show any definite trend as a function of dose. Water uptake in samples over the whole pH range (3–11), prepared at different doses, showed an increase in the swelling ratio as dose was increased from 0.07 to 0.14 Mrads. A further increase of dose from 0.14 to 0.25 Mrad resulted in a decrease in the swelling ratio. One would expect a decrease in the swelling ratio with increasing dose; however, the increase observed at the beginning, from 0.07 Mrad to 0.14 Mrad, could be due to the simultaneous degradation/crosslinking upon irradiation. An initial increase in swelling (dose 0.07–0.14 Mrad) could preferably be due to the degradation followed by a decrease in swelling at higher doses (0.14–0.25 Mrad). A decrease in swelling could be explained on the basis of increased crosslinking at higher doses. Similar behavior has been reported by Dergunov et al.[28]

pH of immersion medium

The results of water uptake as a function of pH in G_x, PVP_x, and GV samples are summarized in Table III. Gelatin has an isoelectric point in the range of 4.7–5; below this value gelatin chains will be protonated (NH_3+) and repulsion between them is responsible for higher water uptake. Crosslinked gelatin showed minimum swelling at pH 3 (~280%) and highest swelling at pH 11 (~390%). However in the present study most of the amino groups are used up because of crosslinking with GLU and the free amino groups do not allow a marked increase in swelling. On the other hand, as the pH of the medium increased from 7.4 to 11, an increase in swelling was observed. This could be due to the deprotonation of the acid groups found in the gelatin chains. PVP_x showed maximum swelling (1398%) at pH 11 and lowest water uptake at pH 7.4 (~960%). Water uptake at pH 3 was higher as compared with that observed at 7.4. The irregular trend in the swelling behavior with PVP_x needs clarification. As expected, water uptake in IPNs was lower as compared with hydrogels (PVP_x). In GV samples prepared by taking varying amounts of gelatin, water uptake did not change as a function of pH. This abnormal swelling behavior supports interpenetration of two networks. With an increase in the gelatin component in IPNs, a decrease in swelling behavior was observed at pH 3, 7.4, and 11, which further supports the presence of PVP in the networks.

Effect of crosslink density

Table IV shows the effect of crosslink density on the swelling characteristics of hydrogels. For this purpose, samples were prepared using 0.5 and 1% of BIS. As expected, an increase in the crosslink density resulted in a decrease in the water uptake. As crosslinker concentration increases, the polymeric network will become more compact, thus reducing the pore size, which reduces the amount of water uptake.

Effect of AA content

Figure 2(a–c) shows the plots of percent water uptake as a function of time for GV and GVA samples, prepared using 2.5 and 7.5 mol% of AA at a dose of 0.25 Mrad. Figure 2(a) shows that when NVP was substituted with AA (GA), a marked increase in percent water uptake (~1498%) was observed after 10 days. In GVA samples, as the acrylic acid content increased from 2.5 to 7.5%, an identical trend in the water uptake was observed up to 250 h of immersion, which

