

Preparation and characterization of electrically conductive composites of poly(vinyl alcohol)-g-poly(acrylic acid) hydrogels impregnated with polyaniline (PANI)

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Abstract. Novel electrically conducting composite materials consisting of poly(aniline) (PANI) nanoparticles dispersed in a poly(vinyl alcohol) (PVA)-g-poly(acrylic acid) (PAA) hydrogels were prepared within the polymer matrix by *in situ* polymerization of aniline. The conversion yield of aniline into PANI particles was determined gravimetrically while structural confirmation of the synthesized polymer was sought by Fourier Transform Infrared (FTIR), UV-visible analysis and X-ray diffraction (XRD) technique. Morphology and dimension of PANI particles embedded into the colored optically semi-transparent hydrogels were evaluated by Scanning Electron Microscopy (SEM) analysis. Electrical conductivity of composite hydrogels of different composition was determined by LCR meter while electroactive behavior of composite hydrogels swollen in electrolyte solution was investigated by Effective Bend Angle (EBA) measurements.

Keywords: smart polymers, polymer composites, conducting polymers

1. Introduction

A thermodynamic system capable of transforming chemical energy directly into mechanical work is known as a chemo-mechanical system. Many artificial chemo-mechanical systems made of environmentally sensitive polymer gels are being developed for sensor/actuator system such as controllable membrane separation system and electrically regulated drug delivery system [1].

A gel containing ionic groups can be actuated isothermally by an electric field. When the gel is negatively charged, it swells near the anode and contracts near the cathode, the contraction rate being proportional to the external electric current [2].

The absolute change in volume is by no means insignificant-dimensional changes of say some percents are quite usual. Such a gel bar made of poly-electrolyte materials can bend backwards and

forward by the application of an electric field. Water and ions migrate towards the electrode bearing a change opposite in sign to the net change in the gel, and this coupling of electro-osmosis and electrophoresis is thought to be responsible for the observed chemo-mechanical behavior [3].

Electrically conducting polymers (ECPs) and in particular polyaniline, polypyrrole, polythiophene and their derivatives have been the subject of intensive research for their unique electrical, electrochemical and/or optical properties [4–5] and uncountable applications [6–10]. ECPs are also named ‘conjugated polymers’ because they are macromolecules containing a spatially extended π bonding system, which is the reason of their intrinsic semiconducting nature.

Polyaniline is the one of the most promising conducting polymers due to a good combination of

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properties, stability, price and ease of synthesis by different routes [11–22]. It exists in a variety of reversible protonated and oxidized forms, differing for electrical, electrochemical and/or optical properties like many ECPs [23–25]. PANI is difficult to process because it is soluble only in a limited number of organic solvents.

Electrically conducting polymers can be prepared by the polymerization of aniline in acidic medium, resulting in the formation of polyaniline (PANI) [26]. Influence of polymerization parameters on the molecular weight of polyaniline has been studied [27] and a new aggregation mechanism for shape and aggregation control of PANI nanoparticles was suggested [28]. PANI is known as being stable, most promising, and of low cost so different synthetic routes have been developed like one phase emulsion polymerization process [29], Triton Y-100 [30], potentiometric method [31], polymerization by different oxidizing agents like cupric sulphate [32], iron (III) chloride [33]. PANI nanowires have also been potentiostatically deposited on a stainless steel electrode [34]. The polymerization process for PANI and poly(2-methoxy-aniline) (POMA) nanotubes formation was also investigated [35]. Electrically conducting hydrogel composites made of PANI nanoparticles and poly(H-vinyl-O-/m amino acetophenone of different compositions were synthesized by oxidative polymerization [36, 37]. PANI powder with crystalline semi-conducting ZnS composite by mechanical mixing was also found to increase conductivity [38]. Similarly, PANI/Co₃O₄ was synthesized [39] to overcome the solubility problem of PANI. Lee *et al.* [40] reported direct patterning of conducting water-soluble polymers. Some more aspects of preparation methods and properties of polyaniline blends and composites with organic polymer have also been reviewed [41].

Thus, being motivated by the significant and diversified applications of PANI and related conducting polymers, the present paper aims at synthesizing a PANI impregnated graft copolymer PVA-g-PAA and characterizing it by various analytical techniques such as FTIR, SEM and UV-visible analysis. The selection of PVA and PAA as the hydrogels components of the polymer matrix lies in their unlimited applications in medicine, biology and technology [42–44]. The present paper also

describes the results on electroactive behavior of the graft copolymer impregnated with PANI molecules.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA) (98.6% hydrolyzed) was obtained from 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 persulphate (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 was prepared by using MBA as crosslinker and KPS as polymerizing initiator. Schematically, the reaction mechanism may be displayed as shown in Figure 1. In a typical experiment, 1 g PVA was dissolved in 25 ml of hot double distilled water and to this solution were added precalculated amounts of acrylic acid (43.7 mM), MBA (19.45·10⁻² mM) and KPS (11.10·10⁻² mM). The whole reaction mixture was homogenized and kept in a petri dish (corning glass, 2.5" diameter) maintained at 35 ± 0.2°C for 24 h. After the reaction is over, the whole mass converted into a semi-transparent film and it was purified by equilibrating it in double distilled water for a week. The swollen gel was dried at room tem-

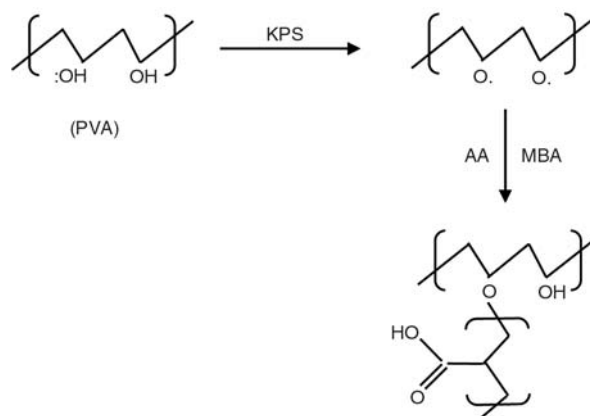


Figure 1. A reaction scheme for graft co-polymerization of PAA onto PVA

perature, cut into rectangular size piece and stored in airtight plastic bags.

