Designing Polyaniline (PANI) and Polyvinyl Alcohol (PVA) Based Electrically Conductive Nanocomposites: Preparation, Characterization and Blood Compatible Study

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Novel electrically conducting and biocompatible composite hydrogel materials comprising of poly (aniline) (PANI) nanoparticles dispersed in a poly (vinyl alcohol) (PVA) – g–poly (acrylic acid) (PAA) matrix were prepared by *in situ* polymerization of aniline. The prepared ionic hydrogels were evaluated for their water uptake capacity in distilled water. While structural insights into the synthesized polymer was sought by Fourier Transform Infrared (FTIR) spectroscopy and X–Ray Diffraction (XRD) techniques, morphology and dimension of PANI particles embedded into the colored optically semi–transparent polymer films were evaluated by Scanning Electron Microscopy (SEM) analysis and Transmittance Electron Microscopy (TEM) while thermal behavior of composite hydrogel was investigated by Differential Scanning Calorimetry (DSC). Electrical conductivity of composite hydrogels containing different PANI percentage was determined by LCR. Considering the potential of electrically conductive nanocomposites materials in biomedical applications the *in vitro* blood compatibility of nanocomposites was investigated by employing several *in vitro* tests.

Keywords: Graft polymer, hydrogel composite, biocompatibility, characterization

1 Introduction

The composite materials have introduced conducting polymers to practical applications in different fields such as sensor and biosensor materials (1), actuators and electromechanical devices (2), biomedical implant materials (3), electronic and optical materials (4), etc. Although a variety of PANI based conducting composites have been synthesized and investigated due to their best combination of stability, conductivity and low cost. However, the desired choice of the best method to produce homogeneous composites with specific characteristics remains an unsolved problem. Stimuli-responsive polymers constitute a versatile class of materials finding a wide spectrum of applications in biomedical, pharmaceutical, and industrial fields (5). These polymers can change their volume significantly in response to small alterations of certain environmental parameters. Thus, the development of manifold stimuli-sensitive hydrogels with sensitivities across temperature (6), electrical field (7), light (8), pH, solvent composition and specific ions (9) have opened up a new dimension of diversified technical applications (10).

Synthetic methods to produce PANI based composite include dispersion polymerization of aniline in the presence of a matrix polymer in a disperse or continuous phase of a dispersion (11). Free radical initiated *in situ* polymerization of aniline in a matrix or in a solution with a matrix polymer (12), electrochemical polymerization of aniline in a matrix (13) and polymer grafting to PANI surface (14) are some alternate routes to design PANI containing nanocomposites. Although these methods are frequently in use, they do, however lack in simplicity and efficiency. (PANI) is an electrically conducting polymer (ECP) having a spatially extended π bonding system, which accounts for their intrinsic semi-conducting nature. Polyaniline is the one of the most promising conducting polymers due to a good combination of properties, stability, price and ease of synthesis by different routes and uncountable application (15). PANI is difficult to process because it is soluble only in a limited number of organic solvents (16). Thus, in the present study, highly swelling grafted hydrogel composed of poly(acrylic acid) and polyvinyl alcohol containing PANI nanoparticles have been prepared by *"in situ"* polymerization of aniline (17). The study mainly focuses on the synthesis and characterization of conducting nanocomposites

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and study of their swelling behavior, biocompatibility, and microhardness.

2 Experimental

2.1 Materials

Polyvinyl alcohol (PVA) (98.6% hydrolyzed) was obtained from the Research Lab, Mumbai, India and used as received. Acrylic acid (AA) was purchased from Merck Limited (Mumbai, India) and purified by vacuum distillation at 55°C. Other chemicals such as aniline (AN), hydrochloric acid, potassium per sulphate (KPS), ammonium persulphate (APS), N, N′–methylene bis acrylamide (MBA) were also of analytical grade and used without any further purification.

2.2 Methods

2.2.1. *Preparation of gel*

A polymer matrix composed of PVA–g–PAA and crosslinked by MBA was prepared following a method reported in the literature (18).

2.2.2. *PANI-impregnation*

The required quantity of AN (10.74 mM) was dissolved in 0.5 N HCl (50 mL) and the gel prepared as above was allowed to soak in the AN solution for 24 h. The aniline (AN) containing swollen gel was dried and then again left in a 0.3M APS bath to soak the required quantity of APS in solution (0.5 N HCl). As soon as the gel swells in APS solution, the entrapped APS initiates polymerization of AN. As the polymerization proceeds, the semi–transparent gel turns black. The PANI impregnated gel is repeatedly washed with distilled water and allowed to dry at 30 ± 0.2°C for 72 h.

The percentage impregnation of PANI into the gel was calculated by using the equation:

$$\% \text{ Impregnatin of PANI} = \left(\frac{W_{PANI} - W_{Dry}}{W_{Dry}} \right) \times 100 \quad (1)$$

Where, W_{PANI} is weight of the dry PANI impregnated gel and W_{Dry} is the initial weight of polymer gel.

