

Interpenetrating Polymer Networks Based on Poly(acrylic acid) and Gelatin. I: Swelling and Thermal Behavior

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ABSTRACT: This article describes the synthesis of full and semi-interpenetrating polymer networks (IPNs) based on poly(acrylic acid) and gelatin as polymers 1 and 2, which were crosslinked sequentially using *N,N'*-methylene bisacrylamide (B_{Am}) and glutaraldehyde, respectively. Various samples were prepared by taking varying amounts of acrylic acid and gelatin in the initial feed. Sequential IPNs were prepared by first polymerizing and crosslinking acrylic acid in the presence of gelatin using redox initiators (ammonium persulphate and sodium metabisulphite) and B_{Am} as a crosslinking agent. Gelatin present in the firm gels was then crosslinked using 4% glutaraldehyde. Characterization of these gels was done by measuring their swelling behavior as a function of pH, temperature, and time. Percent swelling increased with increasing amounts of acrylic acid. The swelling ratio was also determined in the pH range of 1 to 12. Acid/alkali or buffers were used for maintaining pH. A significant increase in the percent swelling was observed when pH of distilled water was above 10. On the other hand, in the case of buffer, the swelling ratio increased with increasing the pH, and a maxima was observed at pH 8.4. A further increase in pH resulted in a decrease in the swelling ratio. Thermal and morphological characterization was done using thermogravimetric analyzer and scanning electron microscopy, respectively. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 217–227, 2001

Key words: interpenetrating polymer networks; hydrogels; gelatin; poly (acrylic acid); swelling behavior

INTRODUCTION

Hydrogels are crosslinked polymeric networks, capable of absorbing large amounts of water and drastically increasing in volume.^{1–3} The swelling properties of these gels have attracted the attention of researchers and technologists, and have

found wide-spread applications in drug delivery devices, separation processes, sensors, contact lens devices, and many other fields.^{4–16} They can respond to external stimuli such as heat, pH, chemical environment, etc., and behave as intelligent materials.^{17,18} Among these, pH-sensitive hydrogels have been extensively investigated for potential applications in controlled release systems.

Although some hydrogels have excellent biocompatible characteristics, they have poor mechanical properties. It is not possible for any single polymer to simultaneously meet the desired

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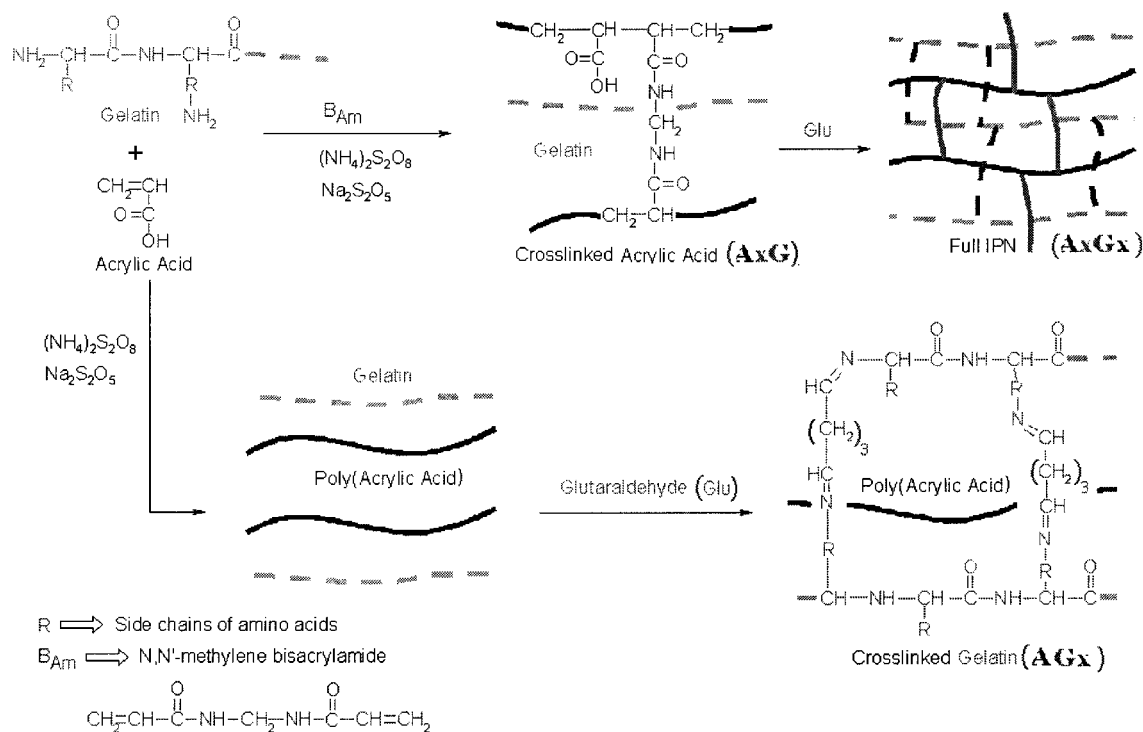


