Preparation and Characterization of Polyvinyl Alcohol Based Biomaterials: Water Sorption and *In Vitro* Blood Compatibility Study

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ABSTRACT: Semi-interpenetrating polymer networks (semi-IPNs) based on polyvinyl alcohol (PVA) and crosslinked polyacrylamide (PAM) were prepared by redox polymerization and further characterized by FTIR, ESEM, and XRD techniques. The semi-IPNs of varying compositions were investigated for their water sorption behavior, and the network parameters like average molecular weight between crosslinks (M_C) and crosslink density were evaluated from water imbibition measurements. The semi-IPNs were also judged for their *in vitro* blood compatibility by blood clot formation and percent hemolysis test. It was noticed that the chemical architecture exert a profound effect on the over all performance of the biomaterials. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2402–2408, 2006

Key words: interpenetrating networks; biocompatibility; swelling

INTRODUCTION

Hydrogels are three-dimensional hydrophilic polymeric networks, which may absorb water from 10 to 20% (an arbitrary lower limit) up to thousands of times their dry weight. Hydrogels may be chemically stable or they may degrade and eventually disintegrate and dissolve. These hydrophilic materials are also coined as "hungry networks" and have been widely employed in variety of applications such as artificial implants,[1] in medicine and pharmacy, agriculture, controlled drug delivery systems,[2] dialysis membranes,[3] burn dressings,[4] etc. To serve as biomaterials the hydrogel must meet certain prerequisites such as adequate water sorption, good mechanical performance, and above all, a fair level of blood compatibility.

The properties of hydrogels may be effectively modified by preparing an interpenetrating polymer networks (IPNs) or semi-IPNs, which are technically defined as a mixture of two or more polymers in which at least one has been polymerized in the immediate presence of other. The IPNs have gained much interest in recent past because of their greatly improved properties in comparison to those of the constituent polymers when present as a blend.

Among various hydrophilic polymers employed in designing IPN materials, the polyvinyl alcohol (PVA) has been a polymer of priority in biotechnical and biomedical communities.[5–7] PVA is used as a basic material for a variety of biomedical applications including contact lens materials,[8] skin replacement materials,[9] reconstruction of vocal cords,[10] artificial cartilage replacement, etc because of their inherent nontoxicity noncarcinogenicity, good biocompatibility, and desirable physical properties such as elastic nature, high degree of swelling in aqueous solution, and good film forming property.[11]

Good deals of efforts have been put into the development of PVA based hydrogels in viewpoint of their water sorption capacity and blood compatibility. For instance, Chandy and Sharma[12] prepared blend membranes of poly(vinyl alcohol) and chitosan and evaluated their blood compatibility and permeability behavior for low molecular weight compounds. Adopting a novel route of hydrogel synthesis, Bajpai and Sani[13] prepared binary blends of polyvinyl alcohol and casein by freezing–thawing method and investigated water sorption and blood compatibility properties. Kim and coworkers[14] prepared interpenetrating network (IPN) hydrogel of polyvinyl alcohol and polyvinyl pyrrolidone and studied their water retention capacity. In another study, Kim and coworkers[15]

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prepared and characterized IPNs of PVA and polymethacrylic acid and studied their water sorption behavior.

Thus, the great potential of PVA based hydrogels in biomedical and pharmaceutical fields has stimulated the authors to prepare and characterize a semi-IPNs of PVA and crosslinked polyacrylamide and examine their water uptake behavior and *in vitro* blood compatibility. The selection of polyacrylamide (PAM) as the other constituent of the semi-IPN lies in its wide acceptance as biomaterial in biomedical community because of its enormous hydrophilicity, nonionic nature, and ease of derivatization into ionic counterparts.