2.3 Characterization

2.3.1. *Fourier transforms infrared (FTIR) spectra*

The FTIR spectra of PANI powder, polymer hydrogel and PANI–Impregnated matrix were recorded on a FTIR spectrophotometer (FTIR–8400S, Shimadzu).

2.3.2. *X–Ray diffraction (XRD) analysis*

In order to investigate the crystalline nature of the prepared native and PANI–impregnated gels, the X–ray diffraction

spectra were recorded using a Philips (Holland) automated X–ray powder diffractometer. The dried gels were placed on the glass slide specimen holder and exposed to X–rays in a vertical goniometer assembly. The scan was taken between 10 to 90° with a scanning speed of 2.4° min^{-1}. The operating target voltage was 35 kV, tube current was 20 mA and radiation used were FeKα ($\lambda = 0.193$ nm).

The crystallinity CrI, is calculated from the relation:

$$\text{CrI} = 1 - t \times \frac{\text{AmW}}{\text{CrH}} \quad (2)$$

Where, t is the scale factor relating the height of CrH to full scale (total blackness). The relationship between crystallite size (CS) and diffracted X-ray line broadening is given by Scherrer (19) as

$$\text{CS} = \frac{K \lambda}{\beta \cos \phi} \quad (3)$$

Where λ is the wave length of X-rays, β is the pure diffraction broadening (in radians), ϕ is the Bragg's angle, and K is a constant depending upon the crystalline shape, usually taken as unity.

2.3.3. *Microscopic analysis*

The scanning microscopic analysis (SEM) and transmission electron microscopy (TEM) analysis of native and PANI impregnated films were performed on a scanning electron microscope (LEO 435 VP Variable Pressure Scanning Electron Microscope) and transmittance electron microscope (TEM Morgagni 268 D, Fei Company, The Netherlands), respectively.

2.3.4. *Thermal analysis*

Differential scanning calorimetry (DSC) measurements were carried out on a TA instruments Inc DSC-2920 with nitrogen as purging gas at the purge rate 50 ± 5 mL/min. The experiments were performed from room temperature to 400°C at a heating rate 10°C/min.

2.3.5. *Electrical conductivity*

The electrical conductivity of prepared gels was measured by Four prob LCR meter (Masstech Digital M/M No. MAS 830L) as detailed in the literature (17).

2.3.6. *Swelling measurements*

In order to evaluate water uptake potential of native and impregnated gel, a gravimetric procedure was followed (20). The degree of water sorption was calculated by the following:

$$\text{Swelling Ratio} = \frac{W_{Swollen}}{W_{Dry}} \quad (4)$$

Where, $W_{Swollen}$ = Weight of swollen gel, and W_{Dry} = Weight of dry gel.

2.3.7. *Blood compatibility tests*

Blood compatibility of native and impregnated hydrogels was evaluated by performing *in vitro* test like thrombus formation and haemolysis assays as reported elsewhere (21–22).

2.3.8. *Mechanical property analysis*

Shore D (Durometer) was used to measure microhardness of native gel and PANI impregnated gel with varying PANI contents.

2.3.9. *Reproducibility of data*

All measurements were carried out at least three time and the average value was utilized for presentation of results. It was found that the experimental errors had never been greater than 3%.

3 Results and Discussion

3.1 Characterization of Gels

3.1.1. *FTIR spectra*

Figures 1(a) and (b) represent the FTIR spectra of PANI powder and PANI impregnated PVA–g–PAA gel film. The characteristic peaks appeared in Figure 1(a) at 824, 1144 and 1312, 1505, and 1590 cm^{-1} indicate aromatic C–H, aromatic amide, and aromatic C–C stretching vibrations, respectively. The spectra (b) of PANI impregnated PVA–g–PAA gel film contain peaks at 876, 1150, 1347, 1500 and 1614 cm^{-1} indicating the presence of aromatic C–H, aromatic amide, and aromatic C–C stretching vibrations which confirm the impregnation of PANI into the gel (polymer matrix).

