

Interaction of Gamma Radiation with PVA/PANi Composite Films: Structural and Morphological Studies

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ABSTRACT: Polyvinyl alcohol (PVA) films containing two different concentrations of polyaniline were prepared by solution casting technique. These films were irradiated with gamma radiation for various doses. Structural and morphological studies of control PVA as well as PVA/PANi composite films were carried out before and after the gamma radiation. Polyaniline is one of the interesting conducting polymers and has the property of changing its color and conductivity when switched between different oxidation states. This unique property of polyaniline

was monitored by investigating UV/vis absorption spectra and changes in electrical conductivity. The changes observed could be correlated to the total dose received by the films. It is therefore proposed that PVA/PANi composite films can be used for fabricating radiation dosimeters. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2243–2252, 2008

Key words: polymers; composite materials; aniline; radiation effects; color changes

INTRODUCTION

Recently γ -irradiation and electron beam radiation technologies have been used extensively for many industrial applications like food irradiation, sterilization of medical goods, radiation crosslinking of polymers, etc. All these processes involve highly energetic radiation and therefore need to be executed safely. Standardization, measurement, and control of these radiation doses delivered during processing have also become essential.

Irradiation of metals, alloys, and semiconductors have been reported for over many years but polymers, being the newer types of materials, have not been studied in details. Polymeric materials are the simplest akin to human body and therefore finds applications in several areas such as medicine, biotechnology, and pharmaceutical products. Therefore, the effects of irradiation need to be studied extensively. The exposure of polymers to gamma radiation induces structural defects and degradation of initial structure by scission and emission of atoms, molecules, and molecular fragments.^{1,2} It generates a num-

ber of charged species, ions, free radicals and induces either scission or crosslinking or both. This leads to changes in density, solubility, molecular weight as well as optical and electrical properties. The magnitude and nature of changes depend on the composition of the polymer and energy of ionizing radiation. In addition to γ -radiation, ion beams and electron beams are also used for irradiating polymers.³ Interest in such studies has gained significance in recent years in view of potential applications in integrated electronics, phosphors, and surface modifications.

PVA is one of the important polymers and is available in the form of powders, fibers, and films. It is used industrially for sizing, adhesives, and emulsification. The effect of γ -irradiation on the films of PVA has already been reported.⁴ During the studies it was noticed that there is appreciable change in color of PVA films after irradiation. Our further research in producing composite films of PVA with various conducting polymers like polypyrrole, polyaniline, etc., has led us to look for the possibilities of correlating the changes in structure, properties and color with the total dose. In this respect, polyaniline is important because of its unique property of producing changes in color and electrical characteristic as it switches between different oxidation states.⁵ Further, with the introduction of new radiation processing there is a great need for dosimeters, which should be reliable, cheap, and easy to use. For this,

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the materials that respond to radiation by visual changes in color is most suitable as a dosimeter. Such a change should be easily identified and quantified with the radiation dose delivered.

PANi can be easily synthesized by chemical and electrochemical oxidation of aniline monomer and exists in different oxidation states. PANi has got several interesting applications like optical displays, electromagnetic interference shielding, corrosion protection, printed circuit boards, etc. It was thought that PANi could also play an important role in radiation process control.⁶ However, its main limitation is its poor mechanical property. This limitation can be overcome by preparing conducting polyaniline composites which possess the mechanical properties of the insulating host matrix and electrical properties of conducting polyaniline as guest. Making composites of PANi is little tricky because its conducting form (emeraldine salt, ES) is not soluble when compared with its undoped, nonconducting form. Some of the derivatives of PANi emeraldine base (EB) are highly soluble in common organic solvents.⁷ Sevil et al. have synthesized 2-chloro-polyaniline, which is soluble in tetrahydrofuran to some extent.⁷ This study reports the well-known method of *in situ* polymerization of PANi using PVA as a host matrix. Composite films of PVA/PANi were prepared, which were initially green in color. Green color of the films could be changed to blue by deprotonating PANi with 1N NH₄OH. This blue color is due to EB form of PANi. When these blue colored films were exposed to γ -rays for different doses, it was seen that PANi reprotonates as indicated by green color of the films. This article reports the structure, morphology, and color changes of PVA/PANi films by γ -radiation and determine its suitability for the development of plastic dosimeters. These changes in color were confirmed using UV/vis spectrophotometer. We have also studied in detail, how the presence of PVA assists in reprotonating the blue-colored film to green one.

EXPERIMENTAL

Materials

PVA was obtained from Loba Chemie, Mumbai, India. The DP value of PVA was in the range of 1700–1800. Aniline, ammonium persulphate (APS), and ammonium hydroxide were obtained from S. D. Fine Chemicals, Mumbai, India.

Methods of film preparation

Preparation of PVA films

Four percent solution of PVA was prepared by dissolving PVA powder in distilled water at 50°C. A

clear PVA solution was obtained. Films of this solution were prepared by pouring it on a flat polypropylene Petri dish. The thickness of the film was controlled by the volume of solution added. Every time 5 mL of stock solution was poured on the Petri dish. The solvent was evaporated away by heating the dish by keeping it under infrared lamp. The films were removed from the Petri dish. We denote this film as PVA [W].

Similarly another 4% PVA solution was prepared in acidic medium (1M HCl) instead of distilled water. Films from this solution were prepared in similar manner. We denote this film as PVA [H]. All the films were stored in a vacuum desiccator for further investigation.