Figure 1 Schematic representation of the synthesis of various IPNs.

demands in terms of both properties and performance. Interpenetrating polymer networks (IPNs) makes it possible to combine partially compatible or incompatible polymers and provide unique possibilities for controlling the mechanical and physicochemical properties.^{19,20} IPNs have several advantages over simple hydrogels or blends because the synthesis and crosslinking of two or more different polymers is done in the immediate presence of each other, so that the crosslinked chains are intermingled, resulting in considerable phase mixing, thereby restricting the domain size.²¹ Another advantage of this method is that chemically incompatible systems can also be combined.

Because the properties of IPNs are influenced by the conditions of synthesis, composition, degree of crosslinking, and compatibility, it was considered of interest to investigate systemically the effect of acrylic acid/gelatin content on the swelling characteristics of IPNs crosslinked using *N,N'*-methylene bisacrylamide/glutaraldehyde as crosslinking agents. Semi-IPNs were also prepared to investigate the effect of crosslinking of the components on the swelling and thermal behavior. The effect of the environment, i.e., pH, temperature, etc., on the swelling characteristics has also been evaluated.

EXPERIMENTAL

Materials

Acrylic acid (AAc) (G. S. Chemicals), *N,N'*-methylene bisacrylamide (B_{Am}) (SISCO research lab, Mumbai), gelatin (Ge) (type-B) (S. D. Fine Chem. Ltd., Boisar), glutaraldehyde (Glu) (25% LR) (S. D. Fine Chem. Ltd), sodium metabisulphite (S. D. Fine Chem. Ltd) and ammonium persulfate (SISCO Research Lab, Mumbai) were used as obtained.

Preparation of Interpenetrating Polymer Networks (IPNs)

Schematic representation for the synthesis of full and semi IPNs are shown in Figure 1. A detailed procedure for the synthesis of full and semi IPNs is given below.

Full IPNs (AxGx)

Full IPNs of acrylic acid and gelatin were prepared by sequential polymerization using *N,N'*-methylene bisacrylamide and glutaraldehyde, respectively, as crosslinking agents using the procedure reported earlier,²² after suitable modification.

Table I Sample Designation and Monomer Ratios in the Preparation of Full IPNs

Sample Designation	Acrylic Acid (g)	Gelatin (g)
AxGx-1	1	1
AxGx-2	2	1
AxGx-3	3	1
AxGx-4	4	1
AxGx-5	5	1
AxGx-6	1	2
AxGx-7	1	3
AxGx-8	1	4
AxGx-9	1	5

Two grams of gelatin was dissolved in 20 mL of oxygen free distilled water with continuous stirring at 37°C until homogenous solution was obtained. To this solution, 2 g of acrylic acid (AAc) and 0.215 g of *N,N'*-methylene bisacrylamide (B_{Am}) were added. The reaction mixture was then made oxygen free by purging nitrogen. Free radical polymerization and crosslinking of AAc was carried out using ammonium persulphate (0.1 mol %) and sodium metabisulphite (0.1 mol %) as redox initiators. This reaction was left overnight at room temperature, resulting in the formation of firm gels. The gels were carefully dislodged from the walls of the container, and were immersed in 4% glutaraldehyde (Glu) solution for 20 h to crosslink the gelatin chains. The IPNs were washed extensively with water to remove water-soluble moieties and then dried in vacuum to constant weight.

Several samples were obtained by varying the ratio of AAc : Ge by following the above procedure. The feed composition and sample designations are given in Table I. The total monomer concentration in reaction mixture (w/v) was kept constant (20%) in all these preparations. The concentration of crosslinking agent, i.e., B_{Am} (for AAc) and Glu (for Ge) were kept as 0.5 mol % and 4% (w/v), respectively.

Semi IPNs (AxG), (AGx)

Semi-IPNs were prepared in a similar manner as full IPNs except that only one of the polymers, poly (acrylic acid) [PAAc] or Ge was crosslinked. AxG-1, AxG-3, and AxG-5 are the sample designations for semi-IPNs where PAAc was crosslinked and the AAc : Ge ratios were 1 : 1, 3 : 1, and 5 : 1, respectively. AGx-1, AGx-3, and AGx-5 are

the sample designations for semi-IPNs where Ge was crosslinked and the AAc : Ge ratios were 1 : 1, 3 : 1, and 5 : 1, respectively. The sample designations and monomer feed ratio for the preparation of semi-IPNs are given in Table II.