3.1.2. *X-ray diffraction analysis*

The XRD patterns of the prepared native and PANI–impregnated gels are shown in Figure 2(a) and (b), respectively. Figure 2(a) shows a prominent peak near 20° which corresponds to the (101) plane of the PVA crystal.
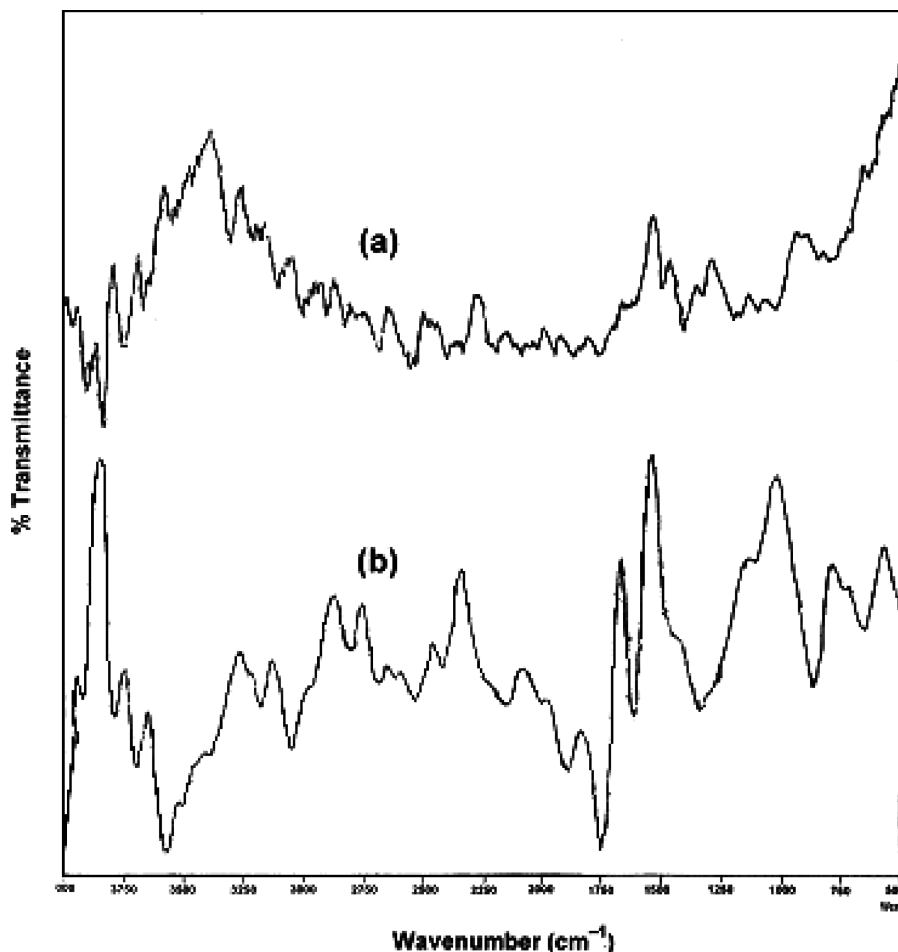

Fig. 1. FTIR spectra of (a) PANI powder and (b) PVA–g–PAA impregnated PANI gel.
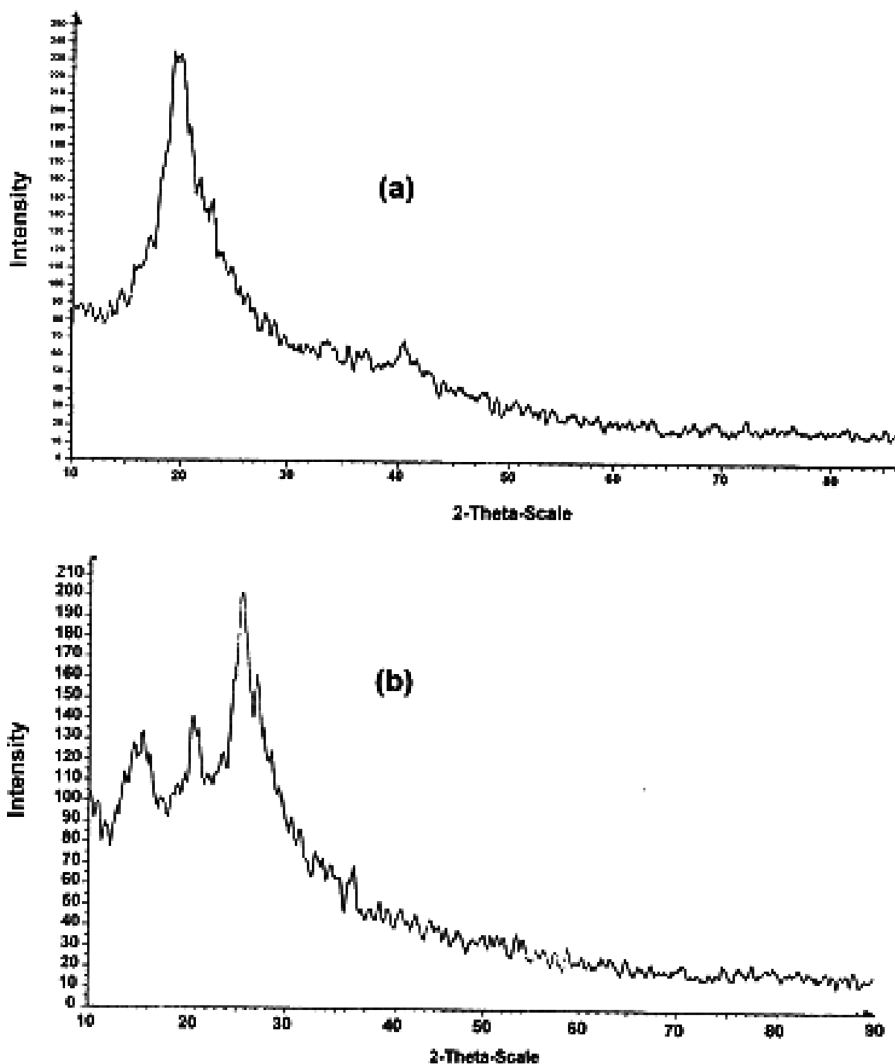
Fig. 2. XRD–spectra of (a) Native (PVA–g–PAA) and (b) PANI–impregnated gel.