Preparation of PVA + PANi composite film

The standard method of preparation of polyaniline was followed with the only difference that it is done in the PVA medium.⁸ Concentration of PVA was kept constant while aniline monomer was added in two different concentrations (i.e., 2 and 5 wt % with respect to PVA). First 2.4 g of PVA was dissolved in 50 mL of 1M HCl at a temperature of 50°C. A clear solution of PVA was obtained which was then allowed to come to room temperature with constant stirring. To this solution freshly distilled aniline was added and the solution stirred continuously at room temperature for 30 min to form homogeneous mixture of aniline monomer with PVA matrix. This solution was then cooled to 5°C and 10 mL of 1M HCl containing APS was added to it drop wise over a period of 3 h. The weight of APS (oxidant) was chosen in such a way so as to maintain the monomer to oxidant molar ratio of 2 : 1. After complete addition of oxidant, solution was further stirred continuously for another 2 h. The temperature was maintained at 5°C throughout the addition. A homogeneous light green colored solution was obtained. From this solution films were prepared by the same solution casting method as described earlier for PVA films. The uniform light green colored films were obtained resembling the color of ES form of PANi. Lightness of the color was because of the very low PANi content. Homogeneous diffusion of aniline monomer into PVA host matrix was confirmed by uniform color of the films. The thickness of the films was measured at five randomly selected places with a thickness gauge having an accuracy of ± 1 μ m. The average thickness of the film was found to be 40 ± 2 μ m. These films were washed with sufficient quantity of water so as to remove unreacted APS. These films were dried and the thickness was measured again, which was found to have slightly reduced to 38 ± 2 μ m. This reduction in thickness may be due to dissolution of some PVA content of the composite

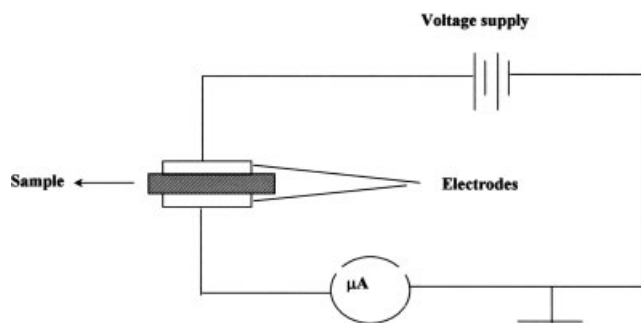


Figure 1 Schematic diagram of two probe conductivity setup.

film, which did not copolymerize with PANi. Some of the dried films were then dipped in a 1N NH_4OH solution for 45 s. These films became blue in color resembling that of the EB form of PANi. These films were again dried and stored in a vacuum dessicator for further investigation.

Irradiation of films

PVA [W], PVA [H], and PVA + PANi films were subjected to γ -ray irradiation for different doses. The Co^{60} source of Gamma Chamber-900 at Radiation Safety Systems Division, BARC, Mumbai, India, was used for γ -irradiation. Dose rate of Gamma Chamber-900 was 4.0 kGy/h. Gamma chamber was calibrated with Fricke dosimeter reference standard.

Structural studies using UV/vis, FTIR, XRD, and SEM

UV/vis spectrum was obtained by using GBC spectrometer model 918. Perkin-Elmer FTIR system model 2000 was used to record the IR spectra in ATR mode in the range $4000\text{--}400\text{ cm}^{-1}$ with 150 scans and a resolution of 4 cm^{-1} . X-ray diffraction studies were performed using Philips X-ray generator PW 1710 equipped with copper tube employed as a source of radiation and the diffractometer model PW 1720 with 2θ varying from 10° to 40° with a step size of 0.01° . The morphological studies were carried out using SEM of JEOL make model 5400. The polymeric films were sputter coated with thin film of gold before the examination. Micrographs were recorded with different magnifications from 100 to $5000\times$.

Conductivity measurement of the irradiated samples

I-V characteristics of the control, gamma-irradiated films were studied using two-probe conductivity setup. I-V characteristics of γ -irradiated PVA/PANi composite films are reported here. As shown in

Figure 1, films were placed between two copper electrodes with a surface area of 1 cm^2 and current was measured using Keithly 617 programmable electrometer at different applied voltages across the two electrodes. All the electrical measurements were carried out in vacuum. Further electrical conductivity was measured using the following formula:

$$\sigma = \frac{1}{R} \frac{T}{A} \quad (1)$$

where $1/R = I/V = \text{slope}$ obtained from the I-V plot. Therefore, $\sigma = (T/A) \times \text{slope}$ obtained from the I-V plot.

σ = conductivity in S/cm; R = resistance in ohms; T = thickness in cm; A = area in cm^2 ; I = current in ampere; V = voltage in volts.