Characterization of Hydrogels

Swelling Studies

Weighed amounts of full and semi-IPN samples were dipped in buffers or distilled water of varying pH. The pH of distilled water was adjusted by adding acid or alkali. At intervals, the swollen gels were lifted, patted dry, and weighed. The swelling studies were carried out until an equilibrium swelling was obtained. Percent swelling was calculated using the following equations:

$$\% \text{ Swelling} = \frac{W_s - W_d}{W_d} \times 100$$

$$\text{Swelling ratio} = \frac{W_s}{W_d}$$

where W_s is the weight of the swollen polymer, and W_d is the initial weight of the dry polymer.

A wide-range buffer based on citrate–borate–phosphate–barbitone, having a pH in the range of 1 to 10, and distilled water with a pH ranging from 1 to 12, were used to study the effect of pH on swelling behavior of the hydrogels. To investigate the effect of temperature, swelling behavior of hydrogels was determined at 25, 35, and 45°C. For swelling studies, an average value of three replicates was taken.

Thermal Behavior

Thermal stability of the full and semi-IPNs was investigated by recording TG/DTG traces in nitro-

Table II Sample Designation and Monomer Ratios in the Preparation of Semi-IPNs

Sample Designation	Acrylic Acid (g)	Gelatin (g)
AxG-1	1	1
AxG-3	3	1
AxG-5	5	1
AGx-1	1	1
AGx-3	3	1
AGx-5	5	1

gen atmosphere using Dupont 2100 thermal analyzer having 951 TG module. A heating rate of 20°C/min and a sample size of 10 ± 5 mg was used in all the experiments. The following characteristic temperatures were noted from the TG traces: (a) initial decomposition temperature (T_i)—it is the temperature at which the sample starts decomposing. It was determined by extrapolating using steep portion of weight loss curve and the initial base line.

Final decomposition temperature (T_f): It is the temperature at which the weight loss was complete. It was also obtained by extrapolation. (b) Temperature of maximum rate of weight loss (T_{max})—it is the temperature at which the rate of weight loss was maximum.

Morphological Studies

Etched and unetched samples of the semi-IPNs were used to confirm the interpenetration in IPNs using scanning electron microscopy. The samples were etched by repeated hot water treatment to wash out the uncrosslinked gelatin/acrylic acid in the semi-IPNs. The morphology of these samples was investigated using Cambridge Stereoscan model S4-10 scanning electron microscope. The samples were cryogenically fractured by dipping in liquid nitrogen for 2 h. The fractured samples mounted on the base plate were coated with silver using the vapor deposition technique. The surface was then scanned using a magnification of 1000 to

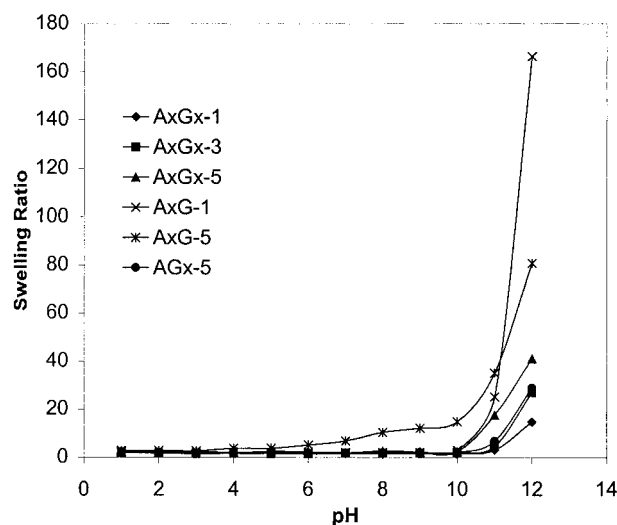


Figure 2 Effect of pH on the swelling behavior of IPNs in distilled water (pH adjusted with acid/alkali) at 37°C.

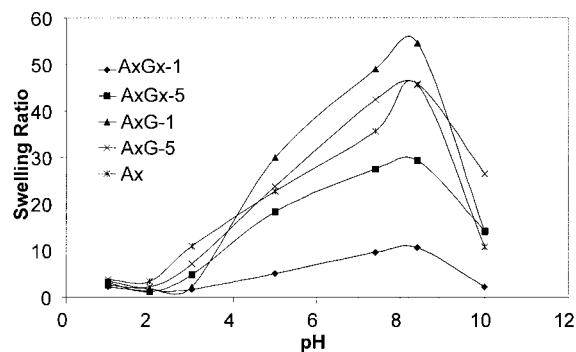


Figure 3 Effect of pH on the swelling behavior of IPNs in wide range buffer at 37°C.

investigate the distribution of two polymer phases.

