

Synthesis of Chitin-Polyaniline Nanocomposite by Electron Beam Irradiation

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ABSTRACT: In this article, we report a novel method to synthesize polyaniline (PANI) nanocomposite. Chitin and PANI are dissolved in a common solvent, *N,N*-dimethyl acetamide, with 5% LiCl, and the solution is irradiated with 8 MeV electron beam for different doses, nanoparticles of PANI in chitin is obtained. The characterization of the composite was done by UV-vis absorption spectrum, FTIR, thermogravimetric analysis (TGA), X-ray diffraction, scanning electron microscopic (SEM), and DC conductivity studies. UV-vis studies show conversion of emeraldine base form to leucoemeraldine base. FTIR

studies show interaction between chitin and PANI. SEM analysis of irradiated composite shows formation of PANI particulates. Average particle size varies from ≈ 40 to ≈ 1000 nm. DC conductivity of blend improves on irradiation. One-dimensional variable range hopping conduction mechanism is dominating in the irradiated blend. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 623–633, 2011

Key words: nanocomposite; conducting polymer; polyaniline; chitin

INTRODUCTION

Polyaniline (PANI) has emerged as one of the most promising conducting polymers, because of its wide spread applications and due to the combination of unique properties such as simple preparation and doping procedure, good environmental stability, and relatively high conductivity and low cost. Unfortunately, poor processability and mechanical properties hinder its potential applications.¹ Several methods have been reported to improve the processability and mechanical properties, such as electrochemical polymerization of aniline in polymer matrix,^{2,3} increasing the molecular weight,⁴ synthesis of PANI in the presence of preformed stable colloidal particles to give conducting polymers,⁵ and blending with other polymers in a cosolvent. The interesting applications of PANI have motivated investigators to study its mechanical properties, thermostability in conductivity, its processability, and so forth, and its use in polymer composites or blends with common polymers. From the technological point of view, these materials are very interesting,

because they combine the electronic conduction of conducting polymer and desired mechanical properties of the insulating polymer.¹

PANI is a high-molecular weight conducting polymer and its general structure is given in Figure 1(a). Depending on the oxidation level, PANI exists in different forms, namely fully reduced leucoemeraldine base (LEB), the half-oxidized emeraldine base (EB), and fully oxidized pernigraniline base. Among these three forms, EB is the most stable and widely investigated polymer. Its conductivity can be tuned via doping from 10^{-10} S/cm up to 100 S/cm and above. The EB form consists of equal number of reduced and oxidized repeating units [see Fig. 1(c)]. By protonic doping the conducting emeraldine salt form is achieved as shown in the Figure 1(d).^{6–10}

Chitin is a natural polysaccharide composed mainly of β -(1 \rightarrow 4) linked 2-deoxy-2-acetamido-D-glucopyranose and partially of β -(1 \rightarrow 4) linked 2-deoxy-2-amino-D-glucopyranose.^{11–13} The structure of chitin is shown in Figure 2. It is the second most abundant natural polymer after cellulose, commonly found in exoskeletons or cuticles of many invertebrates and in the cell walls of most fungi and some algae. It is usually obtained from the shells of shellfish, crab, lobster, or shrimp. Chitin and its deacetylated form have attracted great attention because of their several important advantages such as biocompatibility, biodegradability, high mechanical strength, and nontoxicity.^{11–15}

Nowadays, radiation processing of polymer has gained lots of interest due to its potential applications in various fields. A very few reports are

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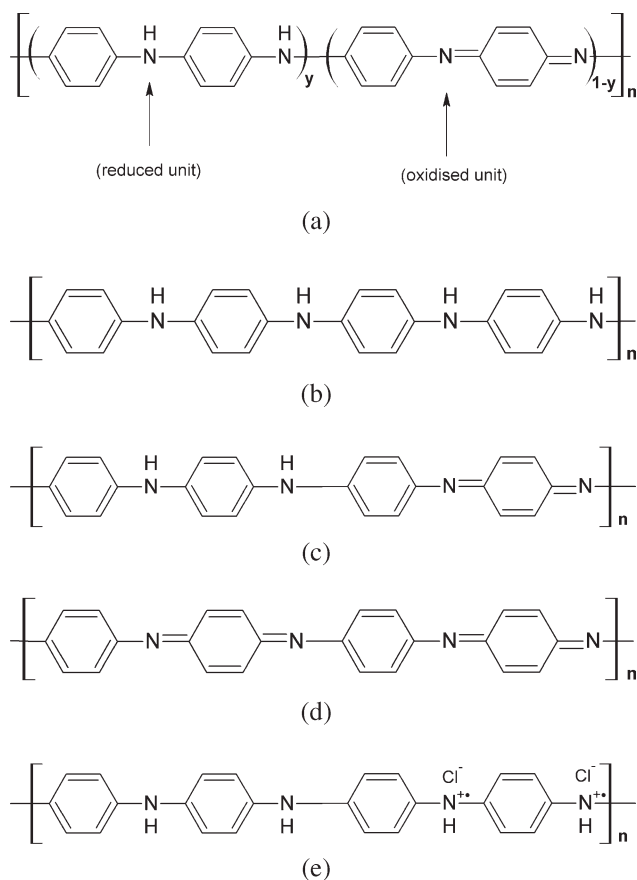


Figure 1 (a) General structure of polyaniline. (b) Structure of LEB. (c) Structure of EB. (d) Structure of PEB. (e) Structure of PES.

available on the radiation processing of PANI and its blends. The conductivity of PANI/PVC blend is increased on irradiating with γ -ray and high energy electron beam due to *in situ* doping.¹⁶ Morphology studies of gamma-irradiated PANI nanofilms have been carried out by Laranjeira et al.¹⁷ Gamma ray irradiation of PANI solution has been reported by Wolszczak et al.⁹ In this article, the results of electron beam irradiation of chitin/PANI blend in solution are presented. In addition to this, e-beam irradiation of EB solution is carried out for comparison. Irradiated samples are characterized by UV-vis, FTIR, X-ray diffraction (XRD), scanning electron microscopic (SEM), and conductivity studies.

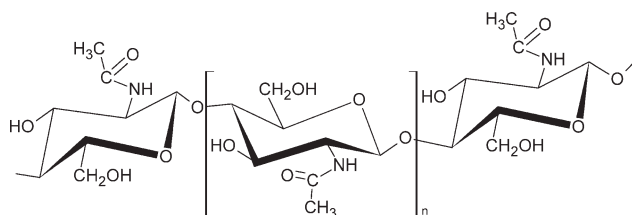


Figure 2 Structure of chitin.