Other minor peaks around 21 and 22° could be attributed to minor crystallites of grafted polyacrylic acid chains. The diffraction patterns of PANI–impregnated gel are shown in Figure 2(b) which not only show a characteristic peak at 20° (due to PVA) but also depicts a prominent peak at 25°, indicative of a characteristic peak of PANI. Thus, the XRD–patterns of impregnated gel provide an additional evidence of PANI formation within the polymer matrix.

The calculated average crystallinity and particle sizes of native and PANI impregnated hydrogels are found to be 0.90, 0.72 and 502,115 Å, respectively. The loss in crystallinity due to PANI impregnation may be explained by the fact that because of *in situ* polymerization of aniline within the matrix, the PANI chains produced due to polymerization may bring disorder in the chains packing and, consequently, may result in a loss of crystallinity.

3.1.3. *SEM*

The morphological features of the prepared native and PANI–impregnated composite films have been studied by recording SEM images of the films as shown in Figure 3(a) and (b), respectively. It is clear from the image (a) that the surface of the native gel is quite homogeneous and shows no cracks, voids or unevenness. This suggests that after grafting of polyacrylic acid chains onto PVA backbone, the matrix remains homogeneous in composition. However, impregnation of PANI into the matrix develops heterogeneity in the matrix is evident from the SEM image (b). It is clear from the image (b) that impregnated PANI molecules form cluster like morphology varying in the sizes from 0.5 to 2 μm. The formation of PANI clusters within the polymer matrix could be attributed to hydrophobic nature of the PANI molecules which may aggregate due to hydrophobic dispersion forces.

Table 1. Effect of varying concentration of constituents of the gel on swelling ratio

	SR (Distilled Water)	Other ingredients
[PVA] (g)		AA – 29.1 mM
1	1.49	MBA – 13.0×10^{-2} mM
1.5	1.49	KPS – 7.39×10^{-2} mM
2	1.42	APS – 0.3M in 0.5N HCl
3	1.42	AN – 10.74 mM in 0.5N HCl
[AA] (mM)		
		PVA – 1 g
14.6	2.07	MBA – 13.0×10^{-2} mM
29.1	1.84	KPS – 7.39×10^{-2} mM
36.0	2.32	APS – 0.3 M in 0.5N HCl
43.7	2.42	AN – 10.74 mM in 0.5N HCl
[MBA] (mM)		
		PVA – 1 g
6.5×10^{-2}	1.61	AA – 43.7 mM
13.0×10^{-2}	1.67	KPS – 7.39×10^{-2} mM
19.45×10^{-2}	2.47	APS – 0.3 M in 0.5N HCl
25.9×10^{-2}	1.60	AN – 10.74 mM in 0.5N HCl
[KPS] (mM)		
		PVA – 1 g
3.69×10^{-2}	1.92	AA – 43.7 mM
7.39×10^{-2}	2.23	MBA – 19.45×10^{-2} mM
11.10×10^{-2}	2.06	APS – 0.3 M in 0.5N HCl
14.80×10^{-2}	1.82	AN – 10.74 mM in 0.5N HCl
[AN] (mM)		
		PVA – 1 g
5.3	1.43	AA – 43.7 mM
10.74	2.45	MBA – 19.45×10^{-2} mM
16.11	2.15	KPS – 11.10×10^{-2} mM
21.48	2.63	APS – 0.3 M in 0.5N HCl
[APS] (M)		
		PVA – 1 g
0.2	3.08	AA – 43.7 mM
0.3	2.84	MBA – 19.45×10^{-2} mM
0.4	3.21	KPS – 11.10×10^{-2} mM
0.5	3.41	AN – 21.48 mM in 0.5N HCl

3.1.4. *TEM*

In order to investigate the size and morphology of the prepared PANI nanoparticles, transmission electron micrograph (TEM) images were recorded as shown in Figure 3(c) and (d), respectively which represent the images of nanoparticles clusters and single nanoparticles. It is clear from the image (c) that the clusters formed have a dimension up to 2 μm, while individual nanoparticles vary in their sizes in the range of 5 to 10 nm. The results obtained from TEM study are consistent to SEM investigations and, thus, confirm the nanocomposite nature of the material.

3.1.5. *Differential scanning calorimetry (DSC)*

In order to gain insight into the thermal properties of the native and PANI impregnated hydrogels, the DSC thermograms were recorded and, as shown in Figure 4(a) and (b), both the thermogram (a) and (b) show a "semi-crystalline" nature of the gel, but the prepared impregnated hydrogel, (b), is less crystalline in nature with respect to native gel (a), which is also confirmed by XRD studies as explained earlier.

The glass transition temperatures (Tg) appears at 47.54°C in the PVA-g-PAA hydrogel i.e., native gel Figure 4(a) is slightly above the pure Tgs of PAA which are 41°C. The observed increase in Tg implies a crosslinked nature of the vinyl polymers.

The glass transition temperatures(Tg) of PANI impregnated hydrogel appears at 49.66°C. This isuggests that the impregnation of PANI particles in the PVA-g-PAA hydrogel matrix should bring about a little enhancement in the glass transition temperatures (Tg) of the prepared gel.