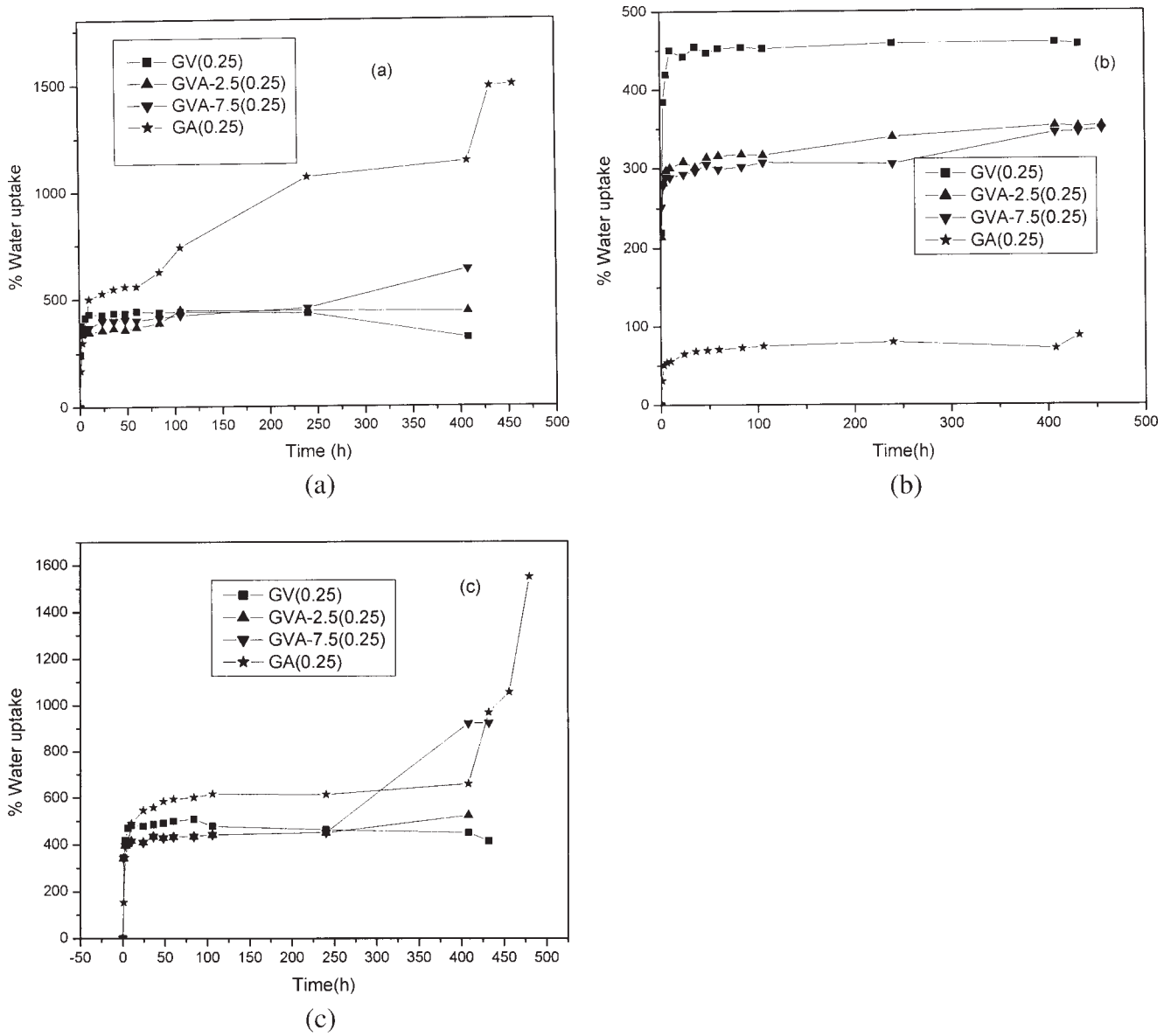

Figure 2 Effect of AA content on the water uptake prepared at doses of 0.25 Mrad at (a) pH 7.4, (b) pH 3, and (c) pH 11.

was followed by a sudden increase after 400 h in GVA-7.5, whereas it was not seen in GVA 2.5%. About an 81% increase in water uptake was observed with GV samples at pH 3 as compared with GA samples. This can be explained on the basis of a PK_a (4.28) value for poly(acrylic acid). Below this pH value (pH 3), AA will be in the collapsed state, which will result in low water uptake. At higher pH, swelling of IPNs can be explained by the presence of a negatively charged carboxylate ion, which will result in repul-

TABLE III
Effect of pH on Percent Water Uptake in Hydrogels and IPNs

Sample designation	% Water uptake at pH of		
	3	7.4	11
G_x (0.25)	280	310	390
PVP_x (0.25)	1250	960	1398
GV (0.25)	459	443	498
G_1V_2- (0.25)	600	513	789
G_2V_1- (0.25)	436	436	504

TABLE IV
Effect of pH and BIS Content on Percent Water Uptake

Sample designation	% Water uptake at pH of		
	3	7.4	11
GV (0.25)[a]	487	458	512
GV (0.25)	459	443	498
GVA-2.5 (0.25)[a]	468	472	654
GVA-2.5 (0.25)	353	445	524

[a] Represents the samples prepared using 0.5% w/w BIS.