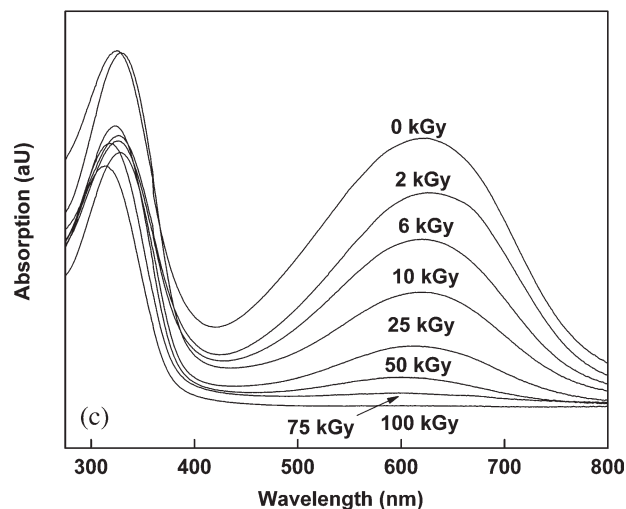
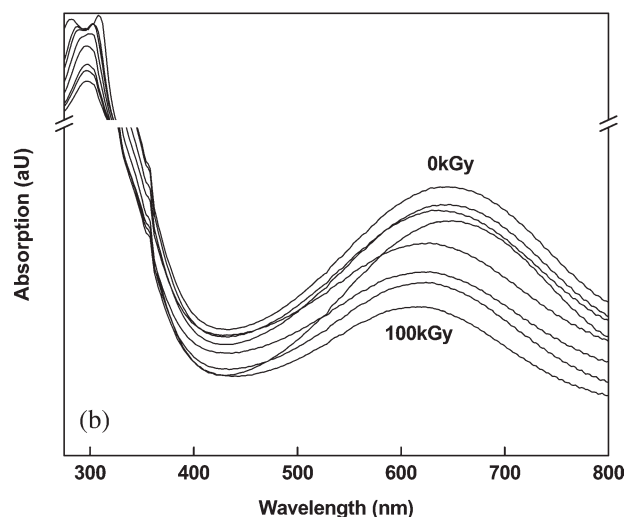
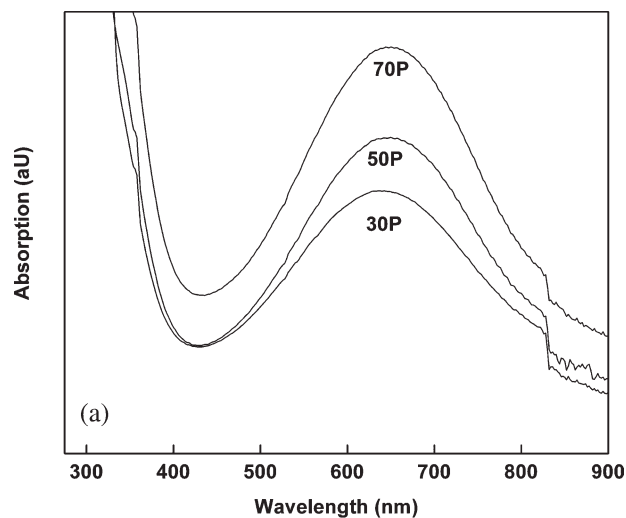


Figure 3 (a) UV-vis spectra of chitin-polyaniline blends. (b) UV-vis spectra of 30P blend irradiated with different doses. (c) UV-vis spectra of EBS irradiated different doses.

TABLE I
Percentage of Conversion of EB to LEB with
Irradiation Dose

Dose (kGy)	LEB (%)			
	30P	50P	70P	100P
0	0	0	0	0
1	2.9	7.3	9.7	12.4
2	5.4	9.4	14.8	19.2
4	7.9	12.8	22.4	29.2
6	13.3	21.6	29.7	33.8
8	31.3	32.0	35.1	45.4
10	32.6	35.6	41.3	56.2
25	45.4	49.7	64.6	72.8
50	57.2	62.1	75.1	88.4
75	63.8	73.5	86.3	94.2
100	70.1	81.7	92.8	99.1

EXPERIMENTAL

Materials and chemicals

Chitin from HIMEDIA, Mumbai, with molecular weight 400,000 g/mol, *N,N*-dimethyl acetamide (DMA; AR grade) and LiCl (AR grade) from SRL, and ammonium peroxy disulphate (APS; GR grade) from MERCK were used as received. Aniline GR grade from MERCK was distilled under reduced pressure before use.

Preparation of PANI

PANI is prepared by chemical oxidative polymerization of aniline by APS in aqueous acidic medium as reported by MacDiramid and Epstein.¹⁸ Aniline (0.25M) is prepared in 1M HCl, and it is cooled to 0–5°C. Precooled 0.25M APS solution in 1M HCl is added dropwise with in 20-min interval, and reaction mixture is maintained at 0–5°C with stirring for 1 h and is taken out of the ice/water bath and again stirred for 3 h. The green precipitate of PANI is filtered and washed with 1M HCl and then with deionized water and finally with acetone, dried for 24 h at 60°C. Thus, obtained green flakes of PANI is powdered and treated with 0.5N NaOH solution for 16 h to get EB. Resultant EB powder is washed with water until it is neutral. Viscosity average molecular weight of polymer is found to be 1.03×10^5 g/mol.

Preparation of nanocomposite

Blends of chitin and PANI with PANI 30, 50, and 70% (30P, 50P, and 70P) were prepared by mixing 0.5% (wt %) chitin solution and 0.5% (wt %) EB solution in DMA with 5% LiCl in required proportions. Details of blend preparation are reported in our earlier publications.^{6,7} So, obtained blend solution

was irradiated with electron beam at Microtron center, Mangalore University. Specifications of electron beam used for irradiation is as follows, beam energy 8MeV, beam current 25–30 mA, pulse repetition rate 50 Hz, pulse width 2.5 μ s, dose rate of 60 kGy/h (Fricke dosimetry) and sample is kept at a distance of 30 cm from the target. During irradiation, the