RESULTS AND DISCUSSION

PVA is obtained from the polyvinyl acetate (PVAc) by esterification and thus was expected to be non-crystalline (like PVAc). But surprisingly it is crystalline with identity period of 2.5 \AA , which is on account of 1,3 glycol linkages and the arrangement of all hydroxyl groups being on the same side of the chain.⁹ The model proposed by Bunn¹⁰ is shown in Figure 2, the unit cell being monoclinic with $a = 7.81\text{ \AA}$, $b = 2.5\text{ \AA}$, $c = 5.51\text{ \AA}$, and $\beta = 91.42^\circ$. One unit cell comprises of two monomer units of vinyl alcohol ($-\text{CH}_2\text{CHOH}$).¹⁰ Many physical properties of polymers depend on the degree of crystallinity. Therefore in the present studies the degree of

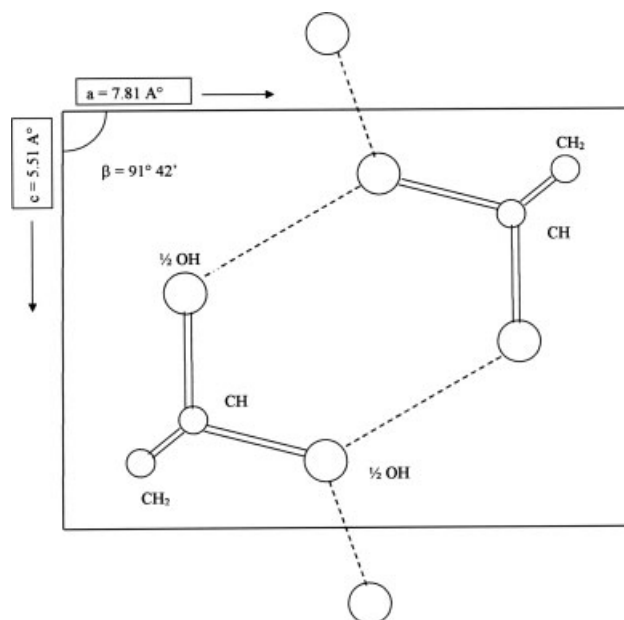


Figure 2 Unit cell of polyvinyl alcohol (monoclinic) (by Bunn).

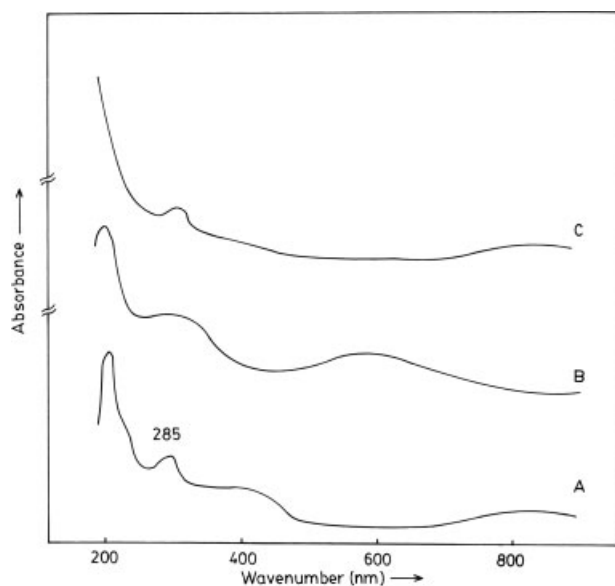


Figure 3 UV/vis spectra of (A) PVA/PANi film (2 wt % aniline) as it is; (B) same film reduced with 1N NH_4OH ; (C) reduced film irradiated by γ -rays for 20 kGy.

crystallinity was calculated using the method of X-ray diffraction and IR Spectroscopy.

UV/vis spectra

UV/vis absorption spectroscopy has been used for finding the changes in the PVA film subjected to gamma irradiation. It was reported⁴ that the control film is transparent and colorless and shows no absorption peak in the visible region. The film becomes yellowish brown after γ -irradiation. The absorption spectrum of the irradiated film showed two absorption bands at 280 and 355 nm. The intensity of the band at 355 nm was found to increase gradually with increasing dose of radiation. This region is violet/blue in color, which is complimentary to yellow orange. Thus the visual observation of change in color is supported by the spectroscopic analysis by the observation of the absorption band at 355 nm. This shows that some chromophores are formed. This can occur due to the scission of hydrogen and hydroxyl groups and the formation of a carbonyl double bond ($\text{C}=\text{O}$).

It is interesting to see how the UV/vis spectra can help in determining the structural changes for PVA/PANi film after irradiation with gamma rays. Figure 3, curve A shows UV/vis spectrum of PVA/PANi composite green (with 2 wt % aniline) film which has a sharp absorption band at 285 nm. The spectrum for PVA/PANI blue colored film (i.e., after deprotonation) shows two broad bands in the regions of 240–340 nm and 500–620 nm (Fig. 3, curve B). The second region corresponds to yellow and orange colors, which are complementary to blue color.

When the same film was exposed to γ -rays for the dose of 50 kGy the blue color of the film changed from blue to green and absorbance in the region 500–620 nm reduced significantly from 0.7 to 0.3. Also a sharp peak at 285 nm (observed for the PVA/PANi green film) started to reappear (Fig. 3, curve C).