EXPERIMENTAL

Materials

PVA (98% acetalized, molecular weight 14,000 Da) was obtained from Research Lab Chem Industries, Mumbai, India and used without further purification. Acrylamide (AM; Research Lab, Pune, India) was crystallized twice in methanol and dried in vacuum over anhydrous silica for a week. *N*,*N*′ methylene bis acrylamide (MBA; Research Lab, Mumbai, India) was used as a crosslinking agent, potassium persulphate (KPS; Loba Chemie Pvt. Ltd., Delhi, India) as an initiator, and potassium metabisulphite (MBS; Qualigens Fine Chemicals, Mumbai, India) as activator, respectively. Bidistilled water was used throughout the experiments.

Synthesis of IPN

Semi–IPNs were prepared by a redox polymerization method as reported elsewhere.[16] In a typical experiment, into 25 mL of PVA solution (2.0 g) were added 2.0 g of acrylamide, 0.13 m*M* of MBA and 1 mL each of potassium metabisulphite (0.01*M*) and potassium persulphate (0.001*M*). The reaction mixture taken in a rectangular glass pellet (50 mm × 50 mm × 10 mm) was kept at 35°C for a week. The prepared semi-IPNs were purified by equilibrating them in distilled water so as to ensure complete leaching of unreacted chemicals, monomer, and polymers. The purified semi-IPNs were cut into equal sized square pieces, dried at room temperature for a week, and stored in air–tight polyethylene bags.

FTIR analysis

The structural characterization of the semi–IPN was performed by recording FTIR spectra of the end-polymer on a Perkin–Elmer spectrophotometer (Paragon 1000 FTIR).

Environmental scanning electron microscopy (ESEM)

The ESEM of the prepared semi-IPN was recorded on a scanning electron micrograph (STEREO SCAN, 430, Leica ESEM) at Indian Institute of Technology, Pawai, Mumbai (India).

X–ray diffraction study (XRD)

The XRD studies were carried out on Rigaku Rotating anode mode RU–H3R, X–ray powder diffractometer, to ascertain the crystalline nature of the prepared semi–IPNs

Water sorption measurements

Since a biomaterial must exhibit an adequate water sorption property so as to exhibit its resemblance to living tissues, the progress of the water sorption process was monitored gravimetrically.[17] In brief, preweighed pieces of semi-IPNs were placed in a water reservoir and allowed to swell till equilibrium. The swollen pieces were then taken out at different time intervals and gently pressed in between two filter papers to remove excess of water and finally weighed in a sensitive electronic balance (No. APX-203 Denver Instruments, GmbH Germany). The swelling ratio was calculated by the following equation:

$$\text{Swelling Ratio} = \frac{\text{Weight of dry IPNs}}{\text{Weight of swollen IPNs}} \quad (1)$$

Biocompatibility tests

The following methods were adopted for estimating *in vitro* biocompatibility of the prepared semi-IPNs.

Blood clot formation

The antithrombogenic property of the hydrogel surface was evaluated by recording the weights of the clots formed as a result of the surface–blood interaction, as described elsewhere.[18] In a typical experiment, the semi- IPNs were equilibrated with saline water (0–9% w/v NaCl) for 24 h in a constant temperature bath. To these swollen IPNs were added 0.5 mL of acid citrate dextrose (ACD) blood, which was followed by the addition of 0.3 mL of $CaCl_2$ solution (4*M*) to start the thrombus formation. The reaction was stopped by adding 4.0 mL of deionized water and the thrombus formed was separated by soaking in water for 10 min at room temperature and then fixed in 36% formaldehyde solution (2.0 mL) for another 10 min, and after drying, its weight was recorded. The same procedure was adopted for PVA and PVC (blood bag manufac-

tured by Hindustan Latex Limited, Thiruvanthpuram, India), respectively.