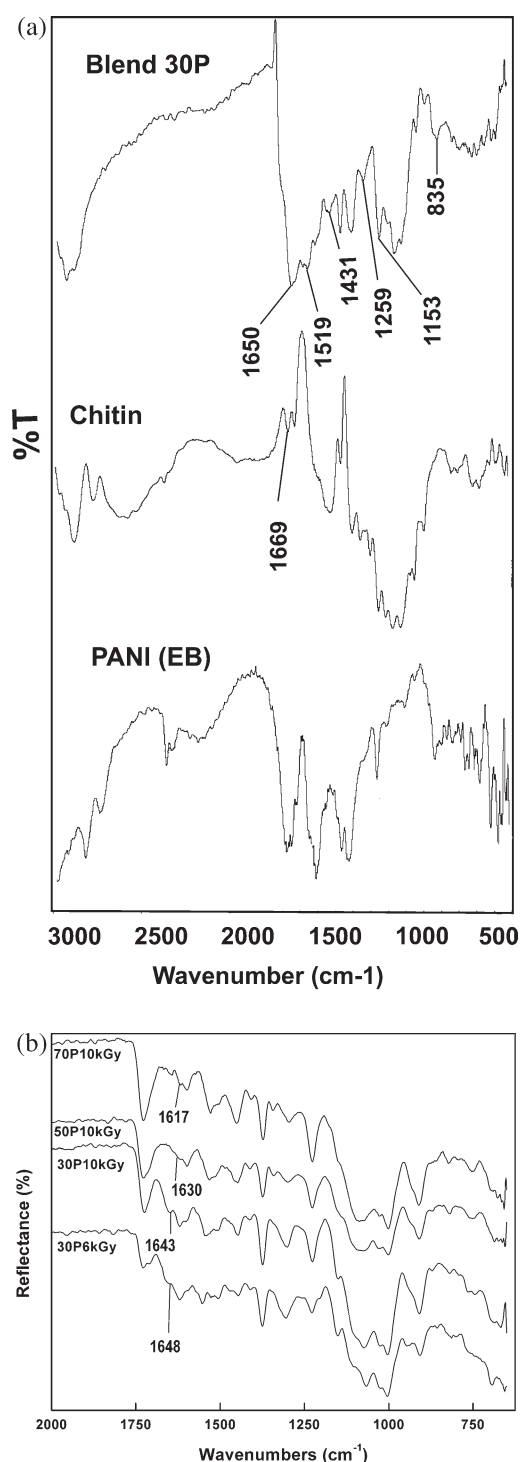
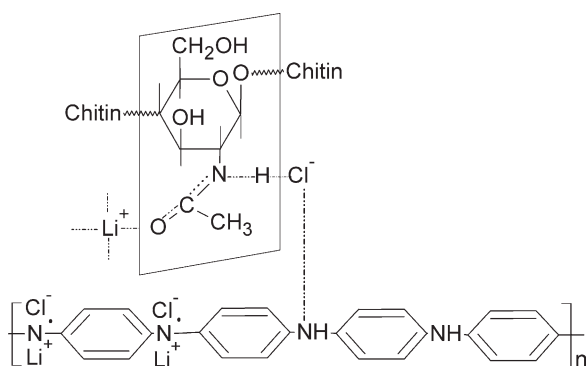


Figure 4 (a) FTIR spectra of PANI (EB), chitin and 30P blend. (b) FTIR spectra of irradiated 30P blend.



Scheme 1 Interaction between chitin and polyaniline.

color of the solution turned blue to brown and above 4 kGy, immediately after the irradiation of blend solution, brown particles were obtained at the top of the solution, and after 20–30 min these particles were uniformly distributed in solution. Irradiated solution was cast into films and used for further characterization. EB solution (EBS) in DMA is also irradiated for comparison. Irradiated PANI solution is dried at 60°C, and the powder thus obtained is used for further studies.

Physical characterization

The irradiated blend solutions were diluted, and UV–vis absorption spectra were recorded between 300–800 nm using Shimadzu spectrophotometer (model UV-3101 PC). FTIR spectra of the films were recorded between 4000 and 400 cm^{-1} with a resolution of 1 cm^{-1} , using Perkin-Elmer Spectrophotometer (model 1000) using the KBr pellet technique. Conductivity of various blend films was recorded by two-probe method using Keithley Electrometer (model 6517A). SEM photographs were taken for surface of samples coated with gold using SEM (Model: JEOL JSM 5800CV). XRD measurements were carried out using a Bruker D8 Advance X-ray diffractometer. The angular range was from 7° to 40° (2 θ). The operating voltage and current of the tube were kept at 40 kV and 20 mA, respectively, throughout the entire course of investigation. TGA was carried out using Perkin-Elmer, Diamond TG/DTA machine, in nitrogen atmosphere, from room temperature (25°C) to 600°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

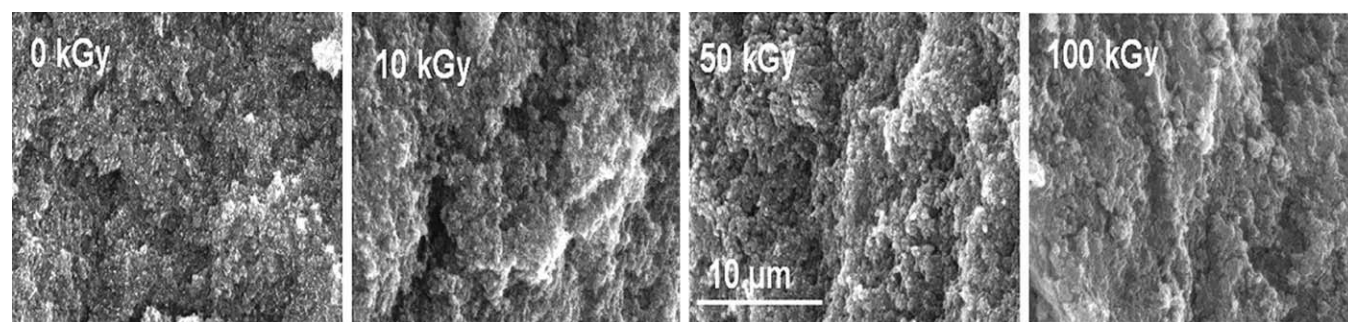
Figure 3(a) shows UV–vis absorption spectra of unirradiated chitin-PANI blend solutions. Absorption peaks are observed at ≈ 330 nm and ≈ 630 nm. These peaks are similar to the absorption peaks observed for PANI, the absorption peak at ≈ 330 nm corresponds to π – π^* transition of the benzenoid ring. The peak at ≈ 630 nm is assigned to

polaron band transition. As the composition of the PANI in the blend increases, the polaron band transition absorption peak shifts to higher wavelength side. An additional absorption edge at ≈ 430 nm is observed for 70P, which also corresponds to polaron transition.^{1,6,7,19} The red shift and absorption shoulder at ≈ 430 nm clearly indicate that as percentage of PANI increases, conductivity of the blend increases.