The observed enhancement in Tg implies the impregnation of PANI particles into the native gel as far as Tg of PANI is concerned, it might have been suppressed because of strong prevailing interactions between various copolymeric segments within the hydrogel matrix. This suggests a marginal influence of Tg of PANI on the thermal properties of the hydrogel.

3.1.6. *Electrical conductivity and effects of PANI*

In order to investigate the effect of content of PANI impregnation in electrical conductivity, the four different PANI contents gel, i.e., 0%, 5%, 10%, and 30% PANI impregnated composites were selected and these samples were prepared by two methods. Firstly, variation of aniline and keeping all the other ingredients constant, and secondly, variation of APS, and keeping all the other ingredients constant.

The plot of room temperature d.c. conductivity vs. wt% of PANI content prepared by both method in hydrogel composites are shown in Figure 5(a) and (b). It is quite interesting to note that although PANI is a conjugated polymer and more responsible for conductivity, the conductivity values of approximately 5% PANI contents hydrogel composite in both the method, are significantly higher than the other higher percentage PANI content hydrogel composite.

The mechanism of electrical conductivity in conducting polymers has been reported in the literature that the dc conductivity of conducting polymers depends on their morphology and certain other factors such as type of monomer, doping level, degree of crystallinity etc. It has been reported that the large increase in conductivity originates from the fact that doped (protonated) polyaniline is a polyelectrolyte, i.e., a macromolecule bearing a large number of ionizable groups .It is also reported that upon reaction with the vapors of the appropriate substance, its molecular
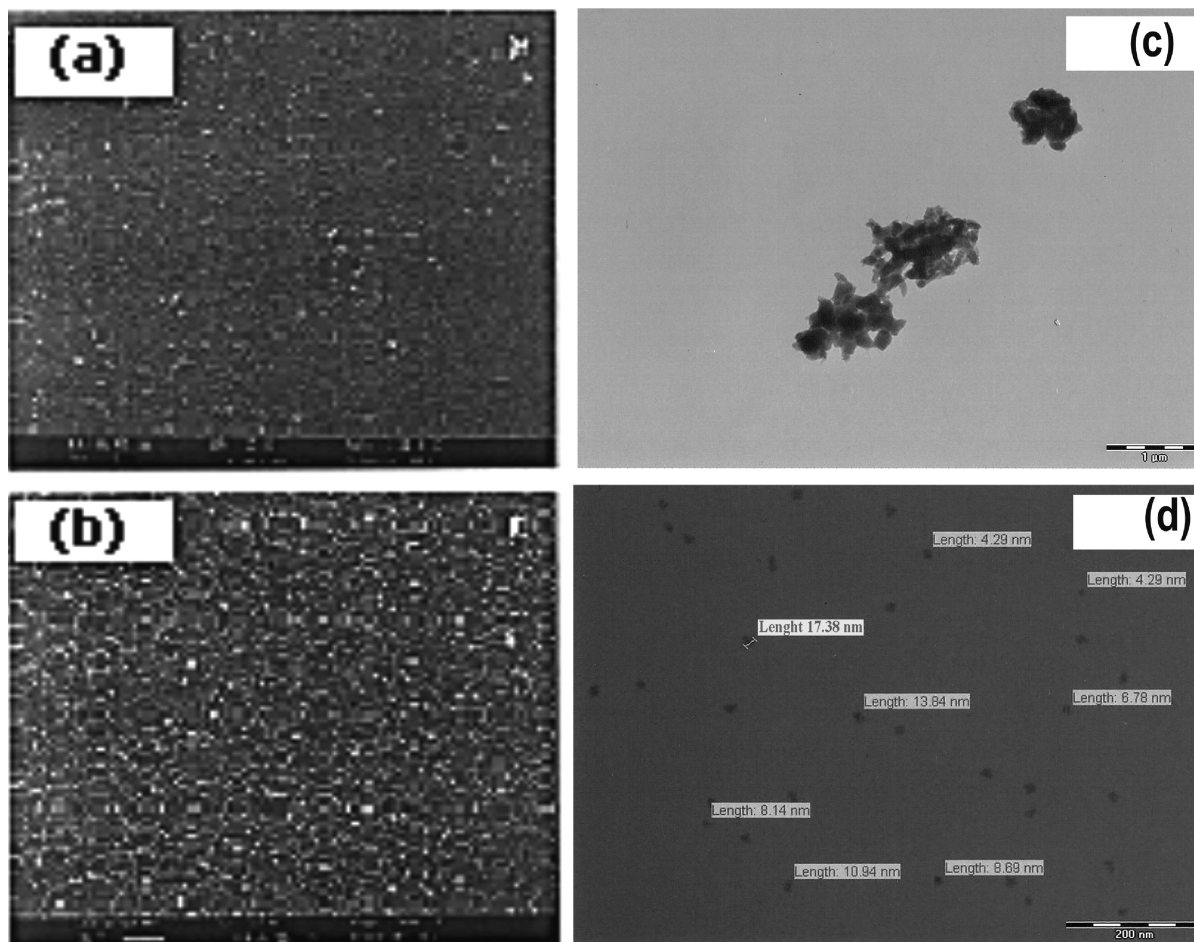
Fig. 3. SEM images of (a) Native (PVA–g–PAA) gel and (b) Impregnated gel and TEM image of PANI particles cluster (c) and particle distribution (d).

conformation changes from compact coil structure to an expanded coil-like structure. The attainment of expanded molecular conformation acts to reduce π -conjugation defects in the polymer backbone and the opening up of coil tends to promote linear conformation necessary for crystallization. Thus, an increase in the crystallinity of the polymer occurs with enhancement of the intermolecular component of the bulk conductivity.