Films of PVA [W] and PVA [H] were also irradiated by γ -rays and changes in color were noted. In the case of PVA [W] films the UV/vis spectrum shows (Fig. 4, curve A) no significant absorption bands. When these films were subjected to γ -irradiation for a total dose of 40 kGy still the absorption spectrum did not reveal any significant change in absorption bands (figure not reproduced). However with the continued irradiation to a further dose of 100 kGy the absorption spectrum showed a peak at 280 nm (Fig. 4, curve C), which was also indicated by the visual observation of slight coloration (yellowish). It is interesting to note that when PVA [H] films, which were colorless initially, did not show any absorption bands (Fig. 4, curve B). Now it is interesting to note that PVA [H] films when exposed to γ -irradiation for 40 kGy became yellowish in color. The UV/vis spectrum of such films, depicted in Figure 4, curve D, clearly shows two absorption bands at 226 and 282 nm, indicating the formation of chromophores.¹¹ Thus, substantial color change at a lower dose rate for PVA [H] films shows that definitely there is some molecular rearrangement taking

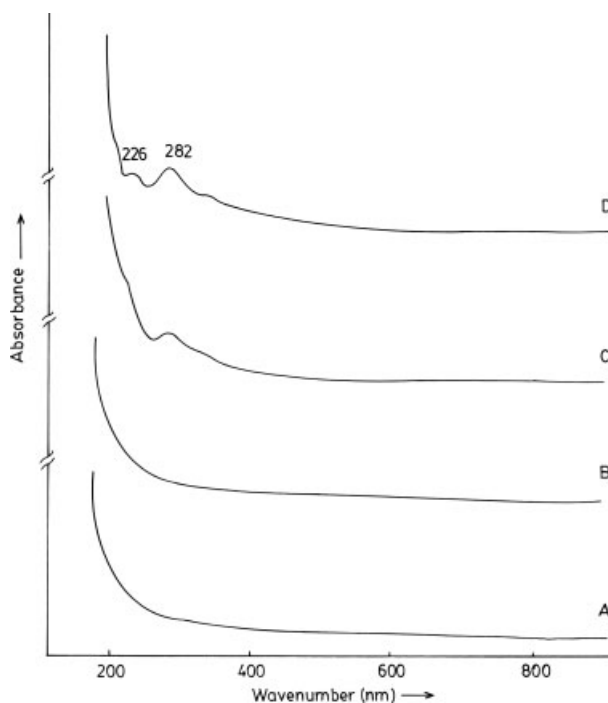
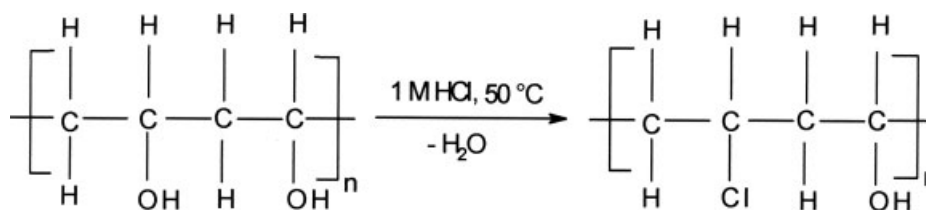


Figure 4 UV/visible spectrum of (A) PVA [W] film, (B) PVA [H], (C) PVA [W] film irradiated by γ -rays at 100 kGy, and (D) PVA [H] film irradiated by γ -rays at 40 kGy.



Scheme 1 Partial chlorination of PVA molecule.

place when PVA is dissolved in 1M HCl when compared with that dissolved in water alone. Therefore, we propose that when PVA is dissolved in 1M HCl, it gets modified by replacement of some of the $-\text{OH}$ groups with $-\text{Cl}$ atoms available from the surrounding HCl. Thus the reaction is expected as shown in Scheme 1.

Further when this chlorinated PVA is exposed to γ -rays for the dose of 40 kGy it liberates HCl as shown in Scheme 2.

This mechanism helps us to understand how certain ions liberated during irradiation assist in protonation processes. It is to be anticipated that the liberated HCl will help in protonation of EB form of PANi in to ES form as shown in Scheme 3. Thus these reaction schemes allow us to understand the significant color changes from blue to green observed in PVA/PANi films after irradiation.

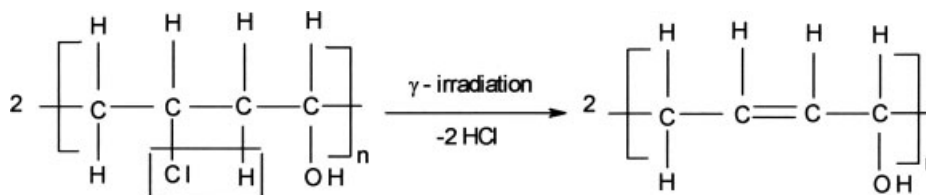
Infrared spectroscopy

Typical FTIR spectra for PVA samples are shown in Figure 5 covering the region $400\text{--}4000 \text{ cm}^{-1}$. The peak positions corresponding to important chemical bonds in PVA are given in Table I.¹² The peak positions corresponding to certain important chemical bonds as reported by Kenny and Wilcockson are listed in column 2 of Table I.¹² The column 3 of Table I lists the positions of absorption bands observed in our samples of PVA.