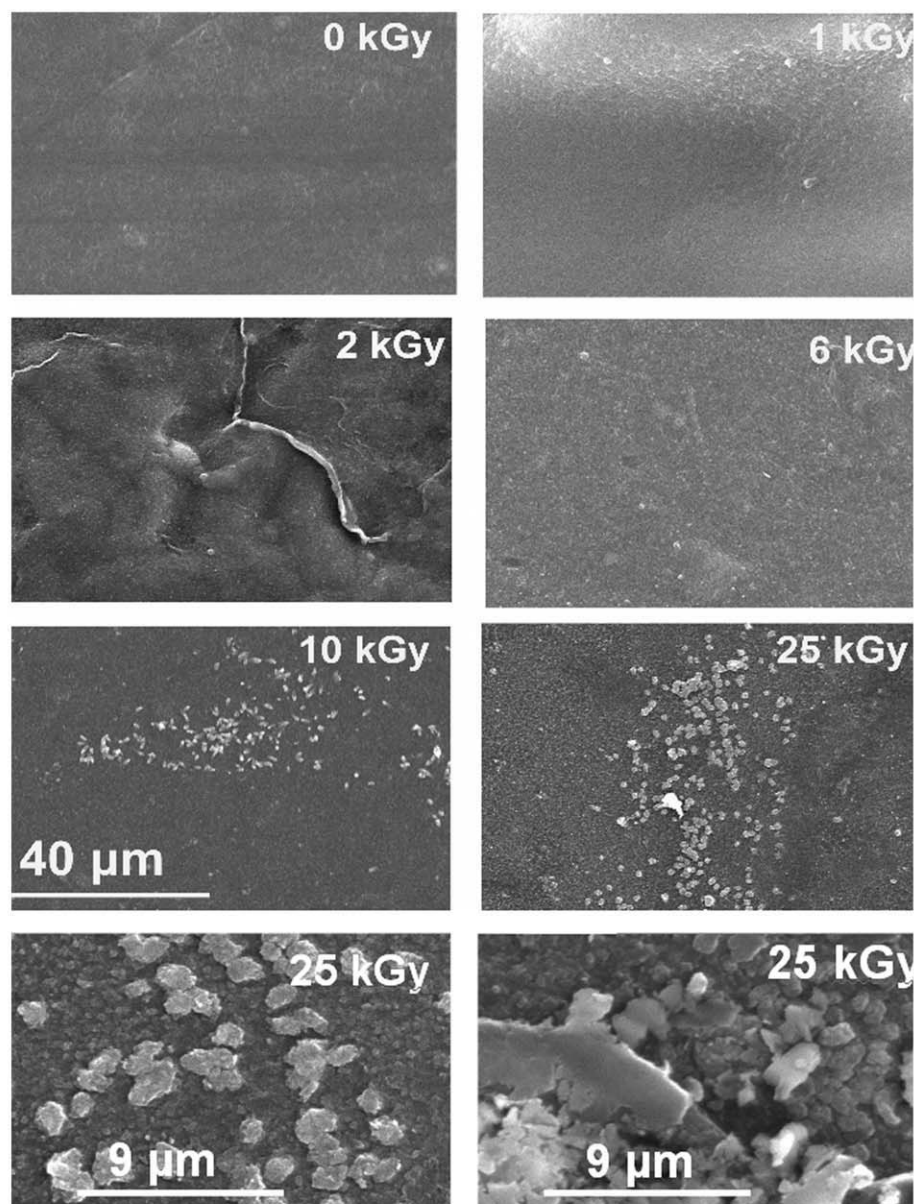
Figure 3(b,c) shows the UV–vis absorption spectra of irradiated chitin-PANI blend solution and irradiated EBS, respectively. For both blend and EBS, the intensity of absorption peak at ≈ 630 nm decreases as irradiation dose increases and shifts to lower wavelength side. This indicates the conversion of EB into LEB during irradiation. Further during irradiation color of the solution turns from blue to brown indicating the formation of LEB, because LEB is brown in color. Intensity of brown color increases with increase in dose. It has been reported that when EB solution in DMF is irradiated with gamma ray, it gets converted into LEB.⁹ Percentage of LEB present in different samples was calculated from the area under the 630-nm peak in UV–vis spectra, considering area under the 0 kGy peak as 100% EB. The percentage conversion of EB to LEB increases as the composition of PANI increases in the blend (Table I).

The IR spectrum of chitin-PANI blend shows significant peaks of both chitin and PANI [See Fig. 4(a)]. The peaks at ≈ 1519 , ≈ 1431 , ≈ 1259 , ≈ 1153 , and ≈ 835 cm^{-1} are characteristic of PANI.^{20–22} All other significant peaks are due to the presence of chitin in the blend. The band at ≈ 1519 cm^{-1} is attributed to the quinoid and benzenoid unit stretching modes of PANI, and band at ≈ 1153 cm^{-1} is attributed to quinoid unit-doped PANI.²⁰ In the IR spectrum of the chitin, the peak is observed at ≈ 1669 cm^{-1} , which is related to carbonyl groups.^{8,15} But in the case of blend, this peak is shifted to ≈ 1650 cm^{-1} . This is due to the interaction between chitin and PANI (Scheme 1).⁶ Figure 4(b) shows the FTIR spectra of irradiated chitin-PANI blend. It is found that after irradiation, the peak at ≈ 1650 cm^{-1} is shifted further to lower wavenumber. This shows that interaction is improved after irradiation.

Figure 5 shows SEM images of EBS and 30P blend irradiated with various doses of e-beam. The change in the morphology of EBS after irradiation may be due to crosslinking [see Fig. 5(a)]. This is confirmed from the dissolution study of irradiated EBS. The irradiated EBS powder did not completely dissolve in DMA, which shows that some degree of crosslinking might have taken place during irradiation. The insoluble fraction increased with radiation dose. Crosslinking of PANI powder on e-beam irradiation is reported in the literature.²³ Before irradiation,



(a)



(b)

Figure 5 (a) SEM images of irradiated EBS. (b) SEM images of irradiated 30P blends for different doses and last photograph is for 70P blend.

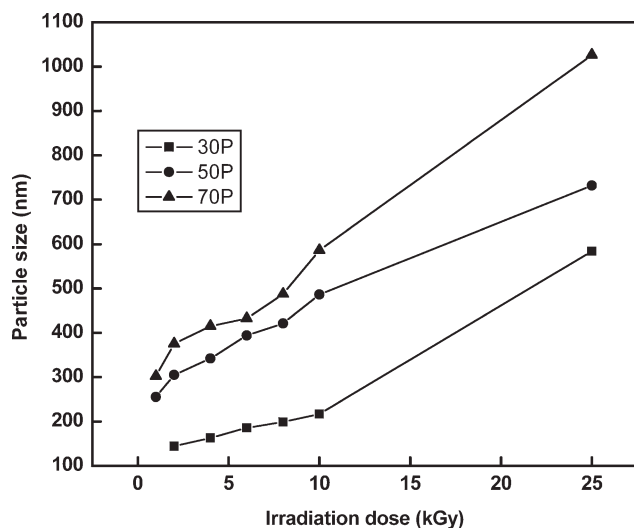


Figure 6 Variation of particle size with dose.

blend shows homogeneous and co-continuous morphology. When irradiated above 2 kGy, PANI particulate formation is observed. The particle size increases as the irradiation dose increases, and it

starts agglomerating above 10 kGy [Fig. 5(b)]. The particle size distribution is determined and average particle size is presented in the Figure 6. It is found that particle size distribution follows Gaussian distribution (Fig. 7). Further, in the case of 50P and 70P blends, formation of PANI particle is observed at lower doses and even particle agglomeration starts at lower dose compared with 30P blend. Particle distribution follows Gaussian distribution in the case of 50P (Fig. 8) and 70P blends also.