RESULTS AND DISCUSSION

Gelatin and poly (acrylic acid) were soluble in water and clear solutions were obtained on mixing varying amounts of gelatin and acrylic acid monomer. However, interpenetrating polymer networks obtained were white/brown and opaque, indicating phase separation upon crosslinking/interpenetration. Poly (acrylic acid) and gelatin crosslinked with *N,N'*-methylene bisacrylamide and glutaraldehyde, respectively, were translucent.

Swelling Behavior

Swelling behavior of a material depends upon its composition, pH, and temperature. The effect of

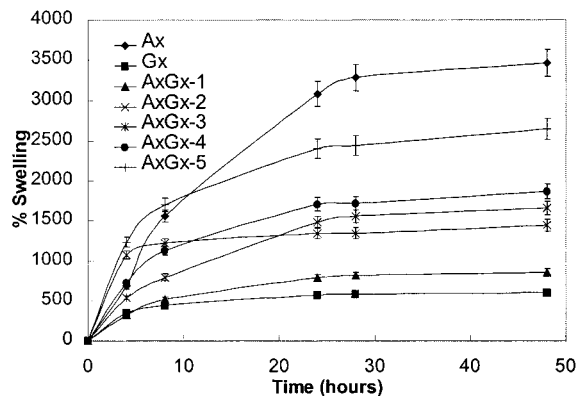


Figure 4 Effect of acrylic acid content on percent swelling in AxGx samples (pH 7.4, temperature 37°C).

Table III Results of % Swelling as a Function of pH and Temperature for Full IPNs

Sample Designation	Temperature (°C)	% Swelling at pH of			
		3.0	5.0	7.4	8.4
Ax	25	1154	2669	4565	5046
	35	985	2171	3465	4458
	45	978	2974	3494	3987
Gx	25	326	391	551	620
	35	329	423	602	645
	45	342	480	641	637
AxGx-1	25	64	412	845	876
	35	68	409	859	963
	45	76	502	937	1037
AxGx-2	25	88	732	1286	1353
	35	101	769	1447	986
	45	134	813	1386	1393
AxGx-3	25	137	904	1593	1755
	35	160	1075	1664	1865
	45	121	1257	1781	2042
AxGx-4	25	212	1593	2080	2086
	35	207	1042	1869	2326
	45	315	1321	2088	2063
AxGx-5	25	400	1554	2726	2495
	35	384	1727	2648	2835
	45	516	1921	2736	3249
AxGx-6	25	72	361	600	668
	35	76	259	616	667
	45	78	352	686	712
AxGx-8	25	125	264	470	619
	35	127	313	560	591
	45	137	346	626	636
AxGx-9	25	155	259	468	543
	35	183	309	585	660
	45	153	338	603	676

these parameters on the swelling behavior is described in the following text.

Effect of pH

Figures 2 and 3 depict the effect of pH on the swelling ratio, in distilled water (pH 1–12) and buffers (pH 1–10). In full and semi-IPNs the swelling behavior in distilled water showed a significant increase above pH 10 (Figs. 2, 4). Above pH 10, the PAAc network is charged, repulsive forces sets up between them, and the polymer chains exist in an expanded conformation that is responsible for a significant increase in the swelling ratio.

In buffers, the swelling ratio increased rapidly as the pH of buffers was increased from 5.0 to 8.4 in all the samples. The pKa value of poly(acrylic acid) is 4.28;^{22,23} therefore, at pH less than 4,

poly(acrylic acid) chains are in the collapsed state, thus reducing the swelling ratio. However, as the pH increases above 6 and 8, the poly(acrylic acid) forms carboxylate ions, which cause repulsion between the network, resulting in rapid increase in the swelling ratio. Electrostatic repulsion between the carboxylic acid in the polymer chains, the ions present in the buffer solution and the ionic osmotic pressure generated from mobile counterions to charged ions in the network may also be responsible for the increase in swelling.^{24–26}

On the other hand, crosslinked gelatin has an isoelectric pH (PI) in the range of 4.7 to 5.1. Below the PI value the gelatin chains remain protonated. As a result, the chains contain NH_3^+ ions, and the cationic repulsion between them could be responsible for their high swelling.²⁷ The

Table IV Results of % Swelling as a Function of pH and Temperature for Semi-IPNs

Sample Designation	Temperature (°C)	% Swelling at pH of			
		3.0	5.0	7.4	8.4
Ax	25	1154	2669	4565	5046
	35	985	2171	3465	4458
	45	978	2974	3494	3987
Gx	25	326	391	551	620
	35	329	423	602	645
	45	342	480	641	637
AxG-1	25	113	2843	3864	4662
	35	124	2904	4794	5356
	45	147	4321	5778	7290
AxG-3	25	382	2355	4108	3728
	35	370	2113	3747	3809
	45	559	2845	3759	4424
AxG-5	25	542	2225	2683	4474
	35	618	2283	4149	4490
	45	665	2138	3534	4664
AGx-1	25	92	666	1182	1268
	35	90	735	1165	1489
	45	117	835	1587	1665
AGx-3	25	125	1170	1669	1844
	35	121	1198	1836	2108
	45	176	1552	2089	2022
AGx-5	25	206	1395	2194	2332
	35	250	1384	2478	2441
	45	388	1904	2734	2808

crosslinked gelatin sample (Gx) degrades completely after 24 h of immersion in solution of pH 1.