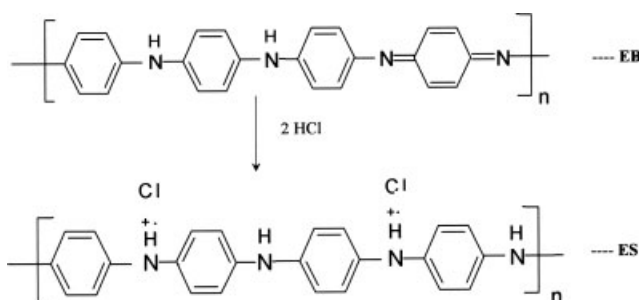
The FTIR study of PVA [H] and PVA + 5% PANi samples was also carried out to understand the transformation of color and structure. Typical FTIR spectra for PVA [H] and PVA + 5% PANi samples are shown in Figure 5 covering the region $400\text{--}4000 \text{ cm}^{-1}$. Two new peaks were observed in the FTIR

spectra of composite films at 1506 and 1587 cm^{-1} due to benzoid and quinoid structures, respectively (shown in Scheme 3).¹³ The relative intensities of these two peaks can be used to determine the relative number of these groups or rather the degree of oxidation. In the FTIR spectra of green film of PVA + 5% PANi there is absorption band corresponding to benzoid only at 1506 cm^{-1} (Fig. 5, curve C). When the film was converted to blue by reaction with 1N NH_4OH the absorption peaks due to both benzoid and quinoid were present due to conversion of ES to EB form (Fig. 5, curve D) (EB contains both benzoid and quinoid rings as shown in Scheme 3). However it can be clearly seen that when the blue colored film was irradiated by γ -rays the intensity of the band at 1587 cm^{-1} due to quinoid ring decreased (Fig. 5, curve E). These observations suggest that EB form of PANi present in blue-colored composite film gets converted to ES form, rendering the film green color. This observation is also supported by UV/vis spectrophotometric studies.

Now it is interesting to see the changes that take place when the composite of PVA + PANi is prepared and converted to blue color and then irradiated with gamma radiation. For the clarity of understanding the earlier work for PANi powder prepared by standard method can be referred.⁸ We recorded the FTIR spectra of green PANi powder, obtained in our investigations, which showed a broad peak at 3421 cm^{-1} due to the $-\text{NH}$ stretching. When this sample was treated with 1N NH_4OH , the absorption band shifted to 3438 cm^{-1} and the intensity of the band increased significantly. To quantify the changes, the ratio of intensity with another standard band at 2925 cm^{-1} due to $-\text{CH}$ stretching was calculated and it was seen that the ratio



Scheme 2 Release of HCl from chlorinated PVA after γ -irradiation.



Scheme 3 Protonation of base form of PANI into salt form.

increased from 1.12 for green to 1.57 for the blue powder. By applying the same criterion for the PVA + PANi film, it could be seen in the present studies that the ratio was 0.5 for green film which increased to 1.0 for the blue. When the blue film was irradiated by γ -radiation to 50 kGy, it was noted that the ratio again fell to 0.78.

IR spectra are useful for determining the crystalline percentage of PVA. It has been shown in our earlier paper that the ratio of absorbance of bands at 1143 and 1432 cm^{-1} can be taken for calculating the percentage crystallinity.⁴ It can be seen that for samples of PVA alone when irradiated with gamma rays, there occurs decrease in the percentage crystallinity. Such method of calculation has been used for cellulose and polyester.¹⁴ The method is based on determining the ratio of absorbance of two bands in the IR region which are dependent on crystallization.

On the basis of assignments of the bands it was concluded that there occurs breaking of C—C and C—O bonds. Further intensity of absorption band at 1736 cm^{-1} , arising due to carbonyl bond (C=O), increases rapidly when PVA alone was irradiated with gamma rays.

X-ray diffraction studies

The change in the percentage crystallinity of the PVA films due to irradiation can be studied by the X-ray diffraction technique. Figure 6 shows the X-ray diffractograms for the PVA control, γ -irradiated PVA and PANi composites. Control PVA exhibits a typical peak at 19° assigned to diffraction from a mixture of planes with Miller indices (101) and (10 $\bar{1}$). It was seen that the intensity of this peak decreased gradually from the control to the irradiated ones.⁴ Additional new peaks appeared at 14° and 17° and their relative intensities went up with the increasing dose. This showed that structural rearrangements take place due to irradiation process. It was shown in our earlier paper that this occurs due to the breaking of —H and —OH bonds and rotation of the molecular chains.⁴ In case of PVA + 5% PANi composites some interesting observations were made. The composite made by standard method that is green in color shows that there is only one peak at 19.2° due to PVA (the peaks at 14° and 17° were absent) and three low intensity peaks at 21.4°, 23°, and 25° due to PANi appeared.¹⁵ When this film was deprotonated to blue using 1N NH_4OH , it was noted that the main peak shifted to