2.2.2. PANI impregnation

Required quantity of AN (10.74 mM) was dissolved in 0.5 N HCl (50 ml) and the gel prepared 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 0.3 M APS bath to soak 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 via the mechanism shown in Figure 2.

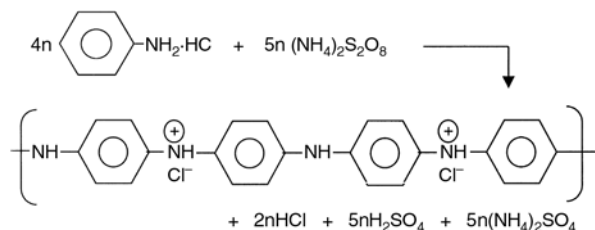


Figure 2. Reaction scheme showing the polymerization of aniline

As the polymerization progresses, the semi-transparent gel turns into black. The PANI impregnated gel is repeatedly washed with distilled water and allowed to dry at $30 \pm 0.2^\circ\text{C}$ for 72 h.

The percentage impregnation of PANI into the gel was calculated by the Equation (1):

$$[\%] \text{ Impregnation of PANI} = \left(\frac{W_{\text{PANI}} - W_{\text{Dry}}}{W_{\text{Dry}}} \right) \cdot 100 \quad (1)$$

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

In order to achieve the objectives undertaken in the study, hydrogels of different composition were prepared by varying the amounts of PVA, AA, MBA, KPS, AN and APS in the feed mixture of the hydrogel.

2.3. Characterization

2.3.1. Fourier Transform Infrared (FTIR) spectra

To gain insights into the structural information of the prepared PANI impregnated gel, the FTIR spectra of PANI powder, polymer hydrogels and PANI-impregnated matrix were recorded in a FTIR

spectrophotometer (FTIR-8400S, Shimadzu). For recording FTIR spectra of native and PANI impregnated films, quite thin and transparent films of respective samples were prepared by solution casting method and the prepared films were directly mounted on spectrophotometer.

2.3.2. UV-visible analysis

UV-visible analysis was also carried out on a double beam UV-VIS spectrophotometer (Systronics, 2201, Ahmedabad, India). For scanning UV-spectra, thin films of samples (native and PANI impregnated) were prepared of sizes $3 \times 1 \times 0.05 \text{ cm}^3$ by solution casting method and put in to the quartz cuvette in vertical orientation.

2.3.3. X-ray diffraction (XRD) analysis

In order to gain insights into the crystalline nature of the prepared native and PANI impregnated gel, 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 $2.4^\circ \cdot \text{min}^{-1}$. The operating target voltage was 35 kV, tube current was 20 mA and radiation used was $\text{FeK}\alpha$ ($\lambda = 0.193 \text{ nm}$).

2.3.4. Particle size analysis

The distribution of particle size of prepared PANI powder was measured by a particle size analyser (Fritsch Particle Sizer Analysette). The PANI particles were prepared as described below:

A known quantity of aniline ($10.74 \cdot 10^{-2} \text{ mM}$) was dissolved into 50 ml of 0.5 N HCl and to this solution of aniline was added 0.3 M APS. The reaction mixture was kept for polymerization at room temperature for 24 hrs and the resulting polyaniline precipitate was filtered, washed and dried at 35°C for 24 hrs. The PANI powder so prepared was stored in airtight polythene bags.

2.3.5. Scanning Electron Microscopy (SEM) analysis

The SEM of the prepared native and PANI impregnated gels were recorded on a scanning electron microscope (Philips 515) for their surface morphological structure.

2.3.6. Electrical conductivity

The electrical conductivity of prepared gels were measured by Four probe LCR meter (Masstech Digital M/M No. MAS 830L) with the help of silver electrode pressed on both sides of the gel. The electrical conductivity of gels of different compositions was also measured.

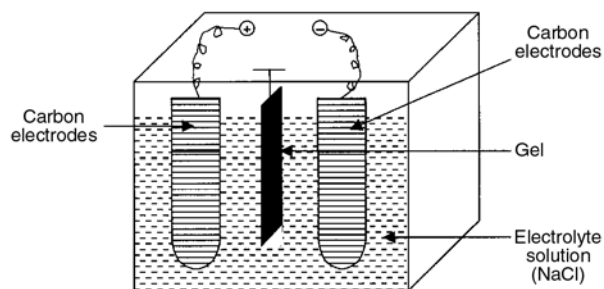


Figure 3. A home-made apparatus for measuring effective bend angle

2.3.7. Effective Bend Angle (EBA) analysis

In order to demonstrate the sensitivity of the gel to the applied external electric field, the bending of the gel under the applied field was measured using a home-made device as shown in Figure 3.

Samples were prepared with varying PANI impregnation percentage and allowed to attain equilibrium swelling in the NaCl aqueous solution at room temperature before electrical stimulation. The same solution was taken in the glass case equipped with two parallel carbon electrodes fixed 30 mm apart at the centre of the glass case. A rectangular specimen having dimensions of $15 \times 1 \times 1 \text{ mm}^3$ was cut and placed vertically at the center of the two electrodes fixing one end of the specimen at the top. The DC voltage was applied across the solution between electrodes and the equilibrium-bending angle was measured with a protractor.

2.3.8. Reproducibility of data

All measurements were carried out at least thrice and average value was utilized for presentation of results. It was found that the experimental errors had never been greater than 1%.