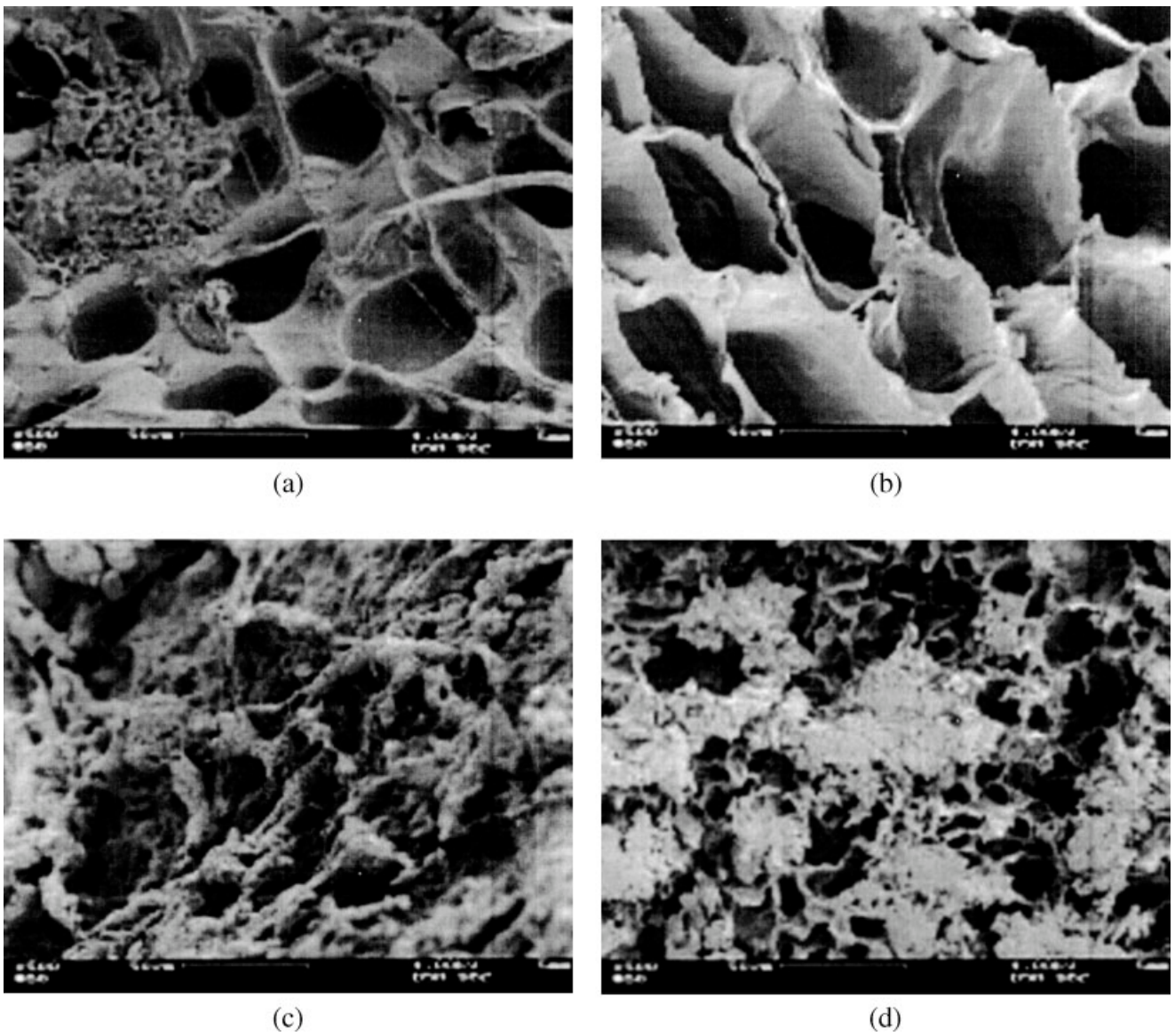

Figure 3 SEM micrographs of freeze-dried (a) G_x (0.25), (b) PVP_x (0.25), (c) GV (0.25), and (d) GVA-2.5 (0.25) (magnification 500×) after equilibrium swelling.

