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Spectroscopic and morphological evaluation of gamma radiation irradiated polypyrole based nanocomposites

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ABSTRACT

Novel electrically conducting nanocomposite materials comprising of poly (pyrrole) (PPy) nanoparticles dispersed homogeneously in a poly (vinyl alcohol)-g-poly (2-acrylamido-2-methyl-1-propanesulphonic acid-co-acrylonitrile) matrix were prepared by *in situ* polymerization of pyrrole. Radiation shielding potential of so designed polypyrrole based nanocomposites was studied by exposure of polymer materials to gamma radiation under varying experimental conditions and structural and morphological changes in irradiated materials were examined by FTIR and SEM techniques. Copyright © 2012 VBRI Press.

Keywords: Electromagnetic interference; polymer composites; conducting polymers.

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Introduction

Integration of macro and nanocomposites has led to the development of a new class of nanocomposite materials which find vital approach in medicine, biology, industry and defense [**1**]. As commercial, military and scientific electronic devices and communication instruments are used more widely, electromagnetic interference (EMI) has become a major problem as it reduces the lifetime and the efficiency of the instrument [**2**]. Electromagnetic interference shielding refers to the reflection or absorption of electromagnetic radiation by a material that acts as a shield against the penetration of the radiation through the shield. Light weight EMI shielding materials are needed to protect the workspace and environment from radiation coming from computers and telecommunication equipment as well as for protection of sensitive circuits [**3**]. Traditionally, metals had been used as materials for electromagnetic shielding but they have certain disadvantages such as high cost, large weight, poor adhesion, corrosion under extreme environments and poor processability. Conducting polymers possess special properties compared to metals that they not only reflect but also selectively absorb electromagnetic radiations [**4**]. These properties have made conducting polymer a useful material in radar or microwave absorbing formulations applied to military and civil purposes such as in stealth technology. There have been some investigations recently on the EMI shielding properties of conducting polymer films or dispersions [**5**].

CPs, in particular polypyrrole and its derivatives has been the subject of intensive research for their unique electrical, electro-chemical and/or optical properties [**6, 7**]. Among the CPs known to date, ones based upon PPy have attracted special interest because of their high conductivity, ease and flexibility in preparation, stability and good mechanical properties. Potential technological applications include electronic and electrochromic devices [**8-9**], biosensor for water pollution [**10**], electromagnetic interference shielding materials (EMI) [**11, 12**] etc.

Polymeric substances exhibit a wide variety of radiation effects. The formation of new chemical bonds after irradiation usually results in irreversible effects. Generally, these are manifested as changes in appearance, chemical and physical states, and mechanical, electrical, and thermal properties. However, not all properties of a polymer are affected to the same degree by radiation.

The radiation stability of a polymer is dependent upon the chemical structure of the material because radiation-induced excitation is not coupled to the entire chemical system, but is often localized at a specific bond. The addition of energy-absorbing aromatic rings to the chemical structure significantly increases the radiation stability of some polymers by aiding in the redistribution of the excitation energy throughout the material. Conversely, the polymers with high aliphatic structures (e.g., ethers and alcohols) are the least resistant to radiation.

Irradiated polymers generally undergo two types of reactions: cross linking and chain scission. The cross-linking process results in formation of chemical bonds between two adjacent polymer molecules. This reaction increases the molecular weight of the polymer until the material is eventually transformed into an insoluble three-dimensional network. Chain scission, or fracture of polymer molecules, decreases molecular weight and increases solubility. Both reactions can significantly alter the physical properties of a polymer. However, the degree and direction of change are not the same for all polymers.

In recent years, electrically conducting polymer composites have gained popularity because of their light weight, resistance to corrosion, flexibility and processing advantages [**13-17**]. All these promising properties allow polymer nanocomposites to be applied in diverse areas such as microwave absorbers [**18, 19**], electronics [**20, 21**], sensors [**22**] and energy storage devices [**23**]. The EMI shielding efficiency (SE) of a composites material depends on many factors, including the filler's intrinsic conductivity, dielectric constant, and aspect ratio [**24, 17**]. The properties of materials not only depend on their chemical structure, but also on their size and morphology [**25**].

Umashankar and coworker [**26**] fabricated nanocomposites comprising of Al/Al-Si alloys and multi walled carbon nanotubes (MWNT) through powder metallurgy and studied their mechanical characteristics. High performance nanocomposites of poly (etheretherketone) and modified clay were prepared by Goyal and Sahu [**27**] using hot processing techniques and their mechanical properties were investigated. Kondawar et al. [**28**] synthesized zinc oxide reinforced polyaniline nanocomposites using microwave radiation techniques and noticed a close relation between the shape of the nanorods and experiments conditions.