The mechanism of formation of PANI particle can be explained as follows: When chitin-PANI blend is irradiated with electron beam, energy is transferred to blend solution, and the following changes occur: (1) the chitin in the blend undergoes chain scission, which is confirmed from the decrease in the viscosity of the blend after irradiation (Intrinsic viscosity 5.6 and 2.3 dL/g for 30P blend before and after 100 kGy irradiation respectively). (2) EB form of PANI gets converted to LEB form. (3) When irradiation dose is sufficiently high, the interaction between chitin and PANI breaks, and PANI gets separated. Separated PANI gets crosslinked and comes out of the solution. This is

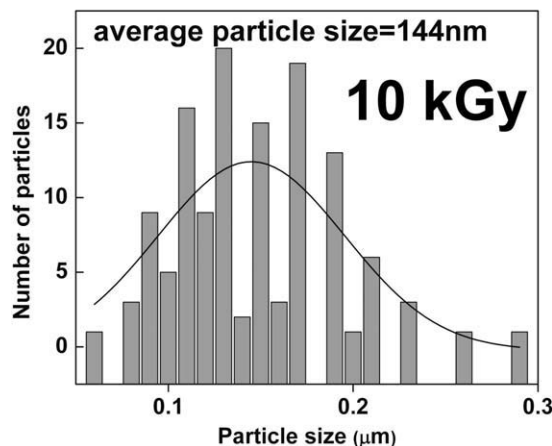
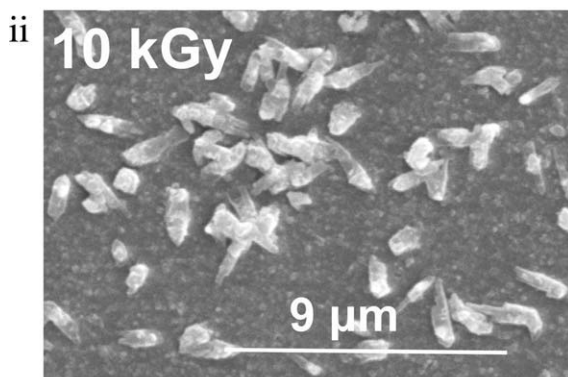
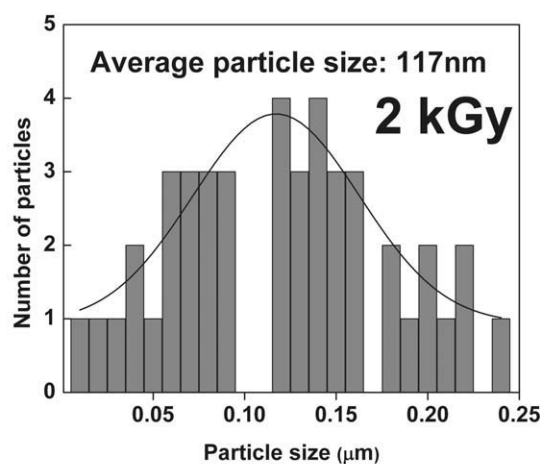
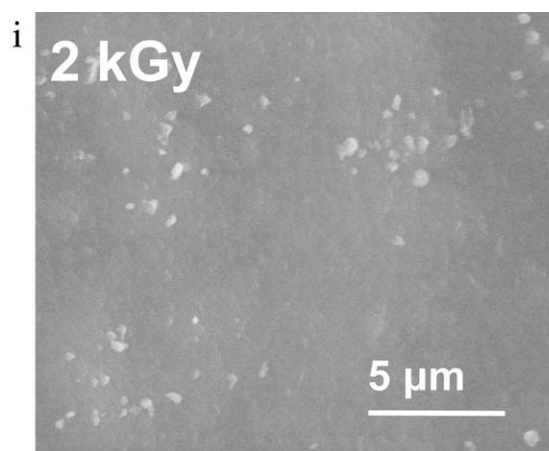


Figure 7 (i) SEM image and particle distribution for 30P2kGy and (ii) SEM image and particle distribution for 30P10kGy.