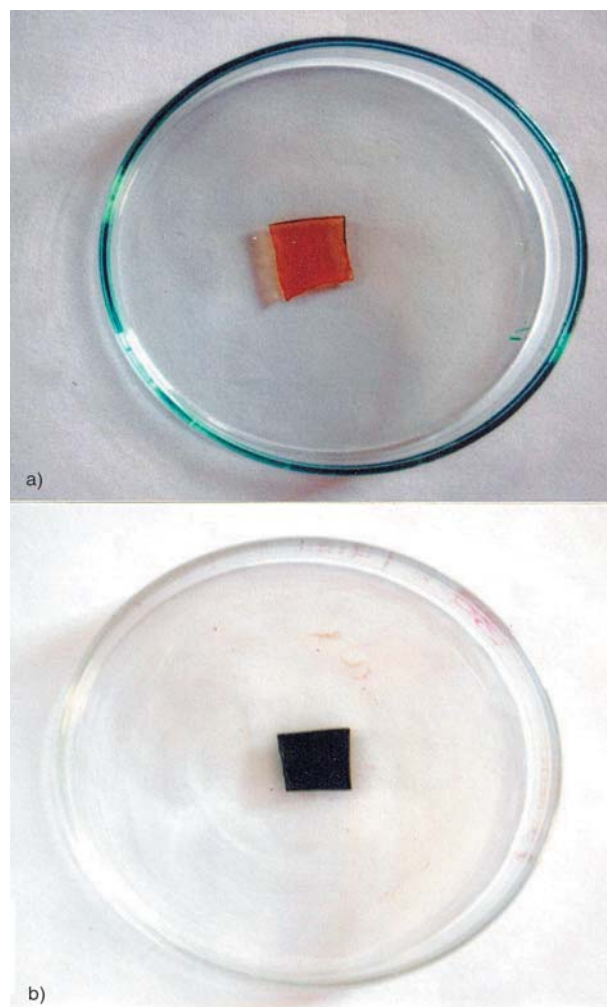


Figure 4. Physical appearance of (a) PVA-g-PAA gel and (b) PANI impregnated PVA-g-PAA gel

3. Results and discussion

3.1. Characterization of gels

3.1.1. Physical appearance

Figures 4a and b depict appearance of the native and PANI impregnated gels which provide a clear evidence of impregnation of PANI into the polymer gel matrix. As evident from the photographs, whereas the native gel is semi-transparent in color while the impregnated gel appears dark-green, which could be attributed to the formation of PANI within the matrix.

3.1.2. FTIR spectra

Figures 5a and b represent FTIR spectra of PVA and PVA-g-PAA polymer films, respectively scanned in the range $400\text{--}4000 \text{ cm}^{-1}$. The characteristic peaks at $1730\text{--}1854 \text{ cm}^{-1}$ are due to the pres-

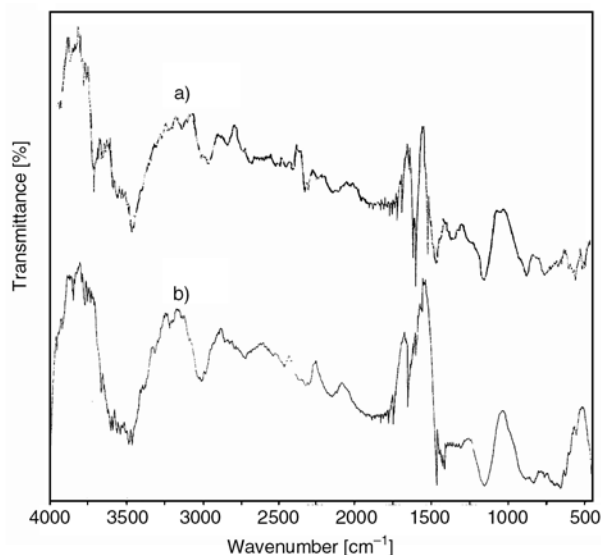


Figure 5. FTIR spectra of (a) PVA and (b) PVA-g-PAA gel

ence of C=O stretching vibration and the peak observed at 650 cm^{-1} is due to the OH out of plane vibration of the carboxylic groups of PAA which appears in the spectra of grafted polymers only, i. e., PVA-g-PAA (Figure 5b). This obviously confirms the grafting reaction. The characteristic peaks at 3468 and 3473 cm^{-1} in both the spectra (a) and (b) are due to the presence of OH groups of PVA, while the spectral bands between 3470 and 3600 cm^{-1} are due to OH stretching vibration of PVA and PAA, respectively, which also confirm the grafting of

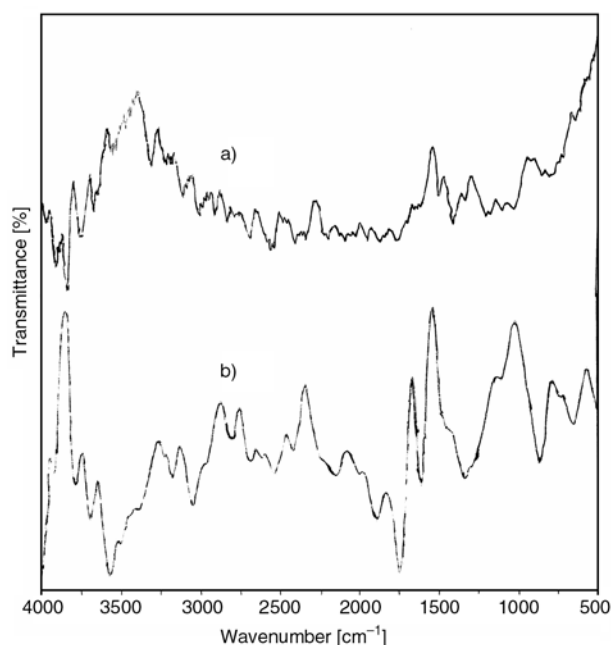


Figure 6. FTIR spectra of (a) PANI powder and (b) PVA-g-PAA impregnated PANI gel

PAA into PVA. The characteristic peak at 1162 cm^{-1} is due to the formation of acetal ring.

Figures 6a and b represent the FTIR spectra of PANI powder and PANI impregnated PVA-g-PAA gel film. The characteristic peaks in Figure 6a appearing 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).

3.1.3. UV-visible spectral analysis

The UV-visible analysis of PVA-g-PAA film and PANI impregnated PVA-g-PAA film was carried out in the range of 200 to 800 nm . It is observed that two characteristic peaks at 334 and at 632 nm in PANI impregnated PVA-g-PAA film spectra (Figure 7b) indicates the presence of PANI into the gel whereas these peaks are not visible in the spectra of PVA-g-PAA (Figure 7a). This obviously confirms the impregnation of PANI into the gel because the emeraldine form of PANI has two characteristic peaks at 334 and 632 nm originating from π - π^* transition of benzenoid rings and the exciton absorption of the quinoid rings, respectively.