Effect of Temperature

The results of swelling characteristics of full and semi-IPNs, respectively, at pH 3, 5, 7.4, and 8.4 in buffer solutions are summarized in Tables III and IV. In the case of Ax, the percent swelling decreased with increasing temperature at all pHs except at pH 5.0, where it showed a decrease as the temperature was increased from 25 to 35°C followed by an increase as the temperature was further raised to 45°C. Swelling in a particular medium is dependent on the crosslink density, pH, and temperature, which in turn, control the diffusion. One expects an increase in the percent swelling with increase in temperature; however, a decrease observed in the case of Ax could be interpreted due to some thermal transition that results in shrinkage. In the case of Gx samples, the percent swelling increased with increasing the temperature irrespective of the pH of the medium. However, the percent swelling was much

less in Gx samples compared to Ax. In all other samples, the percent swelling increased with increasing temperature from 25 to 45°C.

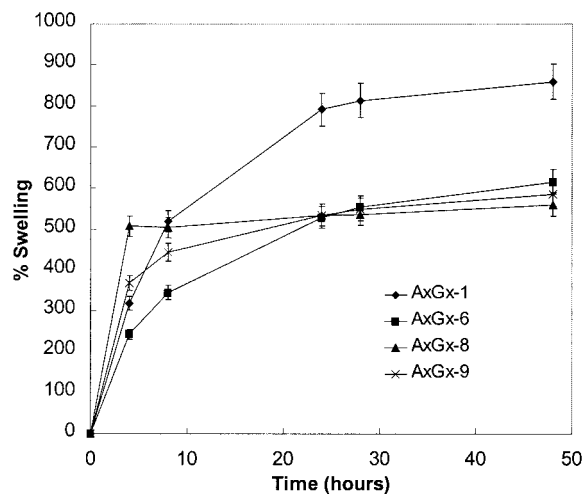


Figure 5 Effect of gelatin content on percent swelling in AxGx samples (pH 7.4, temperature 37°C).