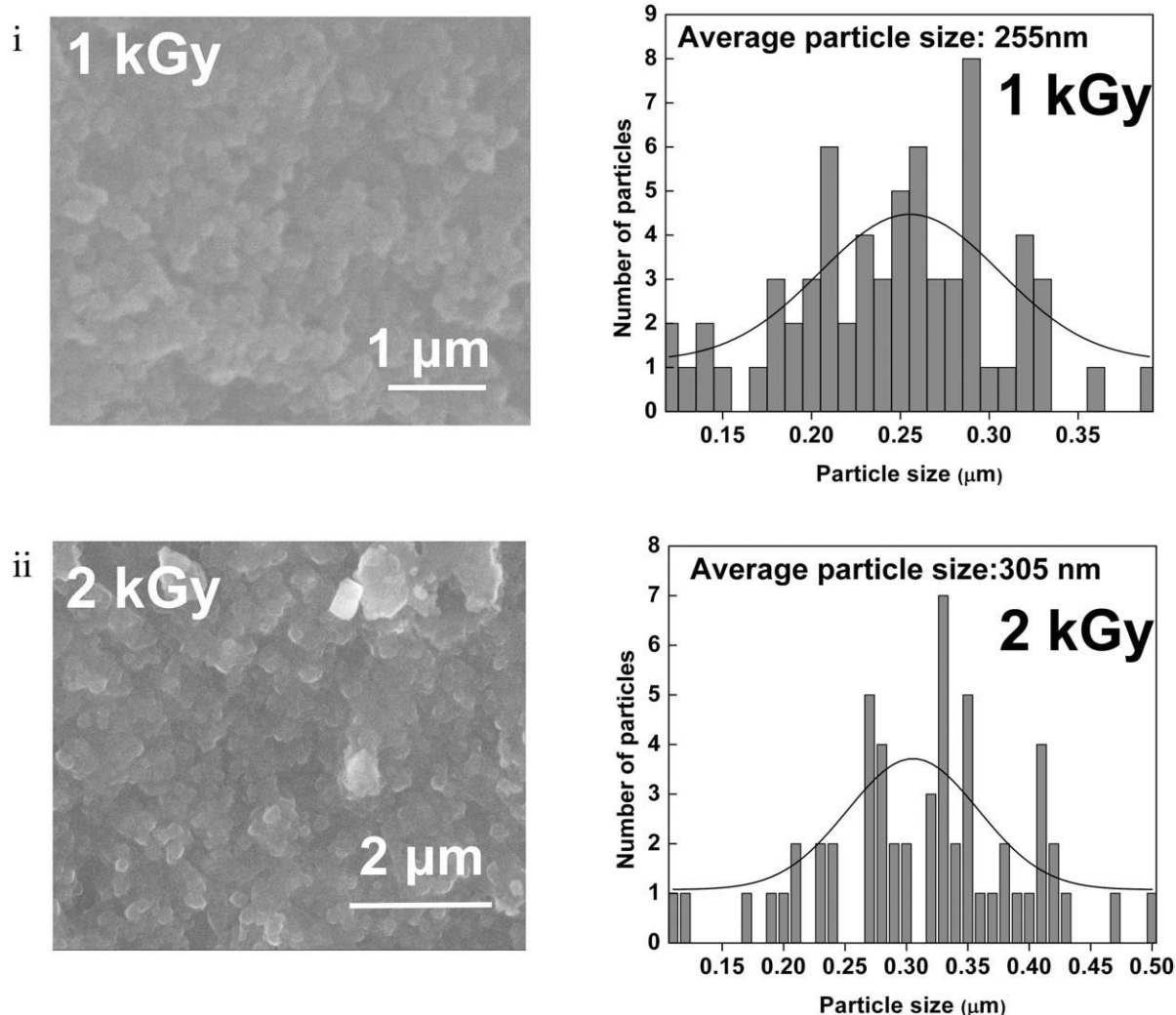


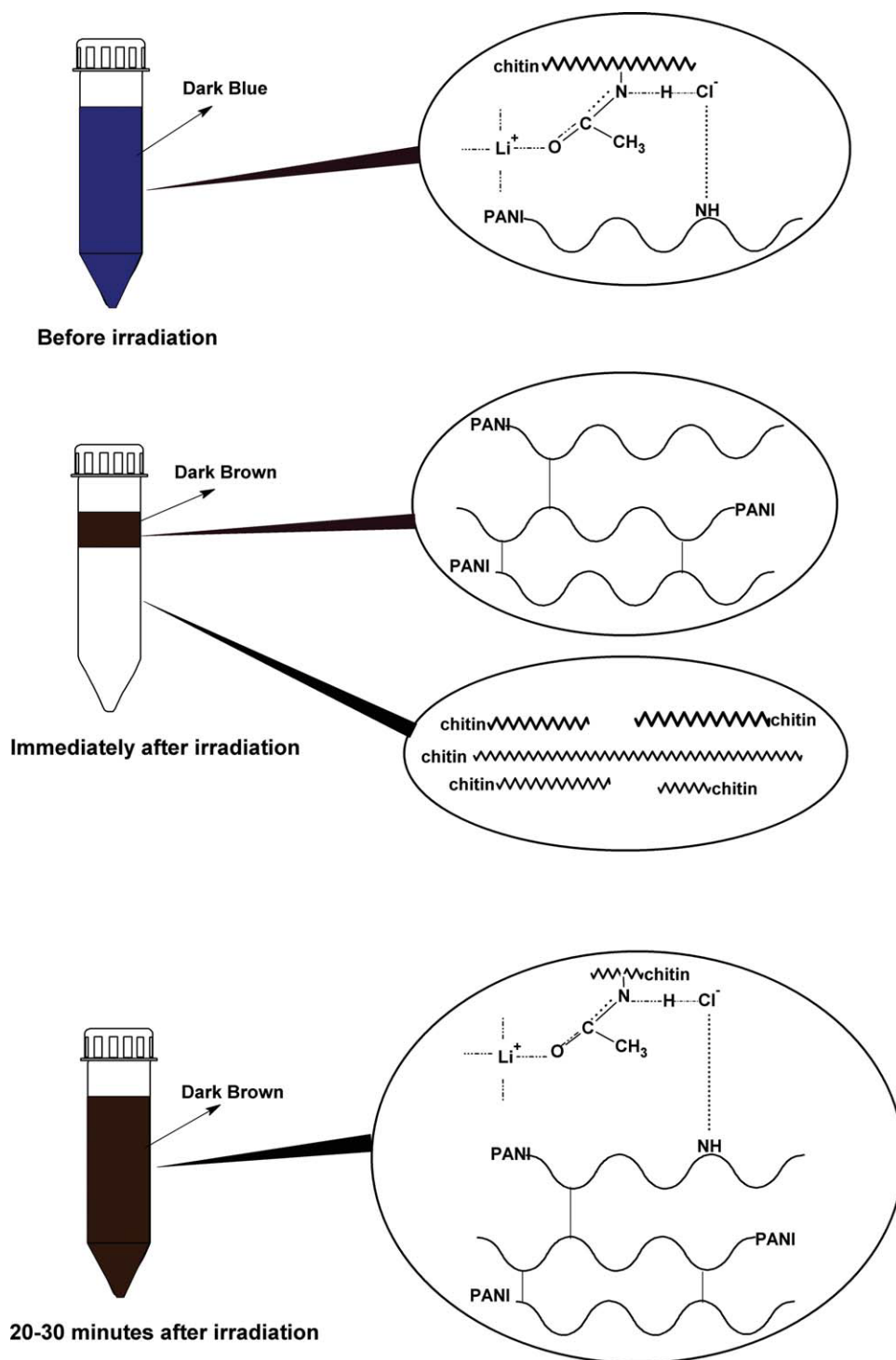
Figure 8 (i) SEM image and particle distribution for 50P1kGy and (ii) SEM image and particle distribution for 50P2kGy.

confirmed from the observation that soon after irradiation two layers are observed, with upper layer brown in color and lower layer colorless. But within a time gap of 20–30 min, the layers vanish and a uniform dispersion is obtained (Scheme 2). This is due to the re-establishment of interaction between chitin and PANI, as evidenced from the FTIR spectra. As the irradiation dose increases, because of the chain scission of chitin, viscosity of solution decreases. Because of the decrease in viscosity, the PANI particles formed cannot remain separated and get agglomerated at higher doses. Same explanation holds good for higher compositions of PANI blends.

XRD analysis of irradiated blend films and EBS are carried out and is presented in Figure 9. Characteristic peak of PANI is observed at $2\theta \approx 19.8^\circ$. A small broadening of this peak in irradiated EBS [Fig. 9(a)] indicates that the more amorphous nature of PANI due to the formation of crosslinks during irradiation. In the case of blends, the intensity of peak reduces and broadening of peak takes place as the

irradiation dose increases. This can be attributed to the crosslinking and formation of PANI particles during irradiation. In Figure 9(b) for 2 and 10 kGy, intensity of peak reduces but for 25 kGy intensity of peak increases. This may be due to the agglomeration of PANI particle or chain scission of chitin at higher doses, which increases crystallinity of the blend. Even for other compositions of blend, same trend is noticed, which is presented in the Figure 9(c).

Figure 10 shows thermogravimetric analysis (TGA) thermograms of EBS and 30P blend irradiated with various doses of electron beam. Initial weight loss is due to the residual solvent present in the both EBS and blend films. EBS becomes more stable after irradiation due to crosslinking. Blend is stable up to 250°C , and then it undergoes degradation. The stability of the blend increases up to 10 kGy and then decreases. The increase in stability is due to the crosslinking of PANI and, at higher doses, the chain scission of chitin in the blend is more, hence thermal stability of blend decreases.