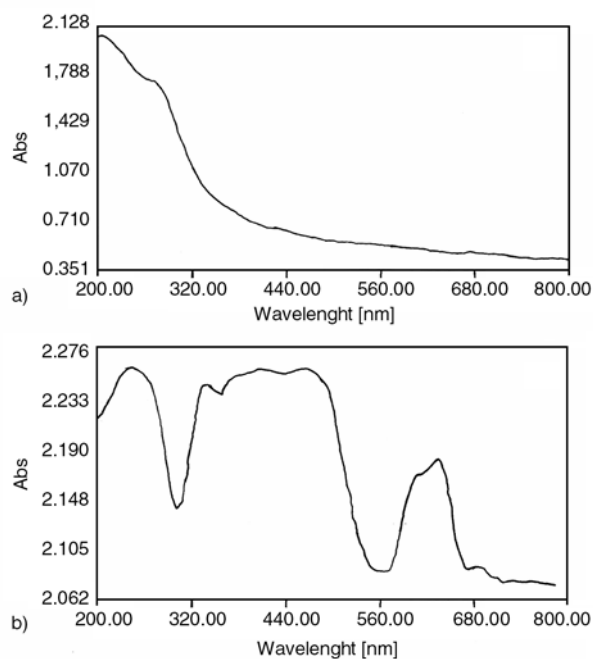


Figure 7. UV-visible spectra of (a) native (PVA-g-PAA) gel and (b) PANI impregnated gel

3.1.4. X-ray diffraction analysis

The XRD patterns of the prepared native and PANI impregnated gels are shown in Figures 8a and b, respectively. Figure 8a shows a prominent peak near 20° , which corresponds to the (101) plane of the PVA crystal. 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 8b which not only shows a characteristic peak at 20° (due to PVA) but also depicts a prominent peak at 25° , which is a characteristic peak of PANI. Thus, the XRD-patterns of impregnated gel provides an additional evidence of PANI formation within the polymer matrix.

A comparison of the peak area of the two diffractograms clearly indicates that upon PANI impregnation, the polymer matrix loses its crystallinity as evident from the increase in broadness of the XRD spectra (b). 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, therefore, may result in a loss of crystallinity.

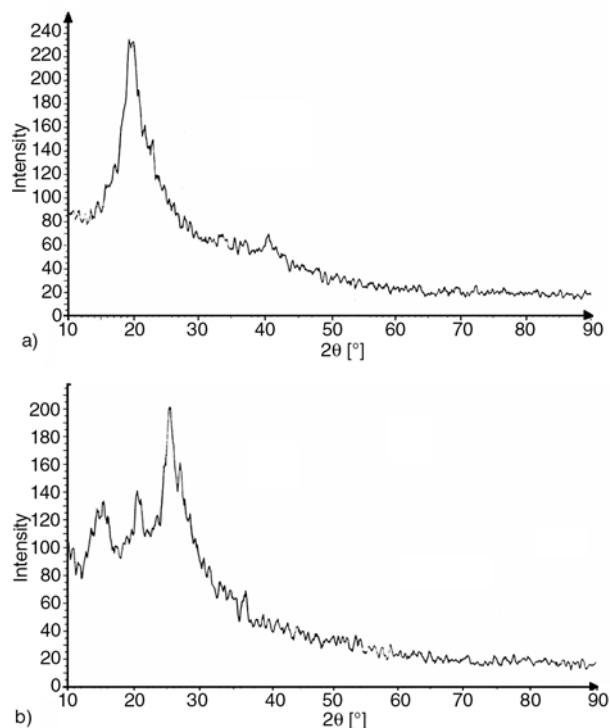


Figure 8. XRD-spectra of (a) native (PVA-g-PAA) gel and (b) PANI impregnated gel

3.1.5. 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 9a 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 as evident from the SEM image (b). It is clear from the image (b) that impregnated PANI molecules form clusters like morphology varying in the sizes 0.5 to $2\ \mu\text{m}$. 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.

3.1.6. Particle size analysis

The particle size distribution curve of the prepared PANI powder is shown in Figure 10 which indicates that the size of the particles vary in the range

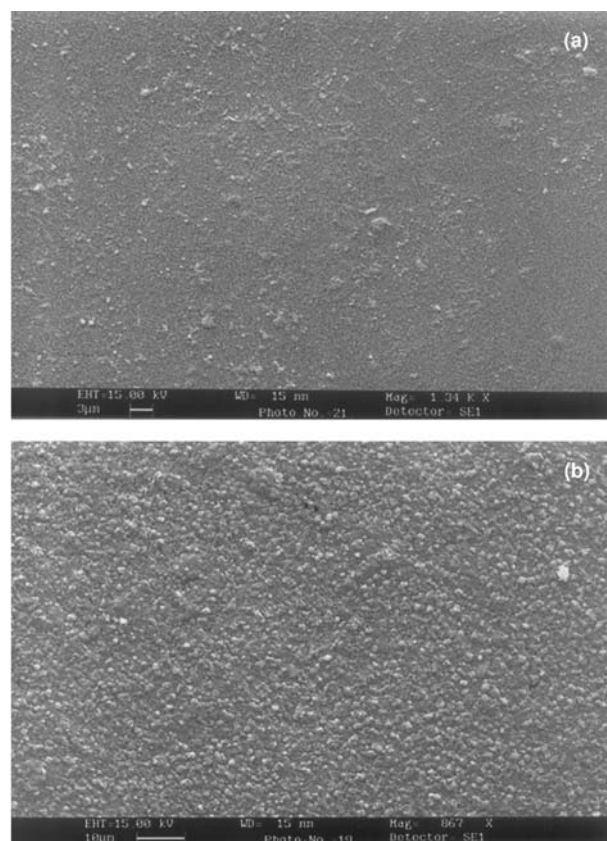


Figure 9. SEM image of (a) native (PVA-g-PAA) gel and (b) impregnated gel

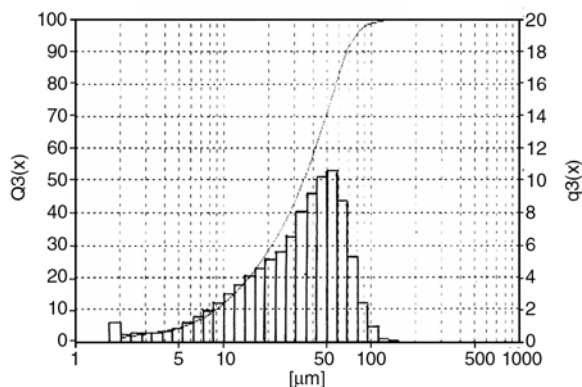


Figure 10. Particle size distribution curve of PANI powder

1 to 100 μm and greatest fraction of particles possess a size of 50 μm . The variation in size of PANI particles could be attributed to varying degree of aggregation of particles under existing experimental conditions.