Percent hemolysis

Hemolysis assay experiments were performed on the surface of the prepared semi-IPNs as reported in the literature.[19] In brief, semi-IPN films were equilibrated in normal saline water (0.9% w/v NaCl) for 24 h at 37°C and human ACD blood (0.25 mL) was added on the semi-IPN films surfaces. After 20 min, 2.0 mL of 0.9% sodium chloride saline was added to each sample to stop hemolysis and the samples were incubated for 60 min at 37°C. Positive and negative controls were obtained by adding 0.25 mL of human ACD blood and saline solution respectively, to 2.0 mL of bidistilled water. Incubated samples were centrifuged for 45 min, the supernatant was taken, and its absorbance (A) was recorded on a spectrophotometer (Systronics, Model No. 106 India) at 545 nm. The percent of hemolysis was calculated using the following relationship:

$$\% \text{ Hemolysis} = \frac{A_{\text{test sample}} - A_{(-)\text{ control}}}{A_{(+)\text{ control}} - A_{(-)\text{ control}}} \quad (2)$$

Adsorption of proteins (BSA)

Protein adsorption experiments were performed to judge the *in vitro* blood compatibility of the prepared semi–IPNs surface. The experiments were performed using a batch method, as reported in other communications.[20] In brief, preswollen gels were mildly shaken with known concentration of BSA solution and after the adsorption experiment, the concentration of protein was estimated in the supernatant solution by UV spectrometer method. The amount of adsorbed BSA was calculated by the following mass balance equation:

$$\text{Adsorbed BSA} = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where C_0 and C_e being the initial and equilibrium concentration of BSA solution (mg ml^{-1}), V is the volume of protein solution, and m the mass of the swollen semi-IPNs, i.e., the adsorbent.

RESULTS AND DISCUSSION

IR spectra

The IR spectra of native PVA and PAM and prepared semi–IPN are depicted in Figures 1(a)–1(c), respectively. A broad band appeared in the spectra (c) at 3485 cm^{-1} clearly marks the presence of hydrogen bonding and suggest for the hydrophilic nature of the semi-IPN. The spectra (a) and (b) also show the existence of OH and NH_2 groups, at 3439 cm^{-1} and 3424 cm^{-1}, respectively. In addition, the peaks that appeared in the range 3000–2900 cm^{-1} indicate the presence of CH_2 groups in all the three spectra. In the spectra (c), a sharp absorption peak located at 1698 cm^{-1} (C═O stretching) confirms the formation of crosslinked polyacrylamide chains in the semi–IPN.

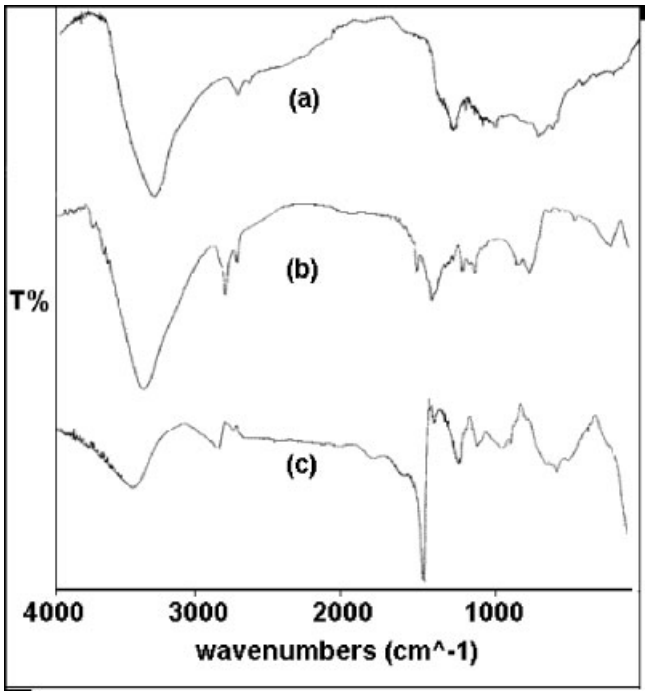

Figure 1 IR spectra of (a) native PVA, (b) native PAM, and (c) PVA-acrylamide semi–IPN.