Morphology and microwave absorbing properties of polypyrrole nanoparticles have been studied by Shamuddian et.al [**29**]. Hakansson et al. [**30**] studied electromagnetic interference shielding and radiation absorption in thin polypyrrole films. The authors doped PPy with anthraquinane-2- sulfonic acid applied on textile fibers irradiated the materials in the frequency range 1-18 GHz. Liu and coworkers [**31**] designed carbon nanotubes – polyurethane composites and evaluated EMI shielding of the prepared materials. They observed that the prepared composite exhibited a reflection dominant mechanism. It was also observed that on increasing the amount of single walled carbon nanotubes the mechanism changed its mode.

Highly adherent and homogenous polypyrrole thin films were deposited on copper substrate by Jamadade et al [**32**] from sodium oxalate solution of different molar concentrations. The EM reflection, absorption, permittivity and conductivity were studied in the frequency range 8-12 GHz. The authors noticed that PPy increases the reflection of copper but decreases the microwave absorption. The absorption was found to be highly dependent on the dopant concentration.

Li and coworker [**33**] prepared CNT added styrene acrylic emulsion based polymer and demonstrated that the MWCNT had a significant effect on dielectric constant of the polymer which ultimately enhanced shielding efficiency of electromagnetic radiation. Ahmadi and coworker [**34**] prepared two phase blends of polystyrene and polyvinyl methylether and studied the effect of electron beam radiation on morphology and properties of two phase blends. It was observed that the irradiation process can play an important role in stabilization of the blends. Sonkawade and coworkers [**35**] studied the effect of gamma rays and neutron radiation on conducting polyaniline for various doses varying from 6 to 50.4 Gy and 15 to 41.9 KGy, respectively. Instrumental techniques like UV-Visible spectroscopy; XRD, Raman spectroscopy etc. were used to investigate the possible effect of irradiation.

The objectives of the present work include designing of the polypyrrole reinforced nanocomposites of polyvinyl alcohol-g-poly (2-acrylamido-2-methyl-1-propanesulphonic acid-co-acrylonitrile) and evaluating the possible structural and morphological changes in the nanocomposites caused by exposure to gamma rays.

The present study bears fair novelty from several viewpoints. Firstly, the method of PPy impregnation within the host matrix guarantees homogeneous dispersion so as to achieve its optimum performance. Secondly, the polymer matrix consists of PAMPS and PAN chains which are ionic and non-ionic, and hydrophilic and hydrophobic, respectively and provides an opportunity to desirably modify the end properties of the material.

Experimental

Materials

Polyvinyl alcohol (PVA) (98.6% hydrolyzed) was obtained from the Research Lab, Mumbai, India and used as received. 2-Acryloamido-2-methyl-1-propanesulphonic acid (AMPS) (99% pure) was purchased from Aldrich-Chemie GmbH, Reidstr.2, D-89555 Steinheim, Germany and used as such. Pyrrole (98% pure) was purchased from Aldrich- Chemie GmbH, Reidstr.2, D-89555 Steinheim Germany, and acrylonitrile (AN) was purchased from Merck Ltd. (Mumbai, India). The later was purified by successive washing it with 0.1 HCl and 0.1 NaOH followed by vacuum distillation at 55°C. Other chemicals such as ammonium persulphate (APS), potassium persulphate (KPS) were also of analytical grade and used without further purification.

Preparation of gel

A polymer matrix composed of PVA–g-P (AMPS-co-AN) was prepared by using KPS as polymerization initiator. In a typical experiment, 2.0 g PVA was dissolved into 20 mL of hot double distilled water and to this solution were added precalculated amounts of AMPS (7.23 mM), AN (30.38 mM) and KPS($11.10 \cdot 10^{-2}$ mM), respectively. The entire 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 was complete, the entire mass converted into a semi-transparent film and it was purified by equilibrating it in doubled distilled water for a week. This swollen gel was dried at room temperature, cut into rectangular pieces and stored in airtight plastic bags.