3.2. PANI impregnation and effects of ingredients

In the present study, AN has been taken as a monomer and in order to get it polymerized within the polymer matrix, it is essential that AN molecules should penetrate into the polymer gel. To achieve the desired objectives of AN polymerization, the monomer AN was dissolved in HCl which formed aniline hydrochloride, thus, yielding cationic species of AN. Now, because of positive charge over the AN molecule, its diffusion into the matrix will be controlled by operative electrostatic forces as well as swelling nature of the hydrogel matrix. It is important to notice here that the polymer matrix is hydrophilic in nature while AN molecules are hydrophobic. In this way one cannot expect hydrophobic/hydrophilic forces being mainly responsible for diffusion of AN. It is, therefore, convincing to consider electrostatic forces as the main factor to cause diffusion of AN into the polymer matrix. Moreover, the presence of PAA segments in the matrix will also contribute to the electrostatic interaction between the entering AN molecules and the matrix itself. Impregnation of PANI into the polymer matrix is basically dependent on the extent of swelling of the polymer film in aniline hydrochloride solution and its subsequent polymerization within the matrix. Thus, the inclusion of aniline into the polymer should definitely be

a function of the chemical composition (and nature also) of the hydrogel and this has been investigated further by varying the concentration of the constituents components of the gel as discussed in the following para.

3.2.1. Effect of PVA

To study the effect of PVA on PANI impregnation, PVA was varied in the range 1.0 to 3.0 g keeping quantities of other ingredients constant. The results summarized in Table 1 reveal that the amount of impregnated PANI constantly increases with increasing PVA concentration in the gel up to 1.5 g. The results may be explained by the fact that with increasing PVA, the hydrophilicity of the matrix increases that allows more aniline to enter into the matrix, which upon polymerization produces greater amount of PANI while beyond 1.5 g of PVA, PANI impregnation decreases. This is due to the fact that the increasing PVA content decreases the interionic repulsion between the PAA chain which allows lesser number of aniline molecules to enter the polymer matrix that results in a decrease in PANI impregnation.

3.2.2. Effect of AA

The influence of AA variation on the extent of PANI impregnation has been investigated by varying the concentration of AA in the range 14.6 to 43.7 mM while keeping the other constituents concentration constant. The results are shown in Table 1, which indicate an increase in the impregnated amount of PANI with increasing PAA content. The increase in PANI impregnation may be explained by the fact that due to ionic nature of PAA, its increasing content in the gel results in interionic repulsion between the PAA chains, which permits a large number of AN molecules to enter the polymer matrix. This results in an enhanced impregnation.

3.2.3. Effect of MBA

The effect of increasing concentration of MBA on the extent of PANI impregnation has been studied by varying its concentration in the range $6.5 \cdot 10^{-2}$ to $25.9 \cdot 10^{-2}$ mM while keeping the other concentration terms constant. The results are shown in Table 1, which show that the amount of impregnated PANI increases initially with the increasing

Table 1. Effect of concentration of constituents of the gel on the amount of PANI impregnation

PVA content [g]	PANI impregnation [%]	Other ingredients
1.0	3.57	AA – 29.1 mM MBA – $13.0 \cdot 10^{-2}$ mM KPS – $7.39 \cdot 10^{-2}$ mM APS – 0.3 M in 0.5 N HCl AN – 10.74 mM in 0.5 N HCl
1.5	3.80	
2.0	3.37	
3.0	1.18	
AA content [mM]	PANI impregnation [%]	Other ingredients
14.6	1.85	PVA – 1 g MBA – $13.0 \cdot 10^{-2}$ mM KPS – $7.39 \cdot 10^{-2}$ mM APS – 0.3 M in 0.5 N HCl AN – 10.74 mM in 0.5 N HCl
29.1	3.57	
36.0	5.75	
43.7	7.55	
MBA content [mM]	PANI impregnation [%]	Other ingredients
$6.50 \cdot 10^{-2}$	12.50	PVA – 1 g AA – 43.7 mM KPS – $7.39 \cdot 10^{-2}$ mM APS – 0.3 M in 0.5 N HCl AN – 10.74 mM in 0.5 N HCl
$13.00 \cdot 10^{-2}$	6.48	
$19.45 \cdot 10^{-2}$	32.69	
$25.90 \cdot 10^{-2}$	19.05	
KPS content [mM]	PANI impregnation [%]	Other ingredients
$3.69 \cdot 10^{-2}$	4.35	PVA – 1 g AA – 43.7 mM MBA – $19.45 \cdot 10^{-2}$ mM APS – 0.3 M in 0.5 N HCl AN – 10.74 mM in 0.5 N HCl
$7.39 \cdot 10^{-2}$	4.07	
$11.10 \cdot 10^{-2}$	10.00	
$14.80 \cdot 10^{-2}$	3.26	
AN content [mM]	PANI impregnation [%]	Other ingredients
5.30	6.25	PVA – 1 g AA – 43.7 mM MBA – $19.45 \cdot 10^{-2}$ mM KPS – $11.10 \cdot 10^{-2}$ mM APS – 0.3 M in 0.5 N HCl
10.74	9.40	
16.11	33.66	
21.48	6.70	
APS concentration [M]	PANI impregnation [%]	Other ingredients
0.2	16.67	PVA – 1 g AA – 43.7 mM MBA – $19.45 \cdot 10^{-2}$ mM KPS – $22.20 \cdot 10^{-2}$ mM AN – 10.74 mM in 0.5 N HCl
0.3	14.19	
0.4	4.21	
0.5	9.09	

concentration of MBA in the range $6.5 \cdot 10^{-2}$ to $19.45 \cdot 10^{-2}$ mM while beyond $19.45 \cdot 10^{-2}$ mM, a fall is noticed. The results may be interpreted by the fact that in the initial concentration range of MBA, the increase observed is due to an enhanced hydrophilicity of the matrix, which in turn, attracts a larger number of aniline hydrochloride molecules to diffuse into the gel which upon subsequent polymerization forms greater amount of PANI. However, beyond $19.45 \cdot 10^{-2}$ mM of MBA, much greater crosslinked network becomes compact and restrains the mobility of both incoming aniline molecules as well as the relaxation of polymer matrix chain. This clearly results in a less amount of PANI impregnation.