ESEM analysis

The morphological features of the prepared semi-IPN are depicted in Figure 2. It is clear from the ESEM image that the surface of the hydrogel is heterogeneous with separated domains that suggest the phase separation during the process of semi-IPN formation. The possible cause of phase separation may be that whereas PVA is a linear polymer, the crosslinked PAM may form clusters of crosslinked chains held to one another via hydrogen bondings between the amide functionals.

XRD analysis

Most of the polymers exhibit a semi crystalline morphology, forming mixed regions crystalline and amorphous domains. The XRD technique has been widely utilized to detect crystallinity in polymer blends. To study the crystalline nature of the prepared semi-IPN, the XRD patterns of native PVA, PAM, and semi-IPN were recorded as shown in Figure 3. The XRD pattern

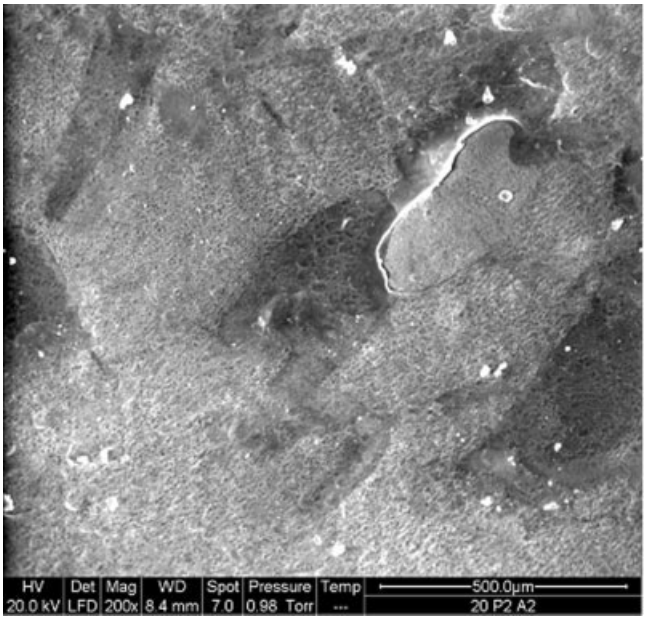

Figure 2 Environmental scanning electron micrographs (ESEM) of semi-IPN.

of semi-IPN indicates their semicrystalline nature. It also shows the interpenetration of crystalline PVA and amorphous PAM polymers and suggest that in the PVA: PAM semi-IPN, as PVA crystallizes the non crystallizable component is rejected from the crystalline region thus resulting in broad amorphous population, which often affects the properties of polymers like glass transition temperature, crystal growth rate, bulk crystallization rate, etc.[21]

Network parameters

An important structural parameter characterizing crosslinked polymer is $M_{C,}$ the average molecular mass between crosslinks directly related to the crosslink density. The magnitude of M_C significantly affects the physical and mechanical properties of crosslinked polymer and its determination has great practical significance. Equilibrium swelling is widely used to determine M_C. Flory and Rehner's early research laid the foundation for analysis of equilibrium swelling.[22] According to the theory of Flory and Rehner, for the perfect network

$$M_c = \frac{-V_1 d_p (V_s^{1/3} - V_s/2)}{\ln(1 - V_s) + V_s + \chi V_s^2} \quad (4)$$

where M_C is the number average molar mass of the chain between crosslinks. V_1 is the molar volume of water (ml mol^{-1}), d_p is the density (g ml^{-1}) of semi-IPN; V_S is the volume fraction of the polymer in the swollen hydrogel, χ is the Flory-Huggins interaction parameter between polymer and solvent (water).

The swelling ratio is approximately equal to $1/V_S$. Here the crosslink density q is defined as the molar fraction of crosslinked units:

$$q = M_o/M_c \quad (5)$$

where M_0 is the molar mass of repeat unit.