In the present composite system, it is noticed that in the approximate 5% PANI content, the polymer composite causes strong interfacial interactions between PANI and PVA-g-PAA hydrogel, thereby changing the molecular conformation of PANI from compact coil structure to an expanded coil-like structure. As a consequence, there may be an enhancement in the conductivity of composite with approximately 5% PANI content. Further, higher volume fractions of PANI may bring about disorder in the chains packing and the matrix develops heterogeneity in the matrix, therefore, it may result in a loss of crystallinity as suggested by the XRD and SEM studies.

Here, it may also be noted that the host matrix, i.e., PVA-g-PAA is highly hydrophilic in nature, which includes PAA as an ionic polymer, whereas PANI is hydrophobic in nature. Therefore, approximately 5% PANI impregnated composite hydrogel not only provides a suitable packed crystalline structure which maintains inter ionic distance to facilitate compact coil structure to an expanded coil-like structure of PANI, but also a suitable moisture content to facilitate ionic carrier as well.

3.2 Swelling Study and Effect of Ingredients

The swelling behavior of the native and impregnated hydrogels with varying ingredients has been measured in distilled water. The results are summarized in Table 1 and may be explained as below.

When the amount of PVA increases in the range from 1.0 to 3.0 g, the swelling ratio decreases which may be attributed to the fact that with an increase in polymer fraction in the hydrogel, the number of network chains increased in unit volume of the gel. This restrains both the inclusion of water molecules into the gel and subsequent relaxation of polymer chains. This obviously decreases the swelling
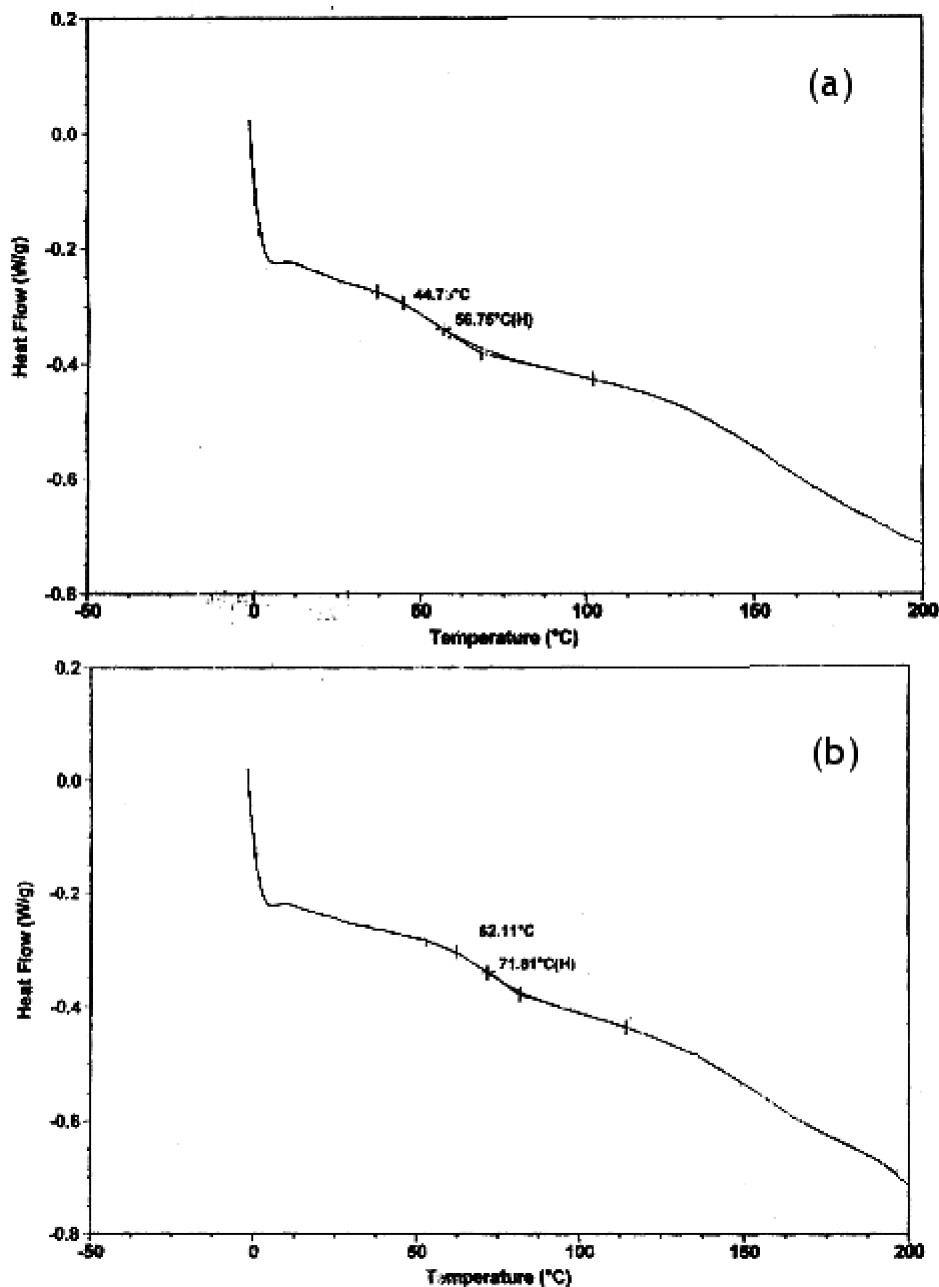
Fig. 4. DSC thermograms of (a) Native (PVA–g–PAA) gel and, (b) PANI–impregnated gel.