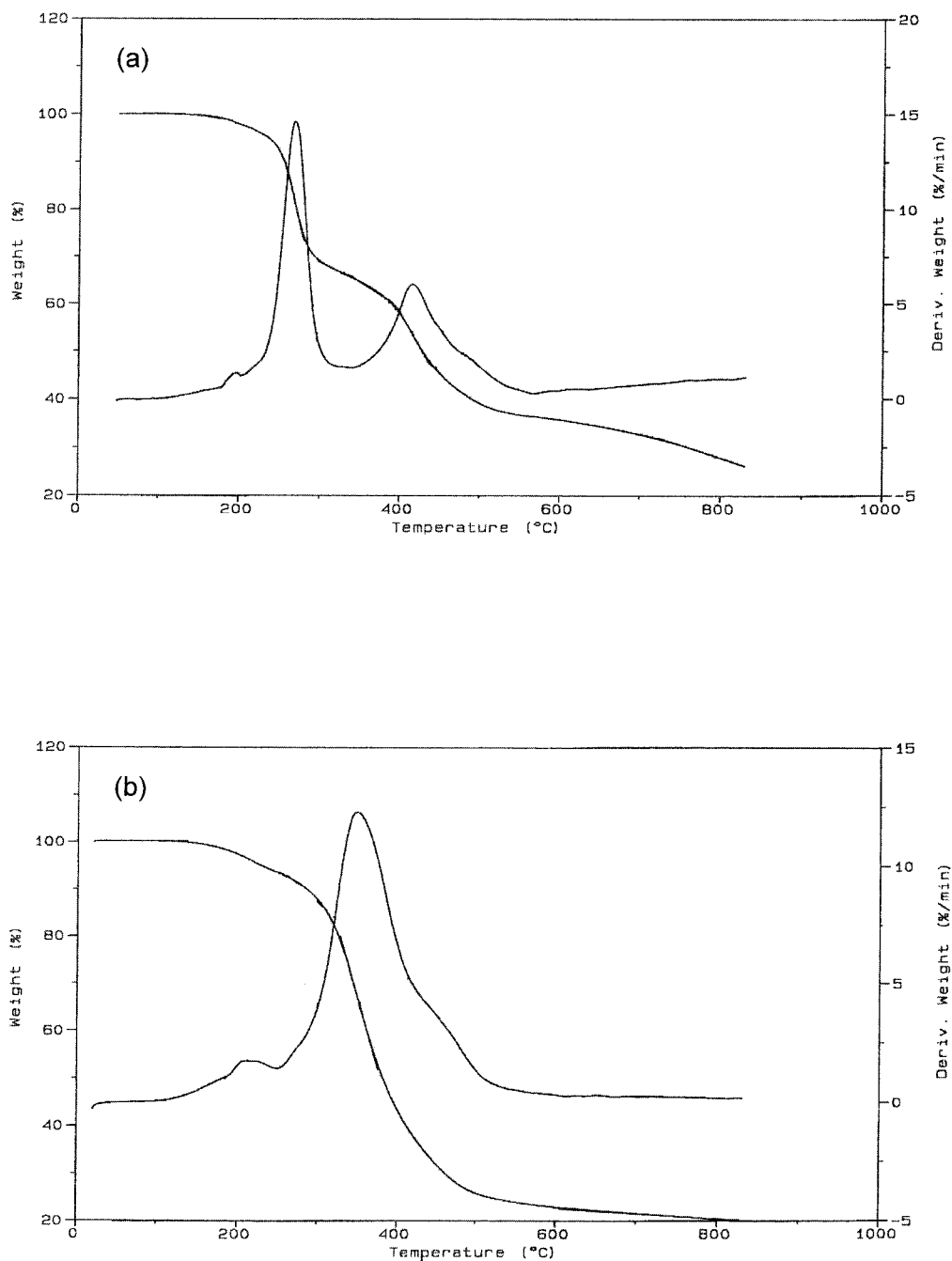


Figure 6 (a–d) TG/DTG traces of samples Ax, Gx, AxGx-1, and AxGx-5.

Effect of Composition

Figures 4 and 5 illustrate the effect of composition on percent swelling in the AxGx samples at a temperature of 35°C and pH 7.4. In all the samples equilibrium swelling was observed after 24 h. Crosslinked poly (acrylic acid) had much higher percent swelling compared to crosslinked gelatin. In the case of the AxGx samples (i.e., AxGx-1 to

AxGx-5), the percent swelling increased with increasing amounts of acrylic acid at all temperatures and pH, whereas increased gelatin content resulted in a decrease in percent swelling. This could be due to an increase in the hydrophilic groups (—COOH) with increasing the amount of acrylic acid in the samples. A similar trend was observed in the case of semi-IPNs (AxG-1 to AxG-