The values of V_1 and χ were taken from the literature.[23] The density of the IPN, d_P,was determined to be 1.12 g cm^{-3}. The values of M_C and q have been calculated for different semi-IPN compositions and summarized in Table I.

Swelling study

The swelling behavior of a material significantly contributes to determine its fate as a biomaterial and, therefore, has to be investigated as a function of the chemical architecture of the IPNs.

Effect of PVA

The effect of the PVA content in the semi-IPN on their swelling behavior has been investigated by varying the concentration of PVA in the feed mixture in the range of 1.0–4.0 g. The results are shown in Figure 4, which reveal that the swelling ratio constantly decreases with increasing concentration of PVA in the feed mixture of the IPN and eventually it attains a minimum value when the hydrogel purely contains

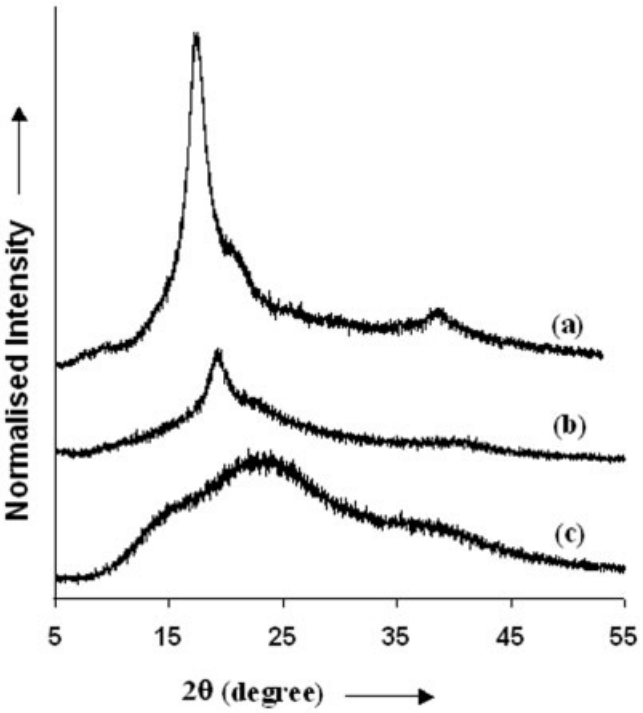

Figure 3 XRD spectra of (a) native PVA, (b) PVA-acrylamide semi–IPN, and (c) native PAM.

TABLE I
Network Parameters of the Semi-IPNs of Different Compositions

Sample	PVA (g)	AM (g)	MBA (m*M*)	SR	M_C	$q \times 10^{-4}$
1	1	2	0.13	5.9	7106	100
2	2	2	0.13	4.5	3894	183
3	3	2	0.13	4.31	3568	199
4	4	2	0.13	3.35	2040	348
5	2	1	0.13	4.12	3226	220
6	2	2	0.13	4.5	3894	183
7	2	3	0.13	5.07	5070	140
8	2	4	0.13	4.35	3625	196
9	2	2	0.065	3.09	1727	412
10	2	2	0.13	4.5	3894	183
11	2	2	0.26	4.8	4531	157
12	2	2	0.39	5.23	5408	131
13	2	2	0.52	5.26	5588	127
14	2	2	0.65	5.1	5226	136

only PVA. The results may be explained by the fact that with increase in PVA content in the semi-IPN, the volume fraction of polymer increases, which results in a decrease in water imbibition capacity. This is because the water molecules will have to travel a longer distance through the semi-IPN to swell them.