Impregnation of polypyrrole

The required quantity of pyrrole (2.73 mM) was dissolved in 3 mL of distilled water and the gel prepared above was allowed to soak in the pyrrole solution for 24 h. The pyrrole containing swollen gel was dried and then again left in a 0.3 M APS solution to soak the required quantity of APS from the solution. When the APS molecules enter into the polymer matrix the APS initiates polymerization of pyrrole. As the polymerization progresses, the semi-transparent gel gradually turns into black. After the polymerization is over, the PPy impregnated gel was repeatedly washed with distilled water and allowed to dry at 35 ± 0.2°C for 24 h. The whole reaction scheme of preparation of nanocomposite hydrogel is shown in **Fig. 1**.

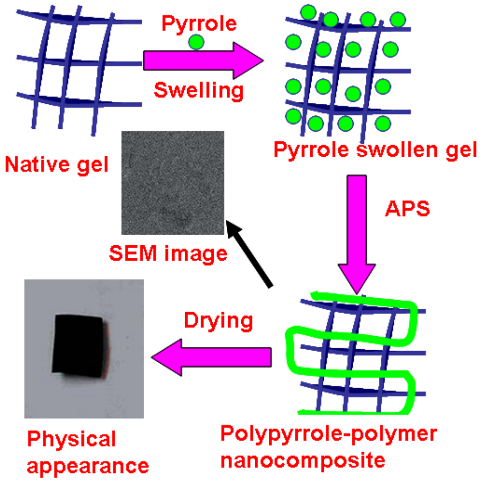

Fig. 1. Schematic presentation of preparation of polypyrrole containing nanocomposite of polyvinyl alcohol based hydrogel.

The percent impregnation of PPy into gel was calculated by the following equation:

$$\%\ \text{Impregnation of PPy} = \frac{(W_{ppy} - W_{DRY})}{W_{DRY}} \times 100$$

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

Irradiation process

Native and PPy impregnated hydrogel films were exposed to gamma rays using 60Co radiation facilities at a constant dose rate and at room temperature. The doses varying from 0.25, 5, 10, 15, 20, 25 MRad were used for irradiation purpose.

Characterization

In order to gain insights into the structural information of irradiated PPy impregnated films the FTIR spectra of PPy powder, polymer hydrogel, PPy impregnated matrix and irradiated PPy impregnated gels were recorded on a FTIR spectrophotometer (Perkin-Elmer, 1000 Paragon). For recording FTIR spectra of native, PPy impregnated and irradiated PPy gels quite thin and transparent samples were prepared by solution cast method and the prepared films were directly mounted on a spectrophotometer and scanned in the range 4000–500 cm^{-1}. Morphological studies of native and irradiated nanocomposite films were performed on scanning electron micrographs (SEM) operated at 10 kV. SEM observations were carried out after gold sputtering the samples with a Philips, 515, fine coater.

Results and discussion

FTIR spectra

Fig. 2 (a) and **(b)** represent FTIR spectra of PVA and PAV-g-P (AMPS-co-AN) polymer films, respectively scanned in the range 4000-400 cm^{-1}. The peaks observed at 1244, 1683, and 2976 cm^{-1} are due to stretching vibrations of SO_3H, CO, and CONH groups of PAMPS which appear in the spectra of grafted gel only, i.e., PVA-g-P(AMPS-co-AN) (**Fig. 2 b**). This obviously confirms the grafting of copolymer chains onto the PVA backbone. The characteristic peak at 3621 cm^{-1} suggests for the presence of hydrated -OH groups and a minor peak at 2976 cm^{-1} implies for C-H stretching of methylene group of constituent vinyl polymers. The spectra also contain a sharp peak at 2359 cm^{-1} which is due to CN stretching of nitrile group of polyacrylonitrile. **Fig. 2 (c)** and **(d)** represent the FTIR spectra of PPy powder and PPy impregnated PVA-g-P (AMPS –co-AN) gel film, respectively. The characteristic peaks in **Fig. 2 (c)** at 923, 1047, 1400 and 3100 cm^{-1} confirm the presence of PPy [**36**]. The spectra **(d)** of PPy impregnated PVA-g-P(AMPS-co-AN) gel film contain peaks at 686, 1168, 1249, and 1600 cm^{-1} indicating the presence of aromatic C-H, aromatic amide ,and aromatic C-C stretching which confirm the impregnation of PPy into the polymer nanocomposite gel.