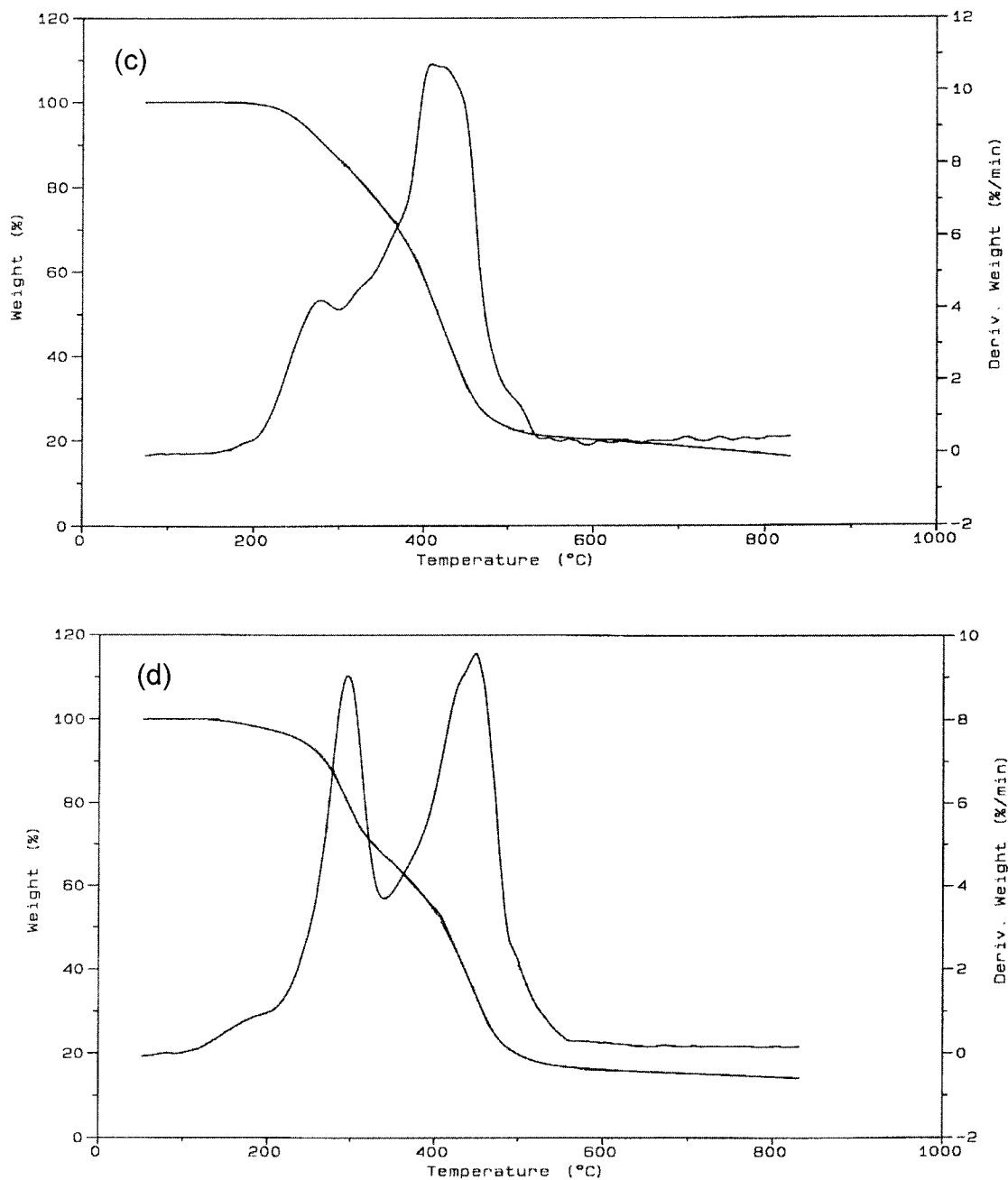


Figure 6 (Continued)

3). Lee et al. also reported that the more PAAC content in the IPNs the higher the swelling ratio.²⁸

Although the AxGx samples have varying amounts of gelatin (AxGx-6 to AxGx-9), the percent swelling showed no definite trend with increasing the amounts of gelatin in the samples.

In the case of IPNs, the percent swelling at all pHs as well as temperatures of measurement was

much lower than the homopolymers (Ax/Gx), thereby indicating the interpenetration of polymer networks that restricts the diffusion of water molecules into the network. A similar behavior has been reported by Chatterji²² in the case of IPNs based on acrylamide/acrylic acid hydrogels.

All the semi-IPNs having 1 : 1 and 3 : 1 ratios of AAc : Ge showed an increase in swelling compared to full IPNs of a similar ratio. In AxG-1 and

Table V Results of Thermogravimetric Analysis of Hydrogels (Heating Rate 20°C/min in Nitrogen Atmosphere)

Sample Designation	T_i (°C)	T_{max} (°C)	T_f (°C)	% Weight Loss	% Char Yield at 800°C
Ax	240	267	284	34	28
	394	416	438	38	
Gx	173	211	250	7	19
	321	353	423	74	
AxGx-1	230	265	300	14	16
	382	417	469	70	
AxGx-3	231	288	304	31	11
	403	432	477	58	
AxGx-5	222	293	311	34	13
	407	446	486	53	
AxGx-8	177	248	260	11	19
	337	363	437	70	
AxG-1	200	273	285	19	15
	382	421	466	66	
AxG-5	231	300	315	36	8
	412	441	474	56	
AGx-1	211	259	260	14	17
	367	414	467	69	
AGx-5	226	288	307	35	12
	405	430	480	53	

AGx-3, in samples prepared by taking 1 : 1 and 3 : 1 ratios of AAc : Ge, a higher percent swelling was observed compared to full IPNs. However, AGx samples prepared by taking a 5 : 1 ratio (AGx-5) surprisingly showed less percent swelling compared to full IPNs. This could be due to the leaching out of uncrosslinked poly(acrylic acid). On the other hand, AxG samples of similar composition (sample AxG-5) showed higher water uptake at all pHs and temperatures compared to full IPN (AxGx-5). The swelling decrease in the case of the full IPNs compared to semi-IPNs could be due to an increase in modulus where both the components are crosslinked.

Thermal Behavior

Figure 6(a)–(d) shows the TG/DTG traces of samples Ax, Gx, AxGx-1, and AxGx-5. All the samples were stable up to 200°C except Gx and AxGx-8, and started losing weight above this temperature. Two-step degradation was observed in all the samples. The relative thermal stability of various samples was evaluated by comparing the T_i (initial decomposition temperature), T_f (final decomposition temperature), T_{max} (temperature of maximum rate of weight loss and percent change at

800°C). The results of thermogravimetric analysis are summarized in Table V.

In the case of IPNs (AxGx samples) T_{max-1} as well as T_{max-2} increased with increasing amounts of acrylic acid. A similar trend was observed in case of semi-IPNs. AxGx/AGx samples rich in gelatin had lower stability as compared to AxGx/AxG samples (rich in acrylic acid).