capacity of the gel. The influence of ionic monomer, acrylic acid, on the swelling ratio of the gel has been investigated by varying its concentration in the range 14.6 to 43.7 mM. The results show that the swelling ratio constantly increases with increasing polyacrylic acid content in the gel. The observed increase may be explained by the reason that with an increase in the concentration of acrylic acid, the number of carboxylic groups present along the polymer chain also increases which is due to enhanced repulsion results in a greater mobility of gel segments. This, in turn, brings about a rise in the swelling ratio.

When the concentration of crosslinking agent (MBA) increases in the range 6.5 to $19.45 \times 10{-}2$ mM, the swelling ratio increases, while beyond $19.45 \times 10{-}2$ mM the swelling ratio decreases up to $25.9 \times 10{-}2$ mM. The results may be explained by the fact that since MBA is a bifunctional monomer, its increasing amount in the gel caused an increase in water sorption capacity, while beyond a certain concentration, the chain density increases which results in a fall in the water sorption capacity.

The effect of PANI content in the hydrogel on its swelling ratio has been studied by increasing the concentration of
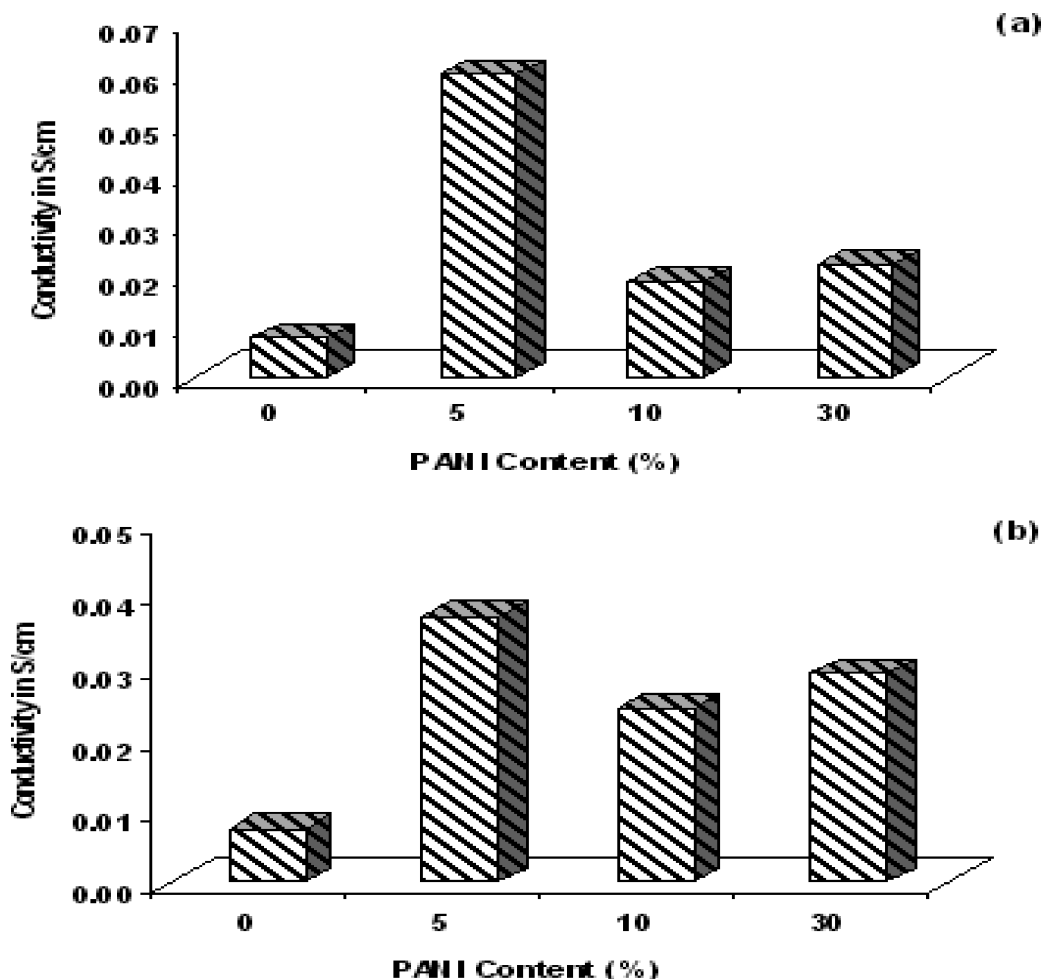
Fig. 5. Electrical conductivity of polymer composite (a) Obtained by AN Variation (b) Obtained by APS Variation.