3.2.4. Effect of KPS

In the present study, the effect of KPS on PANI impregnation has been investigated by varying the concentration of KPS in the range $3.69 \cdot 10^{-2}$ to $14.8 \cdot 10^{-2}$ mM. The results are summarized in Table 1 which clearly reveal that the amount of impregnated PANI increases with increasing KPS in the range $3.69 \cdot 10^{-2}$ to $11.10 \cdot 10^{-2}$ mM while beyond $11.10 \cdot 10^{-2}$ mM, a fall is obtained. The observed increase may be attributed to the reason that as the concentration of KPS increases, the molecular weight (and also size) of polymer chain decreases which results in a formation of network with large number of pores, but of smaller size, which obviously intakes greater number of AN

molecules, thus, giving rise to greater impregnation.

However, beyond $11.10 \cdot 10^{-2}$ mM of KPS, much smaller size of network pores could restrict the diffusion of AN molecules into the polymer gel, and therefore, results in a decrease in the extent of impregnation.

3.2.5. Effect of AN

The effect of AN (monomer) concentration on PANI impregnation within the polymer matrix has been studied by varying the concentration of AN in 0.5 N HCl solution in the range 5.3 to 21.48 mM while keeping the concentration of other constitution of the gel as constant. The results are shown in Table 1 which indicate that the extent of PANI impregnation increases with increasing AN content within the matrix while beyond 16.11 mM of aniline concentration, the extent of impregnation decreases. The observed findings may be explained by the fact that as AN is a monomer of PANI, its increasing concentration in the gel will obviously facilitate more polymerization and therefore, extent of impregnation increases. However, beyond a definite concentration, i. e., 16.11 mM, the decrease observed in PANI impregnation could be due to a lower degree of swelling in AN hydrochloride solution as much greater ionic concentration (because of aniline hydrochloride ion) in the external solution may result in lower swelling which permits less number of AN molecules for polymerization.

3.2.6. Effect of APS concentration

The influence of concentration of APS on PANI impregnation was studied by varying its concentration in the range of 0.2 to 0.5 M keeping other concentration terms constant. The results summarized in Table 1 show that the amount of impregnated PANI decreases with increasing APS concentration. The reason for the observed decrease may be explained by the fact that at low APS concentration, high molecular weight PANI might have been produced whereas at higher APS concentration, the PANI formed would be of lower molecular weight and, therefore, the possibility of leaching of low molecular weight, PANI could not be ruled out. This may consequently result in low impregnation.

3.3. Electrical conductivity and effects of ingredients

The electrical conductivity of polymer composite in different weight ratio of ingredients has been studied and it is found that the electrical conductivity of the gel is enhanced after impregnation of PANI. Moreover, the conductivity also varies with the constituents of the polymer matrix as discussed below.

3.3.1. Effect of PVA

The effect of PVA content on the conductivity of the matrix has been studied by varying the amount of PVA in the range 1 to 3 g. The results are depicted in Table 2, which reveal that the matrix shows an optimum conductivity at 1 g of PVA content while a drastic fall of about 10 times is noticed in conductivity when the concentration of PVA increases to 1.5 g. However, beyond 1.5 g of PVA content, almost no change in conductivity is observed. The results may be explained as below: The conductivity is determined by both the extent of PANI impregnation as well as poly acrylic acid content of the matrix. The former, in turn, is dependent on the hydrophilicity of the matrix. When the concentration of PVA increases from 1 to 1.5 g, the weight fraction of ionic polymer (PAA) decreases in the matrix. This obviously results in fall in conductivity of the matrix. However, beyond 1.5 g of PVA, increase in PVA content does not bring down the conductivity further, which may be attributed to the fact that the matrix acquire an optimum hydrophilic nature and, therefore, does not show further drop in conductivity.

3.3.2. Effect of PAA

In order to study the influence of PAA on the conductivity of the matrix, the concentration of the AA was increased in the range 14.6 to 43.7 mM and electrical conductivity was measured. The results are shown in Table 2, which reveal that the conductivity gradually increases with increasing PAA content in the gel. The results are quite expected and may be explained by the fact that on increasing the concentration of PAA, the number of COO^- groups increases along the macromolecular chain which add to the electrical conductivity of the matrix by

Table 2. Effect of concentration of constituents of the gel on conductivity

PVA content [g]	Conductivity native [S/cm]	Conductivity PANI impregnated [S/cm]	Other ingredients
1.0	$0.38 \cdot 10^{-2}$	$3.33 \cdot 10^{-2}$	AA – 29.1 mM
1.5	$0.19 \cdot 10^{-2}$	$0.37 \cdot 10^{-2}$	MBA – $13.0 \cdot 10^{-2}$ mM
2.0	$0.27 \cdot 10^{-2}$	$0.38 \cdot 10^{-2}$	KPS – $7.39 \cdot 10^{-2}$ mM
3.0	$0.56 \cdot 10^{-2}$	$0.77 \cdot 10^{-2}$	APS – 0.3M in 0.5N HCl
			AN – 10.74 mM in 0.5N HCl
AA content [mM]	Conductivity native [S/cm]	Conductivity PANI impregnated [S/cm]	Other ingredients
14.6	$0.63 \cdot 10^{-2}$	$2.19 \cdot 10^{-2}$	PVA – 1 g
29.1	$0.53 \cdot 10^{-2}$	$2.24 \cdot 10^{-2}$	MBA – $13.0 \cdot 10^{-2}$ mM
36.0	$0.27 \cdot 10^{-2}$	$2.60 \cdot 10^{-2}$	KPS – $7.39 \cdot 10^{-2}$ mM
43.7	$0.46 \cdot 10^{-2}$	$2.79 \cdot 10^{-2}$	APS – 0.3 M in 0.5 N HCl
			AN – 10.74 mM in 0.5 N HCl
MBA content [mM]	Conductivity native [S/cm]	Conductivity PANI impregnated [S/cm]	Other ingredients
$6.50 \cdot 10^{-2}$	$0.01 \cdot 10^{-2}$	$0.32 \cdot 10^{-2}$	PVA – 1 g
$13.00 \cdot 10^{-2}$	$0.01 \cdot 10^{-2}$	$1.27 \cdot 10^{-2}$	AA – 43.7 mM
$19.45 \cdot 10^{-2}$	$0.11 \cdot 10^{-2}$	$2.87 \cdot 10^{-2}$	KPS – $7.39 \cdot 10^{-2}$ mM
$25.90 \cdot 10^{-2}$	$0.22 \cdot 10^{-2}$	$2.87 \cdot 10^{-2}$	APS – 0.3 M in 0.5 N HCl
			AN – 10.74 mM in 0.5 N HCl
AN content [mM]	Conductivity native [S/cm]	Conductivity PANI impregnated [S/cm]	Other ingredients
5.30	$0.75 \cdot 10^{-2}$	$5.97 \cdot 10^{-2}$	PVA – 1 g
10.74	$0.75 \cdot 10^{-2}$	$3.59 \cdot 10^{-2}$	AA – 43.7 mM
16.11	$0.75 \cdot 10^{-2}$	$3.84 \cdot 10^{-2}$	MBA – $19.45 \cdot 10^{-2}$ mM
21.48	$0.75 \cdot 10^{-2}$	$9.10 \cdot 10^{-2}$	KPS – $11.10 \cdot 10^{-2}$ mM
			APS – 0.3 M in 0.5 N HCl