Another cause for the observed fall in the swelling ratio could be that with increasing PVA content in the semi-IPN, the number of hydroxyl and methylene groups increase, which consequently enhances the hydrogen bonding and hydrophobic interactions within the hydrogel. This obviously leads to a lower water sorption by the semi-IPN. Similar type of lower water sorption with increasing content of PVA has also been reported.[24]

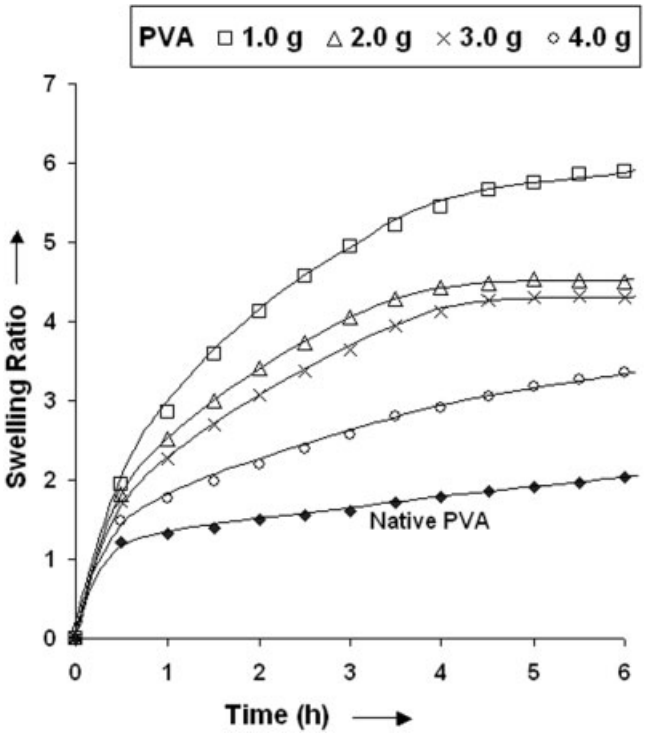

Figure 4 Influence of PVA on the swelling ratio of the semi–IPNs for a definite concentration of [AM] = 2.0 g and [MBA] = 0.13 m*M*.

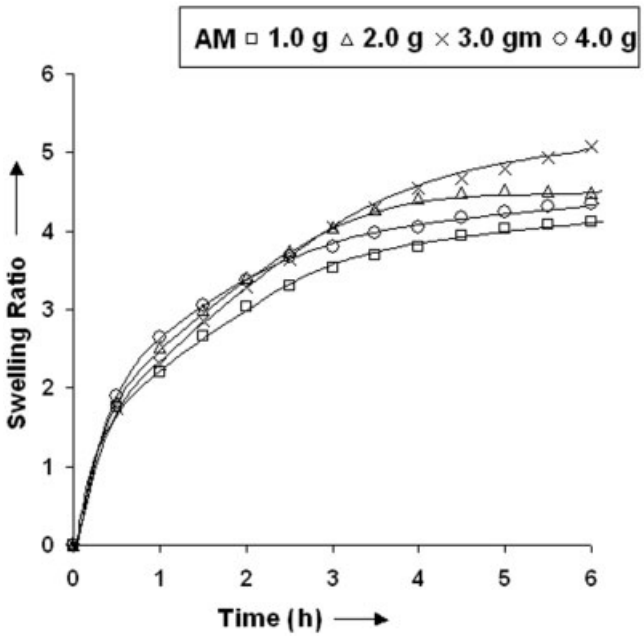

Figure 5 Effect of AM on the swelling ratio of the semi–IPNs for a definite concentration of [PVA] = 2.0 g and [MBA] = 0.13 m*M*.

Effect of PAM

Polyacrylamide being a hydrophilic polymer is known to exert a pronounced influence on the swelling ratio of the semi-IPN. In the present study, the effect of polyacrylamide content on the water sorption capacity of the semi-IPN has been investigated by varying the concentration of AM in the range 1.0–4.0 g for definite concentrations of PVA and MBA. The results are depicted in Figure 5, which reveal that the equilibrium swelling ratio increases up to 3.0 g of AM content in the semi-IPN and then decreases beyond this composition. The reason for the observed increase is quite apparent as PAM is a hydrophilic polymer and has a distinct water associating property. Obviously, its increasing proportion in the semi-IPN composition will result in a greater swelling of the semi-IPN. However, beyond a certain concentration of AM, the network density may increase to the extent that less number of penetrant water molecules enter the semi-IPN and thus cause a lower degree of swelling. The formation of intermolecular hydrogen bounding between PAM chains cause the increase of network density.