Scheme 2 Effect of irradiation onto chitin and polyaniline blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DC electrical conductivity values of various blend films are recorded by two probe method using Keithley electrometer (model 6517A). Conductivity of various irradiated blend compositions and irradiated EBS are presented in the Figure 11. No significant change in the conductivity is observed in EBS after irradiation. Conductivity of various irradiated

blend compositions is shown in the Table II. The conductivity of unirradiated blend films increase as the composition of PANI increases in the blend. That is reported in our earlier publication.⁶ This is because of more and more LiCl gets doped with PANI from the LiCl used as solvent for chitin. Doping of EB with LiCl is already reported by Saprigin

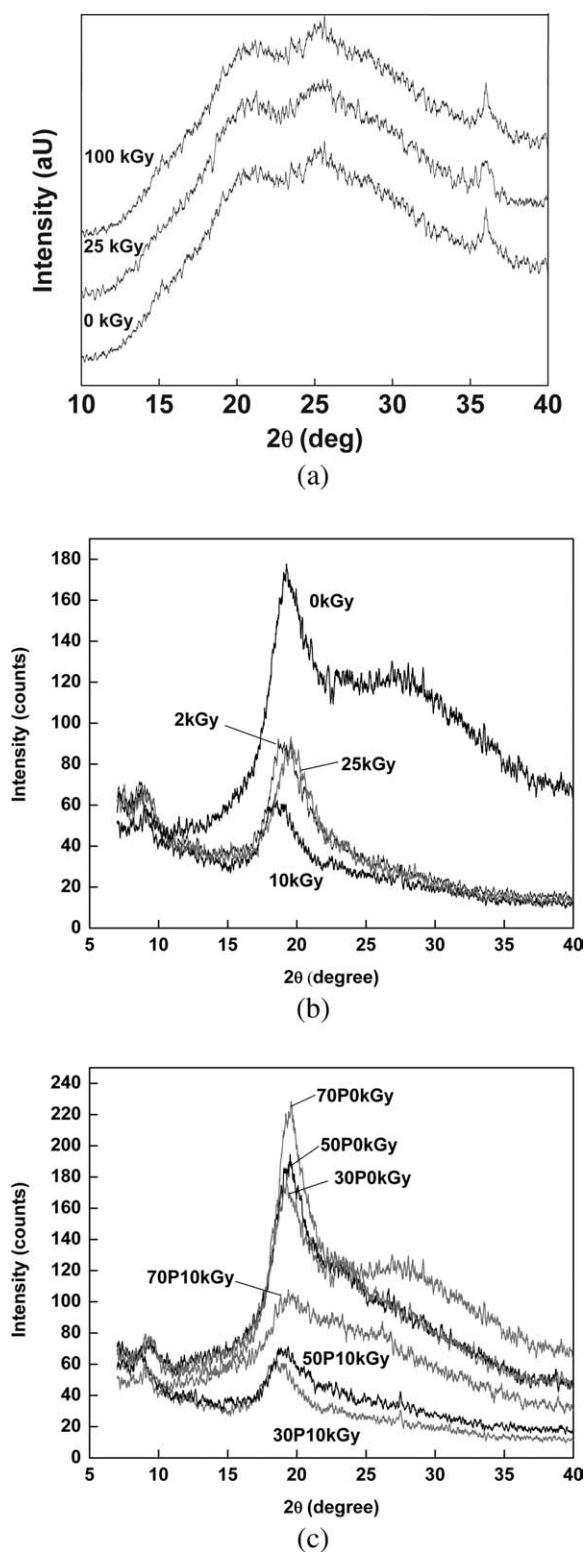


Figure 9 (a) XRD of irradiated EBS. (b) XRD of 30P irradiated blend. (c) XRD for various blends.

et al.,^{24,25} and they obtained the maximum conductivity of the order of 10^{-8} S/cm. In the present case, highest conductivity obtained for unirradiated blend is 2.15×10^{-5} S/cm. This is due to the interaction

between chitin-PANI, which is reported in our earlier publication.⁶ On irradiation, the conductivity increases further and highest conductivity is found to be 2.36×10^{-4} S/cm. This is due to more and more delocalization of charge carriers during irradiation. Further, it should be noted that conductivity in the case of 50P and 70P blends, initially increases with increase in dose and then starts decreasing (Fig. 11). During irradiation, as the composition of the PANI increases in the blend, the percentage of conversion of EB to LEB is more (Table I). But the self-doped (Li^+) LEB is less conducting compared with self-doped EB, and, therefore, conductivity starts decreasing at higher dose. It has been reported that LEB is not so conducting as that of EB form. In addition to this, we have doped these irradiated

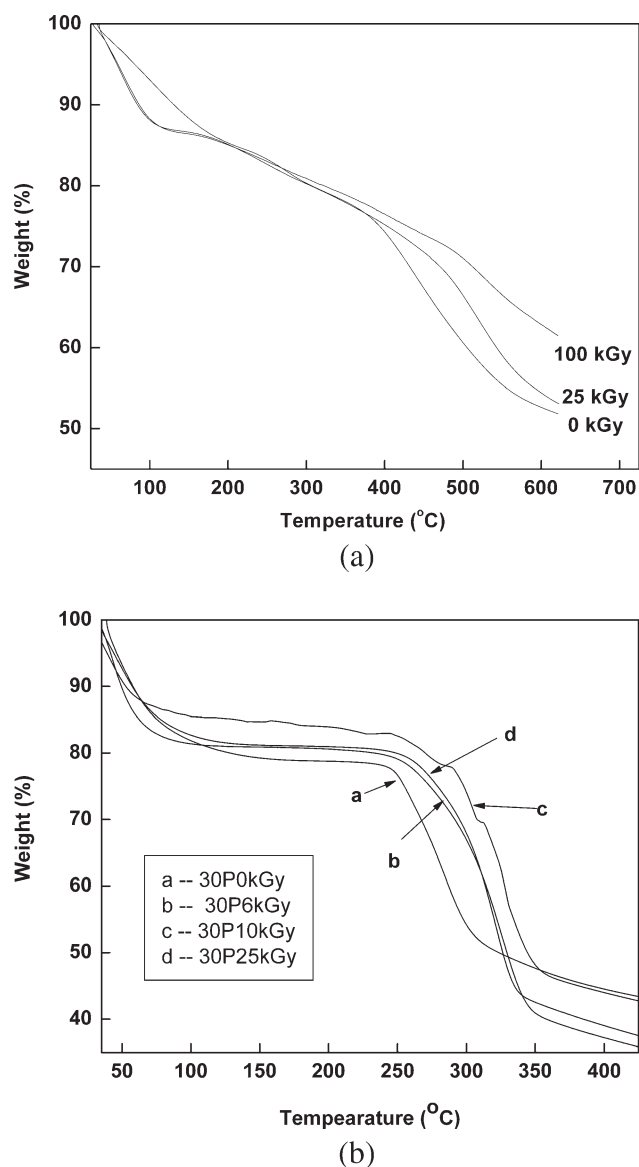


Figure 10 (a) TGA for irradiated EBS. (b) TGA for 30P irradiated blend.