sion in the polymeric network and higher water uptake. As expected, the water uptake was slightly higher with GVA samples as compared with GV samples. The reason for this behavior can be explained due to the alkaline nature of the immersion medium, which supports the deprotonation of the acid group beyond pH 7.0

Morphological characterization

Figure 3 shows SEM micrographs of crosslinked gelatin, PVP, and IPNs based on gelatin : PVP/PVP-AA (sample GVA-2.5) prepared by irradiation using a dose of 0.25 Mrad. Gelatin (G_x) and PVP (PVP_x) showed the formation of large porous structures similar to a honeycomb, with well-defined walls that change upon interpenetration of two network structures, i.e., in IPNs. IPNs of GV showed a coral-type porous network, whereas GVA demonstrated a hybrid of honeycomb and coral networks. Morphological characterization supports the formation of interpenetrating networks.

Thermal characterization

Figure 4 shows TG/DTG traces of hydrogels recorded in a nitrogen atmosphere. A weight loss of ~10% in the temperature range 50–150°C was observed in all the samples. This could be due to the surface and absorbed water. IPNs showed two-step degradation, whereas single-step degradation was observed in the case of crosslinked gelatin (G_x) and PVP (PVP_x). The

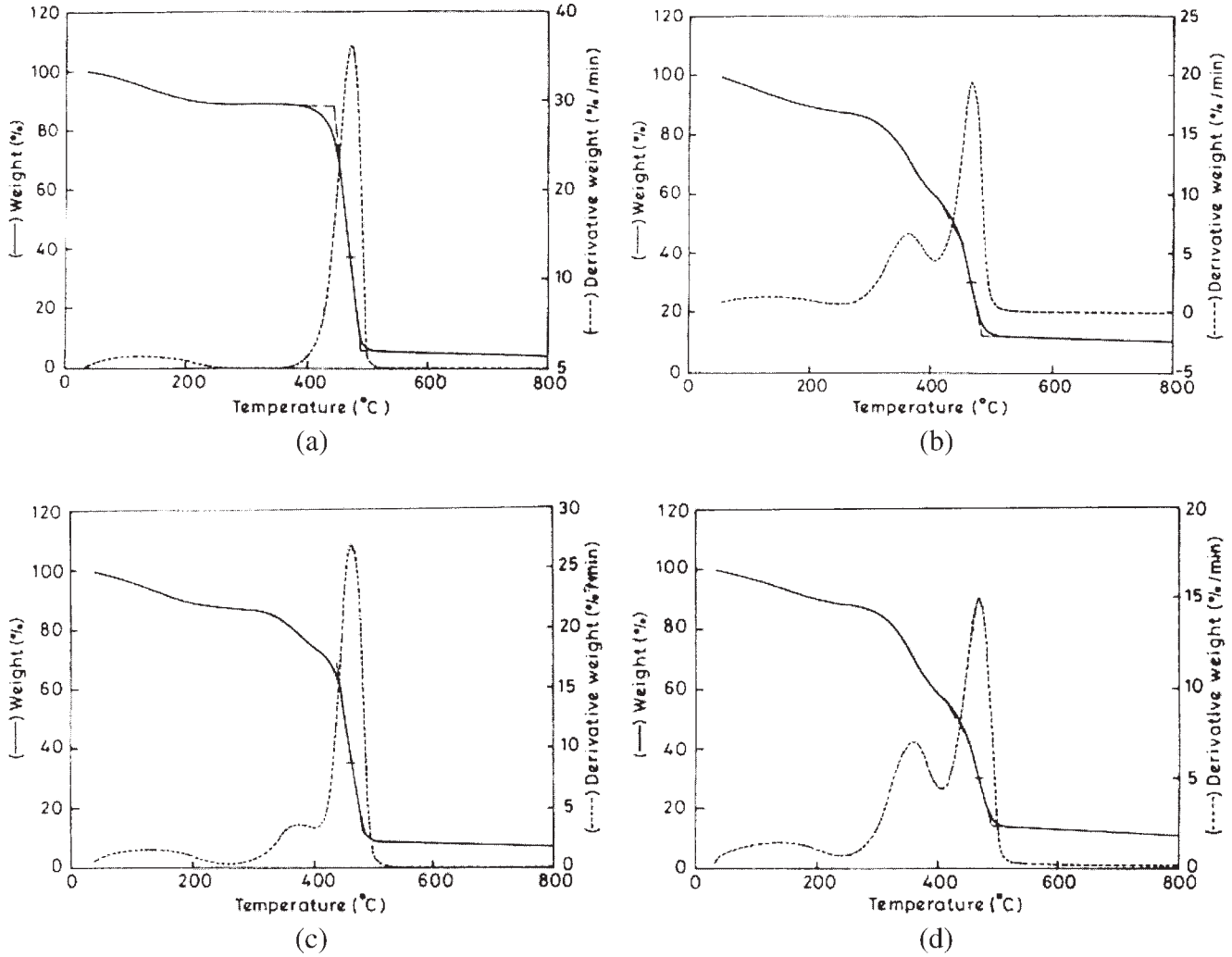

Figure 4 TG/DTG traces of hydrogels (a) PVP_x (0.25), (b) GV (0.25), (c) G_1V_2 (0.25), and (d) G_2V_1 (0.25).

thermal stability of the samples was compared by comparing initial decomposition temperature, temperature of maximum rate of weight loss, final decomposition temperature, and char yield at 800°C. The char yield in all the samples was calculated by ignoring the weight loss up to 150°C and taking the sample weight only after 150°C as the original weight. The results are summarized in Table V. In GV samples, the first step degradation in the temperature range of 250–400°C may be attributed due to gelatin and in the second step (400–500°C) could be due to