Crosslinked poly (acrylic acid) (Ax) and crosslinked gelatin (Gx) show a char yield of 28 and 19%, respectively. If the two crosslinked polymers in IPNs degrade independently, then one would have expected char yield based on the additivity rule. However, the observed values of percent char were lower than the expected values, thereby indicating the interpenetration of polymer chains. The degradation behavior of crosslinked poly(acrylic acid) (Ax) and gelatin (Gx) was affected in the case of IPNs.

In AxGx-1, AxG-1, and AGx-1 (where the ratio of AAc : Ge was kept as 1 : 1), the weight loss in the first step was only 15–17% compared to 34% in crosslinked poly(acrylic acid), whereas in samples such as AxGx-3, AxGx-5, and semi-IPNs AxG-5 and AGx-5, having higher amounts of acrylic acid, percent weight loss in the first step was found to be in the range of 31–36%. This

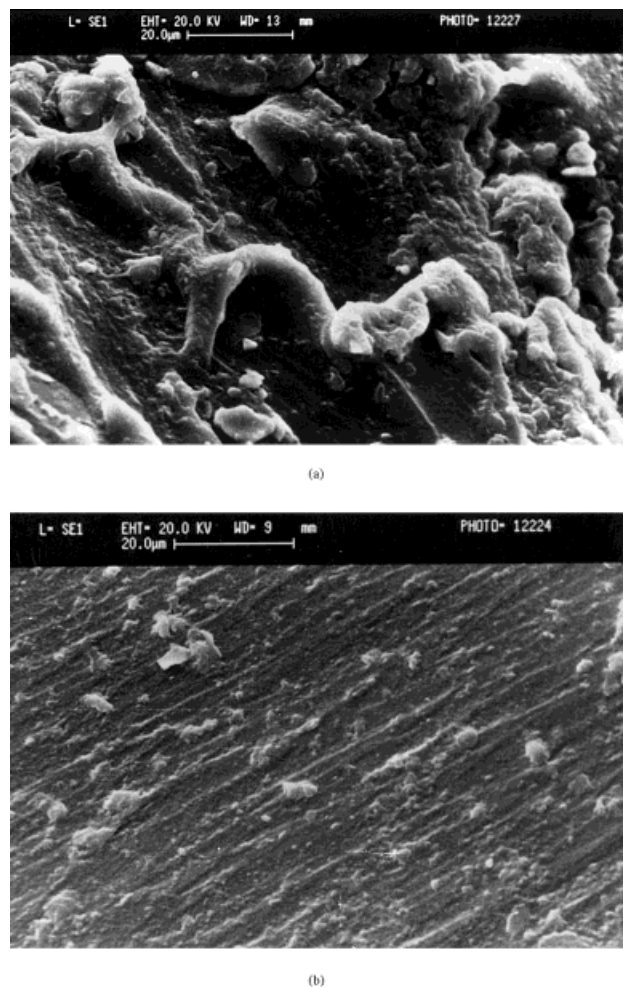


Figure 7 Scanning electron micrographs of (a) etched and (b) unetched AxG-3 samples.

could be due to the fact that the acid groups of acrylic acid are not easily available for dehydration in the case of samples where the ratio of AAC : Ge was kept as 1 : 1, which further supports interpenetration of two networks. The thermal stability of full and semi-IPNs prepared by taking same ratios of AAC : Ge was comparable.

Morphology

Figure 7(a) and (b) depicts the SEM photographs of etched and unetched AxG-3 samples, respectively, at a magnification of 1000. The scanning electron micrographs for full IPNs (AxGx-1, AxGx-5), semi-IPNs (AxG-5 and AGx-5), crosslinked gelatin (Gx), and crosslinked poly (acrylic acid) (Ax) were also recorded. Comparing the SEMs of Ax, Gx with that of full and semi-IPNs, it was observed that full and semi-IPNs show a

two-phase morphology. To further confirm this, in the case of semi-IPNs, the uncrosslinked phase, i.e., gelatin in AxG-5 and poly(acrylic acid) in AGx-3 were etched out using hot water, and the SEM of the etched and unetched samples were compared. The etched samples showed the presence of holes throughout the surface indicating the presence of two-phase structure.

CONCLUSION

IPN hydrogels composed of crosslinked poly (acrylic acid) (PAAc) and gelatin (Ge) were synthesized by a sequential method using redox initiators. *N,N'*-methylene bisacrylamide and glutaraldehyde were used for crosslinking of PAAc and gelatin, respectively. Swelling studies clearly indicated the effect of pH as well as the composition on the percent swelling. Maximum swelling was observed at pH 8.4 when buffers were used, whereas a dramatic increase in the swelling property was observed above pH 10 in distilled water.

Thermal behavior clearly showed that the interpenetration of chains restricts the evolution of water, and this effect was maximum when equal amounts of acrylic acid and gelatin were incorporated.

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