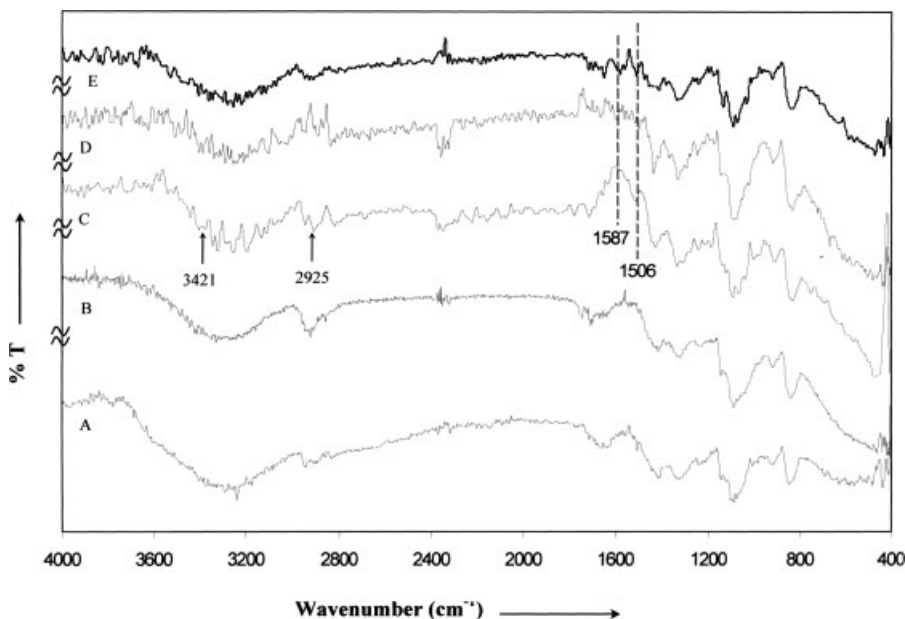


Figure 5 ATR spectra of (A) PVA (H), (B) PVA (H) irradiated by γ -rays for 50 kGy, (C) PVA + 5% PANi green film, (D) PVA + 5% PANi blue Film, and (E) PVA + 5% PANi irradiated by γ -rays for 50 kGy film.

TABLE I
FTIR Absorption Bands of PVA Films

Assignment	Wavenumber as per Ref. 12 (cm ⁻¹)	Wavenumber observed for our sample (cm ⁻¹)
OH stretching	3340	3330–3340
CH ₂ stretching	2942	2940
C=O	–	1736
CH ₂ bending	1430	1432
C–C and C–O–C stretching	1141	1143
C=O stretching	1096	1096
CH ₂ rocking	916	922
C–C stretching	850	849

19.1° and the peaks due to polyaniline also shifted to slightly lower angles. For dosimetric studies, when the blue film was irradiated with γ radiations, it was seen that the main peak shifted to 20.4° and peaks at 15° and 17.3° developed in similarity to our previous studies on irradiated PVA films. In addition the peaks at 22°, 23.6°, and 25.6° could be seen with sufficient intensity and resolution and are on account of presence of PANi. On closer examination it was seen that all these peaks had shifted somewhat to higher angle side meaning thereby that the interplanar distance decreased. This observation is in conformity with earlier studies.¹⁵ The mechanism of such changes can be explained as follows: The polymerization of aniline in the PVA matrix gives rise to some crosslinking of PVA chains by PANi. In addition, during polymerization of aniline, it gets doped with chlorine ions as shown in Scheme 3. This is the ES form and has green color. When it is reduced by ammonium hydroxide, it goes into the EB form with the removal of chlorine ion. Further, under the action of radiation crystallization occurs and therefore there is movement of chains of PVA as well as PANi. These structural changes are manifested and are evident in X-ray diffraction as well as in electron microscopic studies.

The percentage of crystallinities of all these samples were calculated using the method of area under the peaks and the values are given in Table II. Two types of calculations can be done—one by using the

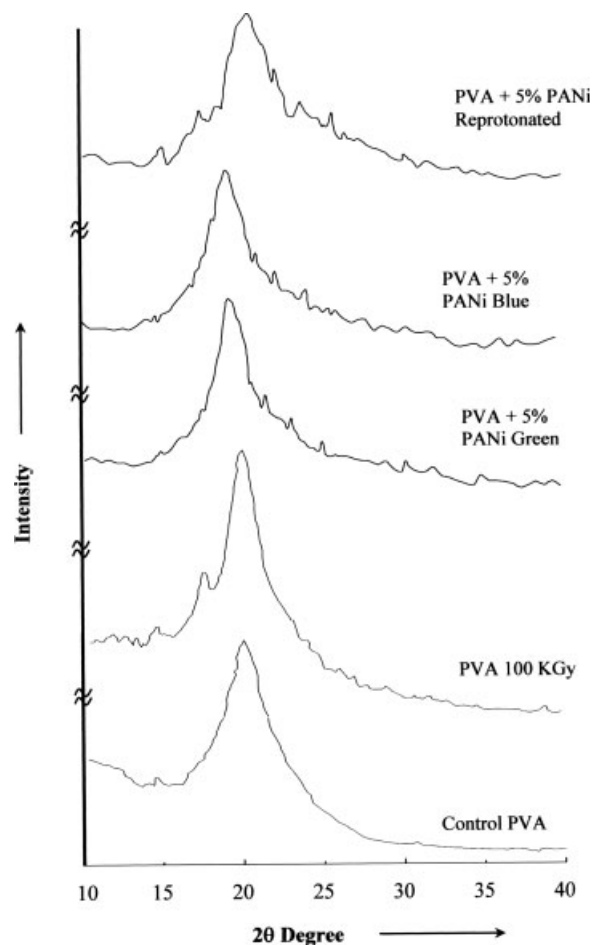


Figure 6 X-ray diffractogram of PVA and PVA + PANi films irradiated by γ -rays.

main peak at 19° and the other on the basis of new peaks appearing at 14° and 17°. The calculations based on peak at 19° were used during the present studies. It can be seen from Table II that in case of the composite films (green), transformation to blue-colored sample occurred with the decrease in percentage crystallinity. However, when it was irradiated there was an increase in the percentage crystallinity as shown in Table II. Thus it shows that the material having ES form has more crystallinity than the one containing the EB form.