PVP. Weight loss in these steps can be used to calculate the composition of samples. GVA samples also showed a two-step degradation. In all the IPNs, T_{max} was higher as compared with hydrogels (G_x and PVP_x) for both the degradation steps. This could be due to formation of interpenetrating networks that in turn delays the degradation. Percent char yield in the case of G_x and PVP_x was found to be at 20% and 15%, respectively. If both the components degrade independently, then char yield should follow the additivity rule; however, in the present study the char yield was lower, which further supports the formation of IPNs. Degradation of both components was affected in the case of IPNs. A similar behavior has been reported in the case of IPNs based on gelatin : AA copolymer.[16]

TABLE V
Results of Thermogravimetric Analysis of IPN Samples in Nitrogen Atmosphere (Heating Rate 20°C/min)

Sample designation	T_i (°C)	T_{max} (°C)	T_f (°C)	%Char yield at 800°C
PVP_x (0.25)	355	476	496	15
PVP_x-2.5	332	470	486	19
GV (0.25)	244	360		21
	400	484	486	
GVA-2.5 (0.25)	267	353	394	24
	400	460	487	
G_2V_1 (0.25)	246	346	400	19
	406	451	488	
G_1V_2 (0.25)	266	366	400	22
	393	473	500	
G_x (0.25)	290	338	397	20

CONCLUSION

The above studies demonstrate that the gamma irradiation technique can be used to make elastic and solid gels and circumvent the problems associated with redox initiation. Thermal and scanning electron microscopy supports the formation of an IPN. The thermal stability of hydrogels (PVP_x, G_x, and PVP_x-2.5) increased when IPNs were formed. Morphological characterization showed the formation of a hybrid pattern in IPNs (GV or GVA samples). The swelling degree was found to be dependent on dose, composition, time, and pH of immersion medium. Dose variation and incorporation of AA has led to the formation of IPNs having rigid as well as elastic structures that may find application as wound dressing and a drug delivery system.

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