Effect of crosslinker (MBA)

Hydrogels possess an additional benefit over other polymeric systems that a minor change in the concen-

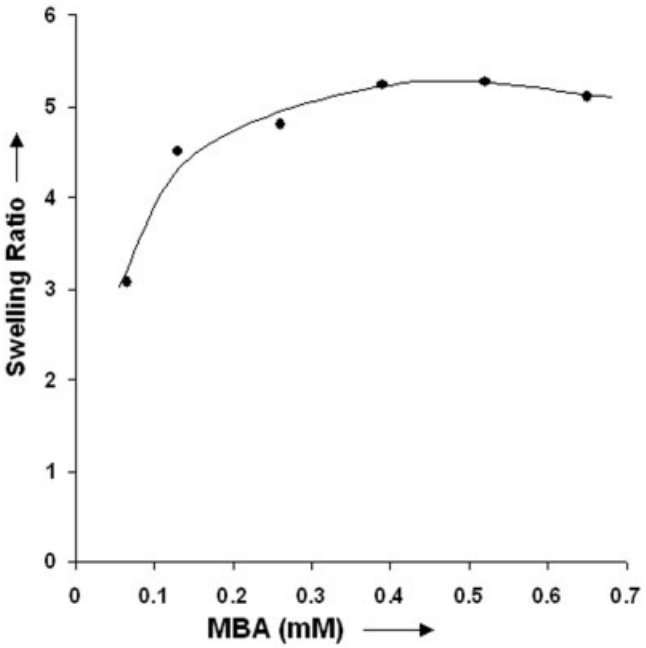

Figure 6 Effect of MBA on the swelling ratio of the semi–IPNs for a definite concentration of [PVA] = 2.0 g and [AM] = 2.0 g.

tration of its constituents brings about a major change in its overall water sorption and related properties. One of the effective ways to cause a dramatic change in swelling ratio of a hydrogel is to employ varying concentrations of crosslinking agent. In the present investigation also, the effect of crosslinking agent on the equilibrium swelling ratio of the semi-IPN has been studied by varying the concentration of MBA in the range of 0.065–0.65 m*M* in the feed mixture of the semi-IPN. The results are shown in Figure 6, which surprisingly reveal that the swelling ratio increases with increasing crosslinker content in the semi-IPN. The results are quite unusual and may be explained as below:

N,*N*′-methylene bis acrylamide is a bifunctional monomer with hydrophilic amide and hydrophobic —CH_2 groups. When the concentration of MBA is increased in the feed composition of the semi-IPN, greater numbers of acrylamide molecules are crosslinked to one another via MBA molecules, thus enhancing hydrophlicity, hydrophobicity and extent of crosslinking in the polymer network. Now in the studied concentration range the hydrophilicity may likely to dominate the hydrophobicity and increased crosslinking effect. The semi-IPN eventually becomes more hydrophilic and thus the swelling ratio increases. It is also clear from the Figure 6, that in the higher concentration range of crosslinker the swelling ratio increases marginally, which suggests that with larger concentration of MBA the hydrophobicity and crosslink density may play a dominating role and may result in a decrease in water sorption capacity.

Blood compatibility

A biomaterial contacting flowing blood often results in a complex interaction at the interface developing a thrombogenicity in the material in the form of a blood clot appearing on the surface.[25] The clot formation is a complex phenomenon and involves many processes like structuring of water molecules on the biomaterials surface, adsorption of plasma proteins, adhesion of platelets, hemolysis, etc.[26] Among various factors influencing blood compatibility, the chemical nature and composition of the materials surface is a significant in determining the ultimate properties of the material. The effect of chemical composition of the gel on the *in vitro* blood compatibility parameters has been investigated (Table II) as discussed below.