TABLE II
Changes in the Percentage Crystallinity of PVA + 5% PANi Samples

Sr. no.	Sample description	Percentage crystallinity on the basis of main peak at 19°
1	PVA control film	64.8 ± 1
2	PVA γ -irradiated 50 KGy	61.7 ± 1
3	PVA γ -irradiated 100 KGy	59.5 ± 1
4	PVA + 5% PANi green	58.7 ± 1
5	PVA + 5% PANi blue	49.3 ± 1
6	PVA + 5% PANi B γ -irradiated 50 KGy	55.2 ± 1
7	PVA + 5% PANi B γ -irradiated 100 KGy	57.8 ± 1

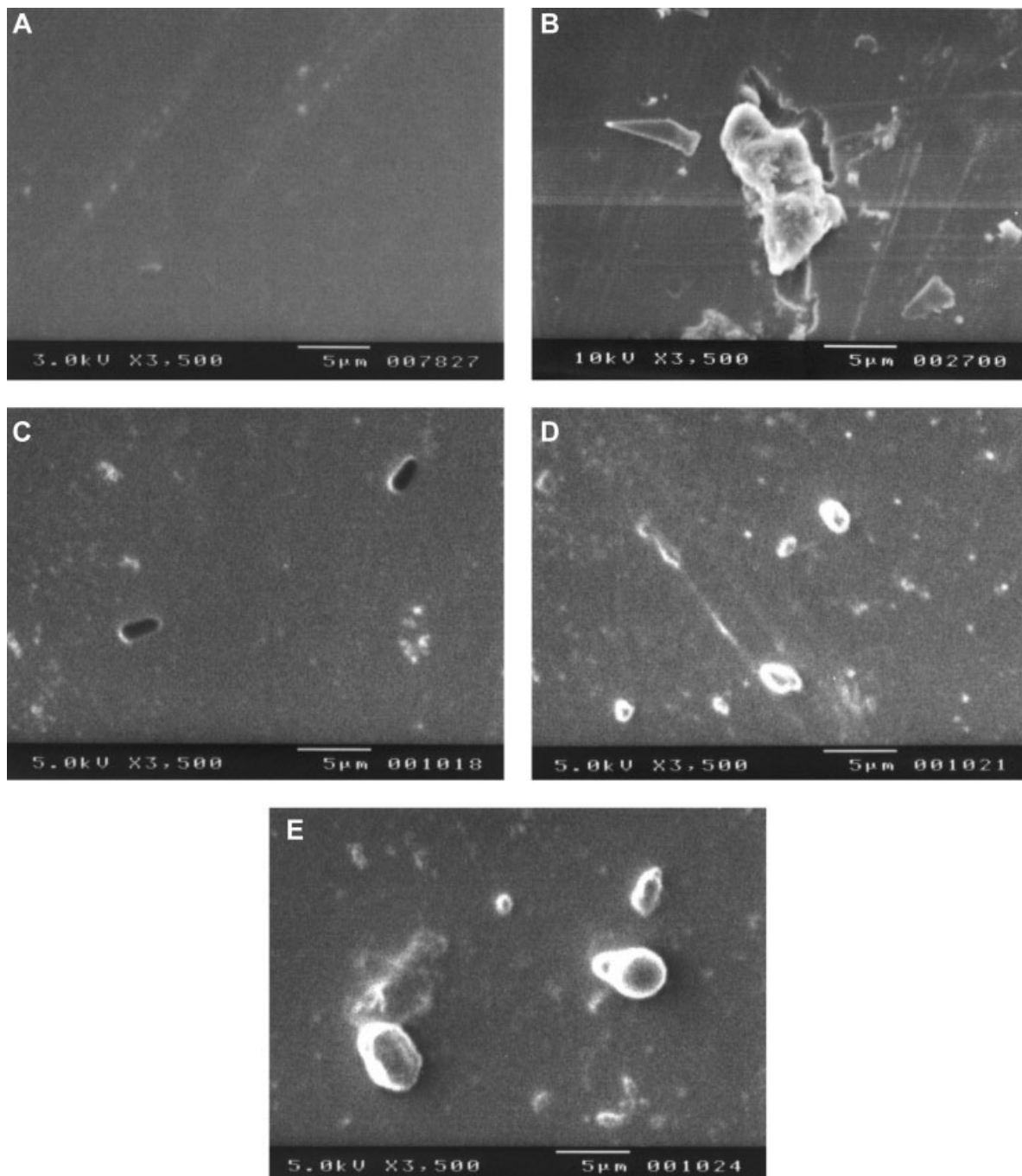


Figure 7 Electron micrographs of (A) control PVA, (B) PVA irradiated with γ -rays for 10 MRad, (C) PVA + 5% PANi green, (D) PVA + 5% PANi blue, and (E) PVA + 5% PANi blue after γ -irradiation for 50 kGy.