facilitating conduction of electrons along the PANI chain.

It is also to mention that with increasing concentration of PAA, percent impregnation of PANI also increases in the studied range, which thus, contributes to the observed increase in conductivity.

3.3.3. Effect of MBA

In the present investigation, the role of crosslinker has been investigated by varying the amount of crosslinker in the concentration range $6.5 \cdot 10^{-2}$ to $25.9 \cdot 10^{-2}$ mM and observing the change in electrical conductivity. The results are shown in Table 2, which show that the conductivity sharply increases with increasing concentration of MBA in the range $6.5 \cdot 10^{-2}$ to $19.45 \cdot 10^{-2}$ mM while after $19.45 \cdot 10^{-2}$ mM of crosslinker; the conductivity acquires a limiting value.

The observed initial steep increase in conductivity with increasing concentration of MBA may be attributed to the fact that with increasing crosslinker concentration, the network density increases which results in a compact network, thus, facilitating flow of electrons responsible for conductivity behavior. However, beyond an optimum

concentration of crosslinking agent, the gels acquire optimum compactness and, therefore, no further increase in conductivity is observed.

3.3.4. Effect of AN

The effect of PANI content on the conductivity of the matrix has been investigated by increasing the concentration of aniline in the range 5.3 to 21.48 mM in the feed mixture of the gel. The results are given in Table 2 which indicate that the conductivity increases with increasing concentration of AN. The results are quite obvious and may be explained by the fact that with increasing concentration of AN solution, greater number of AN molecules will be available within the matrix for polymerization and as a subsequence, the extent of impregnation also increases.

3.4. Bending behaviour of the matrix

Swollen polyelectrolyte gels when kept under an applied electric field normally exhibit a bending towards the electrodes. This is called Electro-mechano-chemical (EMC) behavior and has been recognized as a promising phenomenon in designing smart materials.

3.4.1. Effect of PANI content

Inclusion of PANI molecules within the polymer matrix is expected to enhance the EMC behaviour and, therefore, has been studied by varying the PANI content in the range 0 to 30% at different applied voltages as shown in Figure 11. The results clearly reveal that the effective bending angle (EBA) constantly increases with increasing PANI content. The observed results may be explained by the fact that the greater the PANI content of the matrix, the larger would be the conductivity of the matrix, which in turn, will respond easily to the applied voltage.

It is also noticed from the Figure 11 that at 10 and 30% of PANI content, the bending is exactly same for a given voltage. The reason for the same bending angle at higher PANI content is that the PANI impregnated matrix acquires optimum conductance and, therefore, shows no further bending. Alternatively, it is also likely that the PANI chains are of the matrix may restrain the bending of the matrix. The Figure 12 also indicates that the magnitude of effective bending angle also increases with increasing applied voltage across the electrodes. The increase in effective bending angle may be attributed to the fact that with increase in voltage the charged matrix is attracted more and more towards the electrodes and thus, the bending angle increases.

3.4.2. Effect of voltage

There is a lower critical voltage (LCV) below which no bending of matrix is observed. In the present study, the LCV is found to be 3.0 volt. Thus, the bending phenomenon is observed only after 3.0 V and, therefore, the effect of voltage on bending phenomenon has been investigated in the range 6.0 to 12.0 V for a given PANI content. The influence of applied voltage on the EMC behavior of the matrix has been studied by varying the voltage in the range 6.0 to 12.0 V. The results are depicted in Figures 12 a, b and c which indicate that the EMC behavior of the matrix shows an increase in effective bending angle with increasing voltage at 0.1, 0.2 and 0.3 N NaCl solution. The observed results are quite obvious as with increasing voltage, the charged matrix shows greater attraction towards electrodes and, therefore, bending angle increases.