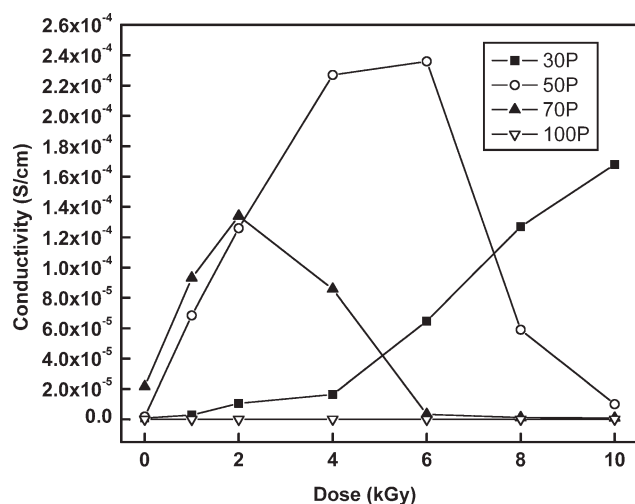


Figure 11 Variation of conductivity with dose for different blends.

blends with 1M HCl. A small amount of increase in the conductivity is observed depending on the percentage of EB form present in the blend (Table II). Unirradiated doped blend shows a DC conductivity of 4.72×10^{-2} S/cm.⁶ Thus, it can be concluded that electron beam irradiation can be used as an alternate method to protonic acid doping. Also it should be noted that irradiated blend films are flexible whereas protonic acid-doped irradiated films are brittle and are difficult to handle. The conductivity attained after irradiation is sufficient to make them interesting materials. 70P-irradiated blend on doping becomes brittle, and, hence, conductivity measurement was not carried out.

In addition to DC conductivity measurements, conduction mechanism in the blend after irradiation is analyzed from the I - V characteristics of irradiated EBS and blends. For EB and LEB, one-dimensional

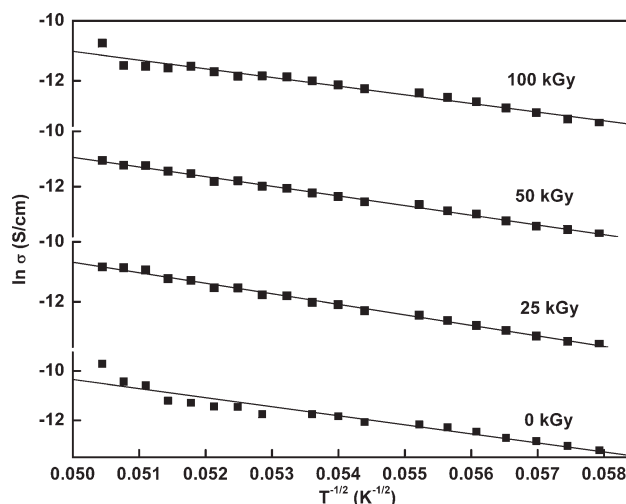


Figure 12 1D VRH plot for EBS.

variable range hopping (1D VRH) mechanism is well established in the literature.²⁶ Figure 12 shows 1D VRH plot for various dose, and it is linear through out the studied range of temperature. Hence in the case of EBS, 1D VRH mechanism is governing the conduction.

The conduction mechanism for unirradiated blends is discussed in our earlier publication,⁷ and it is well established that 1D VRH mechanism is dominating in the undoped blends, and it extends to higher dimension on doping, depending on the percentage of the PANI in the blend and doping time. Hence, irradiated blends are analyzed under the light of VRH mechanism. Figure 13 shows 1D VRH plot for the different irradiated blends. From figure one can see that 1D VRH mechanism is fitting well in the case irradiated blend also. Table III presents T_0 values calculated from the slope of the 1D VRH

TABLE II
DC Conductivity of Various Composites

Sample ID	DC conductivity (S/cm)	
	Undoped	1M HCl doped (24 h)
30P0kGy	8.3×10^{-7}	2.6×10^{-3}
30P1kGy	2.78×10^{-6}	1.22×10^{-5}
30P2kGy	1.05×10^{-5}	3.25×10^{-5}
30P4kGy	1.64×10^{-5}	3.10×10^{-5}
30P6kGy	6.47×10^{-5}	1.00×10^{-4}
30P8kGy	1.27×10^{-4}	1.51×10^{-4}
30P10kGy	1.68×10^{-4}	3.19×10^{-4}
50P0kGy	1.79×10^{-6}	4.72×10^{-2}
50P1kGy	6.85×10^{-5}	—
50P2kGy	1.26×10^{-4}	7.81×10^{-4}
50P4kGy	2.27×10^{-4}	6.17×10^{-4}
50P6kGy	2.36×10^{-4}	4.19×10^{-4}
50P8kGy	5.90×10^{-5}	1.21×10^{-4}
50P10kGy	9.96×10^{-6}	1.86×10^{-5}

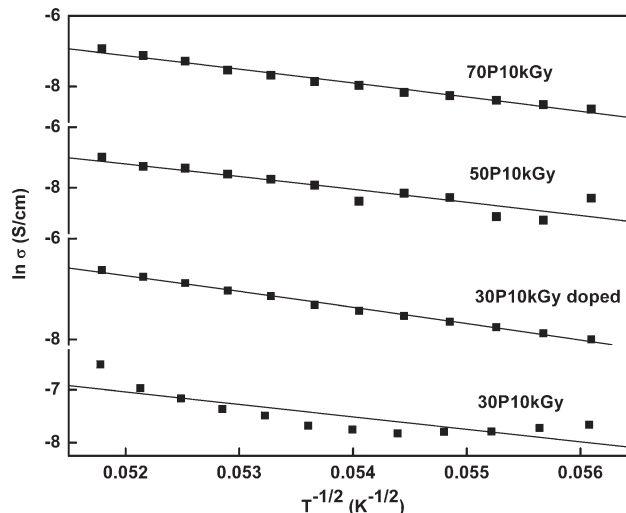


Figure 13 1D VRH plot for irradiated blends.

TABLE III
Mott's Parameters

Sample name	γ	T_0
30P0kGy	1/2	270,400
30P6kGy	1/2	101,124
30P10kGy	1/2	85,849
50P0kGy	1/2	237,169
50P6kGy	1/2	53,361
70P0kGy	1/2	225,641
70P6kGy	1/2	55,225

plot. The value of T_0 decreases as the conductivity of blend increases.

CONCLUSIONS

Electron beam irradiation is an alternate method to prepare PANI nanocomposite stable at ambient conditions. UV-vis spectra show decrease in the intensity of ≈ 630 nm due to formation of LEB during irradiation. IR analysis shows interaction between chitin and PANI. SEM micrograph shows the formation of chitin-PANI nanocomposite. XRD analysis confirms the formation PANI particles in the blend solution and no significant change in intensity of EBS, even after irradiation. Electrical study shows increase in the conductivity due to irradiation up to certain level and then conductivity decreases. In the case of EBS, no significant change in conductivity is found after irradiation. TGA analysis shows that blends are more stable after irradiation. From the $I-V$ characteristic analysis, it is found that 1D VRH mechanism is dominating even after irradiation in the case of chitin-PANI blend. Finally, one can conclude that the formation of PANI particle during irradiation in the blend solution is due to the presence of chitin, where as no particle formation is observed in pure PANI solution irradiated with electron beam.

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