Morphological studies using SEM

Figure 7 shows SEM images of the (A) control PVA film, (B) control PVA irradiated with gamma, (C) PVA + 5% PANi composite film as green, (D) PVA + 5% PANi converted to blue, and (E) PVA + 5% PANi blue after γ -irradiation. In conformity with earlier reports, control PVA film has a smooth surface structure, which shows some granular structure after irradiation [Fig. 7(B)].⁴ The composite film of PVA + 5% PANi, green variety, shows some gran-

ules resembling oblong shape. In addition, the micrograph also shows some diamond/hexagonal shaped crystals [Fig. 7(C)]. On converting this film to blue variety we could infer through accurate measurements that these oblong structural features have grown in size. The average size increases from 0.33 to 0.65 μm . This is possibly due to the release of strain due to removal of chlorine ions. When the blue film was irradiated with γ -rays one could see from the micrograph [Fig. 7(E)] that there is a

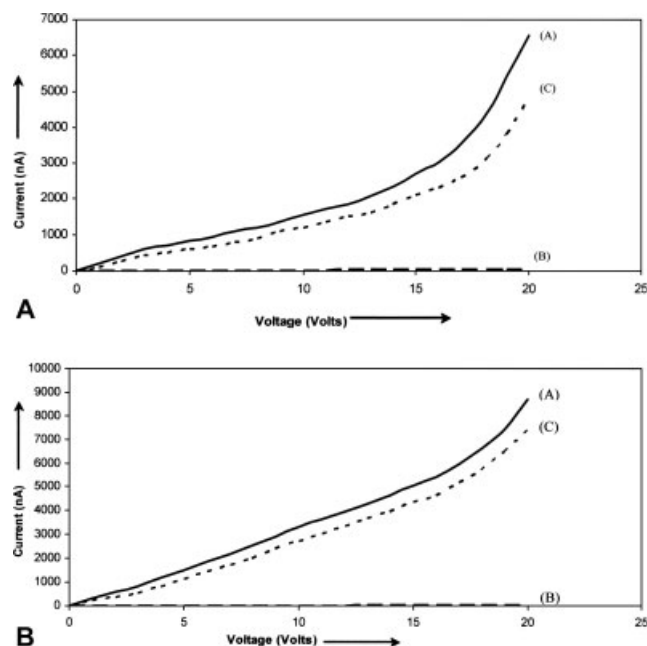


Figure 8 (A) I-V plot of PVA/PANi composite film with 2 wt % aniline with (A) green film, (B) film deprotonated with 1N NH_4OH , and (C) film reprottonated by γ -radiation. (B) I-V plot of PVA/PANi composite film with 5 wt % aniline with (A) green film, (B) film deprotonated with 1N NH_4OH , and (C) film reprottonated by γ -radiation.

growth of some definite shape resembling single crystals (shown by arrow). It can be clearly seen that hexagonal crystals have increased in size for the films after the irradiation.

Thus it can be concluded that the changes in color are also accompanied by the morphological and structural transformations.

Studies of changes in electrical conductivity

The electrical conductivity of the films was studied by measuring current with voltage. Figure 8(A,B) shows I-V characteristics for PVA + PANi films with 2 and 5 wt % aniline, respectively. As shown in Figure 8 the increase in current was steady and slow up to 12 V and then it increased rapidly up to 20 V. Conductivity (σ) was calculated on the basis of I-V plot of low field region (0–12 V). Current of PVA/

PANi films with both concentrations of aniline, treated with 1N NH_4OH , was found to have decreased rapidly and was extremely small even at 20 V. Table III shows the conductivity of both the films (1) in their initial stages, (2) after treatment with 1N NH_4OH , and (3) reprottonated after treatment with γ -irradiation.

It can be seen from Table III that the conductivity of the green film, which is unexposed and immediately after preparation, has a value of 10^{-10} S/cm for 2 wt % aniline content. However, when the aniline content was increased to 5 wt % the conductivity increased to 10^{-9} S/cm. These green films of ES form, when converted to EB (blue) with treatment with NH_4OH , shows almost nonconducting form (conductivity 10^{-12} S/cm). When these blue colored films were exposed to γ -irradiation it was noted that there is a sudden increase in the electrical conductivity and it almost reached the value comparable to controlled green film. This increase in the conductivity when going from blue to the green form is due to the redoped state. It must be mentioned that the value of conductivity even after complete recovery of color (green) is still slightly lower than the controlled unexposed green films, which may be attributed to incomplete conversion to salt form.

CONCLUSIONS

On the basis of these studies it is found that PVA undergoes significant structural changes when PANi was blended to form the composite films of PVA/PANI. These films have green color, which could be changed to blue on reaction with NH_4OH . Such films when subjected to gamma irradiation could be reconverted to the original green color on account of liberation of HCl from the PVA host polymeric film. Thus it is found that the PVA + PANi composite films can be used as plastic dosimeter as the color of the film changes due to γ irradiation. Electrical conductivity was also found to have decreased when transforming from ES to EB state. After irradiation the reversion to ES state enhances the conductivity again. Therefore, the changes in color and

TABLE III
Conductivity of PVA/PANi Composite Films

Status of PVA/PANi composite film	Conductivity of films (S/cm)		
	Green colored film (Unexposed) (1)	Blue colored film (Treated with 1N NH_4OH) (2)	After γ -irradiation of blue colored film (3)
With 2 wt % aniline	5.9×10^{-10}	5.3×10^{-12}	2.8×10^{-10} for 50 KGy 3.9×10^{-10} for 100 KGy
With 5 wt % aniline	1.26×10^{-9}	5.7×10^{-12}	1.04×10^{-9} for 50 KGy 1.14×10^{-9} for 100 KGy

electrical conductivity can be used for the purpose of dosimetry.

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