AN in the range 5.3 to 21.48 mM. The results indicate that the swelling ratio increases with increasing concentration of AN. The observed increase in the swelling ratio may be explained by the fact that due to the ionic nature of PANI macromolecules, its increasing amount in the hydrogel results in greater ionic repulsion among the network chains. This causes network chains to expand and accommodate more water, thus increasing the swelling ratio of the hydrogel.

3.3 Evaluation of Biocompatibility

In the present study, the assessments of biocompatibility were made on the basis of two *in vitro* tests, viz thrombus formation, and haemolysis assay. The tests were carried out for native and impregnated gels and the results are presented in Table 2. The results indicate that the impregnation of PANI into the hydrogel increased the blood clot formation marginally, whereas % haemolysis decreased. This may be attributed to the reason that impregnation of PANI into the hydrogel produces a rough surface due to disorder of the molecular structure which causes greater clot formation

specially the π bonding system contained and the PANI particles produces an atmosphere to uptake a higher saline solution and reduce the haemolysis.

3.4 Microhardness Measurement

The impregnation of PANI particles within the polymer matrix is expected to enhance the microhardness values

Table 2. Data showing various in vitro blood compatibility parameters and swelling ratio in saline solution

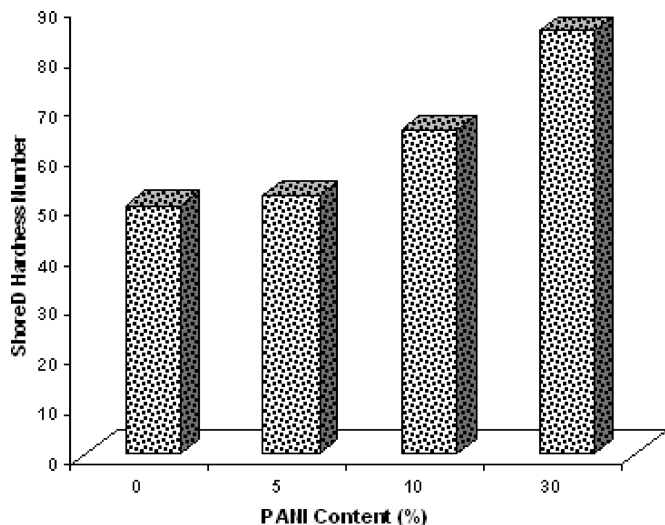| Type of gel	Blood clot (g)	% Haemolysis	Swelling Ratio in Saline solution
Native	0.004	24.9	2.71
5% PANI impregnated	0.0107	36.1	3.38
10% PANI impregnated	0.0082	23.3	1.96
15% PANI impregnated	0.0084	34.2	1.83
30% PANI impregnated	0.0053	21.2	2.30
Glass Surface	0.0352	***	***
PVC (Blood bag)	0.0182	***	***

Fig. 6. Effect of PANI content on Shore D hardness number.

and therefore, has been studied by varying the PANI content in the range 0% to 30% while keeping the other ingredients constant. The results shown in Figure 6 clearly reveal that the hardness of the PANI impregnated polymer matrix increases, with increasing PANI content. The observed increase in microhardness with increasing PANI content may be attributed to the reason that due to the hydrophobic nature of PANI, the chains of aniline rings are quite rigid and, therefore, the PANI impregnated composites will show greater microhardness.

4 Conclusions

Impregnation of polyaniline into poly(vinyl alcohol)–g–poly(acrylic acid) results in a composite hydrogel which shows fair electroconductive and electroactive behaviors. The FTIR spectra of PANI impregnation hydrogel shows characteristic peaks of polyaniline and other functional groups of constituent polymers, i.e., PVA and PAA. The impregnation of PANI into polymer matrix is further confirmed by the XRD analysis, and this impregnation brings about a loss in crystallinity as confirmed by the XRD spectra and DSC thermogram of the native and PANI–impregnated gels. The hydrogel composite shows cluster like morphology varying in size between 0.5 to 2.0 μm. The polyaniline (PANI) particles undergo aggregation and show a wide variation in their sizes ranging from 1 to 100 μm.

The electrical conductivity also varies with varying PANI contents in the composite. The conductivity increases with increasing PANI impregnation, while a drop in conductivity is observed if impregnation is increased up to 10% PANI content. Thereafter, conductivity increased constantly if impregnation is increased further. The native and PANI impregnated matrix not only shows a fair biocompatibility but good swelling properties in both distilled water and electrolyte solution. The contents of PANI in composite hydrogel also show good mechanical strength in increasing order and increased biocompatibility as well.

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