Effect of PVA

When the concentration of PVA is varied from 1.0 to 4.0 g, the amount of blood clot and % hemolysis is

TABLE II
Blood Compatibility Parameters of the Semi-IPNs of Different Compositions

Sample	PVA (g)	AM (g)	MBA (m*M*)	Blood clot (mg)	Hemolysis (%)	Protein adsorption (mg g^{-1})
1	1	2	0.13	5	40.0	8.699
2	2	2	0.13	8	47.6	6.26
3	4	2	0.13	18	52.2	3.804
4	2	1	0.13	9	60.0	6.598
5	2	2	0.13	8	47.6	6.26
6	2	4	0.13	10	45.8	3.401
7	2	6	0.13	10	41.1	2.315
8	2	2	0.065	6	44.8	5.070
9	2	2	0.13	8	47.6	6.26
10	2	2	0.26	11	49.1	5.13
11	2	2	0.65	10	49.8	5.23
12		PVA		5	33.6	7.18
13		PVC		21	47.35	30.42

found to increase with increasing PVA content of the semi-IPN, while a fall is noticed in the protein adsorption. The observed results may be attributed to the fact that increasing PVA in the semi-IPN produces greater hydrophilicity in the material, which causes less adsorption of protein (BSA). It is also recognized that a preferential adsorption of albumin onto a surface prevents fibrinogen, the major blood clotting protein, to get adsorbed onto the surface and, thus, avoid the possibility of clot formation. Obviously, a decreasing adsorption of BSA may favor clot formation and hemolysis and, therefore, the surface may show thrombogenicity.

Effect of PAM

On increasing the concentration of AM in the range 1.0–6.0 g in the feed mixture of the semi-IPN, the amount of protein adsorption and percent hemolysis decreases whereas the weight of blood clot slightly increases. The observed increase in weight of blood clot may be attributed to the decreasing adsorption of BSA, which consequently favors clot formation. Another reason could be that with increasing number of amide groups on the hydrogel's surface, the interaction between the amide group and blood components may result in the formation of blood–clot. The possible reason for the observed decrease in percent hemolysis may be that with increasing AM content in semi-IPN less adsorption of protein imparts blood compatibility to the surface which eventually results in lower degree of percent hemolysis.

Effect of crosslinker (MBA)

When the amount of crosslinker is varied in the range 0.065–0.65 m*M* in the feed mixture, both the weight of blood clot and percent hemolysis are found to increase, while the protein adsorption is not affected significantly. The reason for the observed increasing thrombogeneity may be attributed to the fact that a greaterly crosslinked gel offers more interaction with blood component and, therefore, thrombogenic property increases.

CONCLUSIONS

Macromolecular matrices with interpenetrating polymer network structures may be prepared by polymerizing acrylamide in the presence of PVA and a crosslinking agent (MBA). The prepared semi-IPN contains crosslinked PAM chains held to PVA macromolecules via hydrogen bounding thus forming separate clusters of the two polymers as confirmed by FTIR and ESEM techniques. The semi-IPN also shows semicrystalline nature as evident from XRD analysis.

The semi-IPN exhibits varying water sorption property with changing chemical architecture of the matrix. Increasing amount of PVA content results in a decreasing swelling ratio, while in case of PAM, the swelling ratio initially increases with increasing PAM content in the semi-IPN and decreases beyond a definite amount. The semi-IPN surprisingly shows an increasing water imbibition property with increasing crosslinker content.

The blood compatibility of the semi-IPNs evaluated by *in vitro* methods is also found to depend upon the chemical composition of the material. Whereas the hydrogel is found to offer more blood compatibility with increasing richness in PVA and AM content, the semi-IPN shows decreasing antithrombogenity with increasing crosslinker content of the matrix.

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