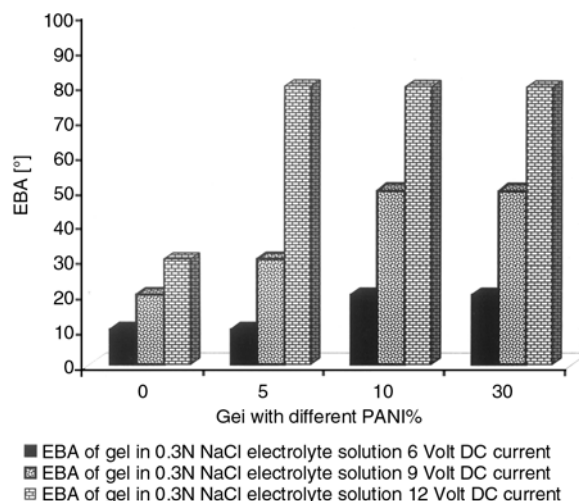


Figure 11. Effect of PANI contents on EBA

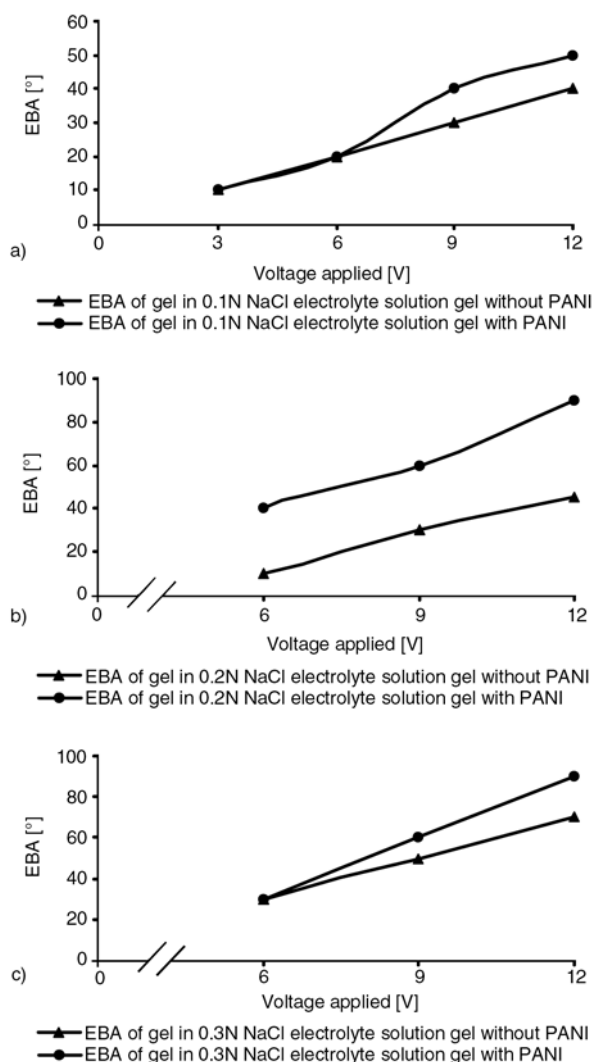


Figure 12. Effects of applied voltage on EBA in (a) 0.1 N NaCl electrolyte solution, (b) 0.2 N NaCl electrolyte solution, and (c) 0.3 N NaCl electrolyte solution

3.4.3. Effect of electrolyte concentration

The concentration of electrolyte solution is an important experimental parameter to exert a significant influence on the effective bending angle of the polymer matrix. The effect of increasing concentration of NaCl solution on bending of the gel has been studied by varying the concentration of NaCl in the range 0.1 to 0.3 N. The results are shown in Figures 13 a, b and c which reveal that the bending angle substantially increases up to 0.2 N NaCl solution and thereafter, it becomes almost constant showing no further increase in bending. The results may be attributed to the fact that increased concentration of NaCl solution facilitates bending of the polymer matrix by binding salt ion to the polyelectrolyte matrix so as to make it more responsive to the applied field. However, beyond 0.2 N NaCl

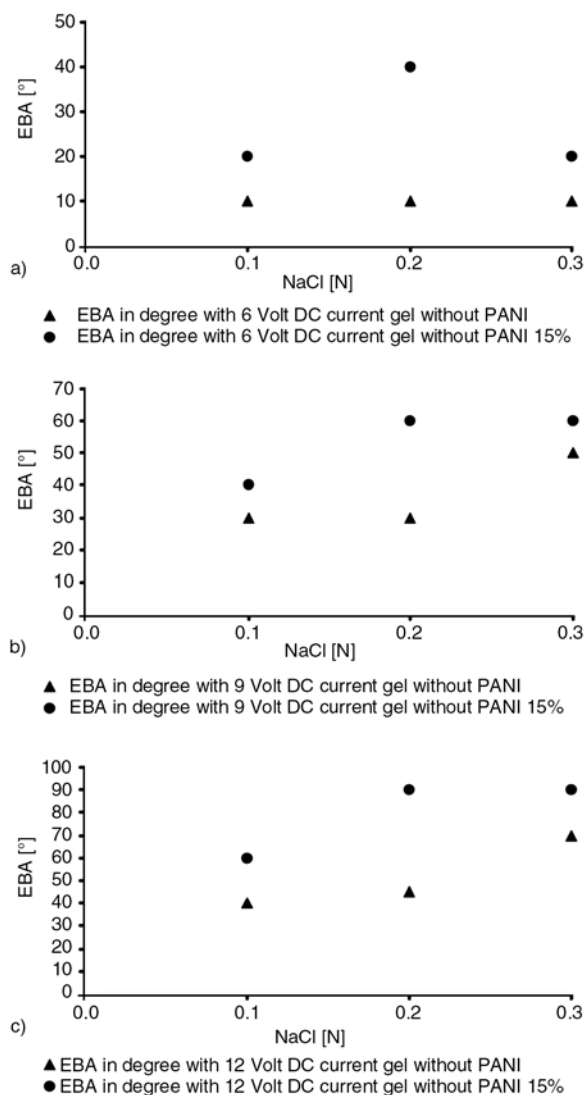


Figure 13. Effect of strength of electrolyte solution in (a) 6 Volt, (b) 9 Volt, and (c) 12 Volt

concentration when the charged centers present along the polyelectrolyte molecules are almost completely ionized, further effect on the effective bending angle of the polymer matrix may not likely to occur. This clearly explains the limiting bending of the matrix at highest applied voltage.

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 impregnated hydrogel show characteristic peaks of poly aniline and other functional groups of constituent polymers, i. e., PVA and PAA. The impregnation of PANI into polymer matrix is further confirmed by UV spectral analysis. The impregnation of PANI within the polymer matrix brings about a loss in crystallinity as confirmed by the XRD spectra 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 extent of PANI impregnation depends on chemical composition of the composite hydrogel. It is noticed that with increasing PVA, MBA, KPS and AN concentration, the amount of PANI impregnation increases up to a certain range and thereafter decreases. On the other hand, whereas an increase in impregnation results with increasing PAA content, a fall in impregnation is observed with increasing APS concentration.

The electrical conductivity also varies with varying composition of the composite. The conductivity increases with increasing PVA and MBA concentration while a drop in conductivity is observed if concentrations are increased further. In the case of AN, the conductivity constantly increases.

The PANI impregnated matrix shows bending behavior when a fixed voltage is applied in the presence of an electrolyte solution (NaCl). The gels show an enhanced bending behavior with increasing PANI content and applied voltage. Moreover, a greater bending is noticed with increasing concentration of electrolyte solution.

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