Irradiation studies

In order to study the interference of gamma radiation on the prepared nanocomposites the samples of varying compositions were irradiated with varying doses of gamma radiation and their FTIR spectra and SEM images were recorded. The following results describe the observed findings:

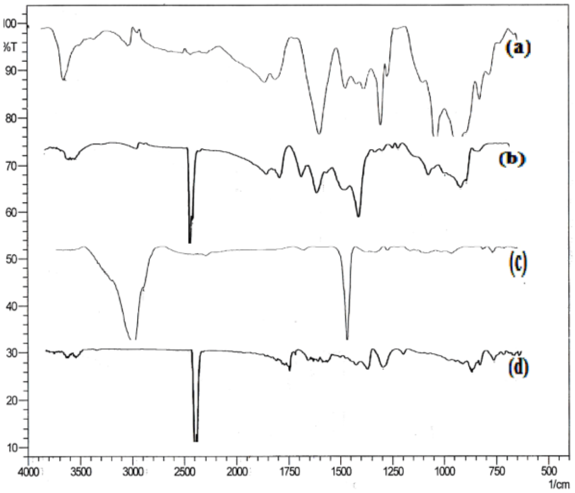

Fig. 2. FTIR Spectra of (a) PVA (b) native PVA-g-P (AMPS-co-AN) gel, (c) PPy powder and (d) PPy- impregnated gel.

Effect of varying radiation doses at low PPy content

The exposure of a polymer matrix to radiation results in several structural effects which arise from macromolecular chain scission and coupling of macro radical chains to impart significant changes in structure as well as properties of the polymer. The effect of varying doses of gamma radiation on a definite composition of nanocomposites was investigated by varying the intensity of radiation in the range 0.25 to 20 Mrad at fixed composition of the material with 0.72 mM PPy content. The results are shown in **Fig. 3 (a)**, **(b)**, **(c)**, respectively which depict the obtained spectral patterns at 0.25, 10 and 20 Mrad doses, respectively. The results clearly indicate that as the radiation dose increases, the number of absorption peaks also increases. The observed changes in spectral pattern may be attributed to the reason that the increasing dose of gamma radiations causes fragmentation of the polymer chains in the sample and results in rapid vibrations of various functional groups of polymer. It is also known that the fragmented chains have greater mobility and thus enable polymer chains to undergo frequent vibrations. This clearly results in FTIR spectra with greater number of peaks.

Effect of varying radiation doses at higher PPy content

When the gamma radiations are incident on the polymer nanocomposites of definite composition having 4.32 mM of PPy, the observed FTIR spectra are shown in **Fig. 4 (a)**, **(b)**, and **(c)** which represents the radiation doses of 0.25, 5.0 and 10 Mrad, respectively. It is clearly from spectra that with increasing dose of radiation the spectral pattern dramatically changes due to enhanced scission of the polymer chains. Moreover it is also evident from the spectra that the intensity of the peaks goes on decreasing with increasing radiation doses. The obtained reduced intensity of spectral peaks may be explained by the fact that at higher PPy content the nanocompsoite shows greater shielding property and therefore the polymer matrix does not undergo severe fragmentation.

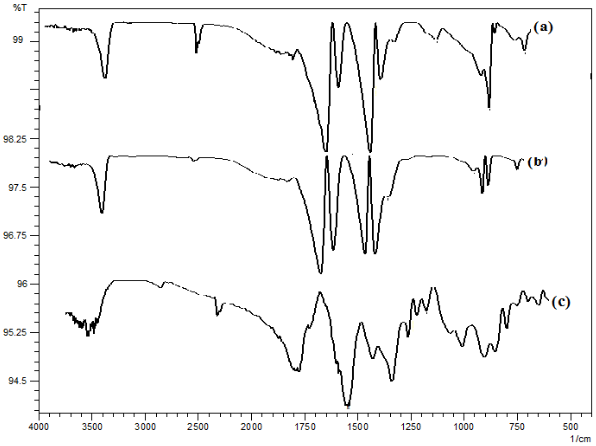

Fig. 3. Effect of varying doses of gamma radiation on spectral pattern of 0.72 mM PPy containing nanocomposites. (a) 0.25 Mrad, (b) 10 Mrad, and (c) 20 Mrad.

Effect of PPy content on irradiation

The interaction of radiation and matter results in changes in properties of the materials which to a great extent depend on the nature of the matter under examination: In the present work the influence of PPy content on irradiation behavior has been studied by varying PPy in the range 0.72 to 4.32 mM at constant radiation exposure of 0.25 Mrad. The results are shown in **Fig. 5 (a)**, **(b)** and **(c)** which demonstrate the observed changes in spectral pattern of the irradiated nanocomposites.

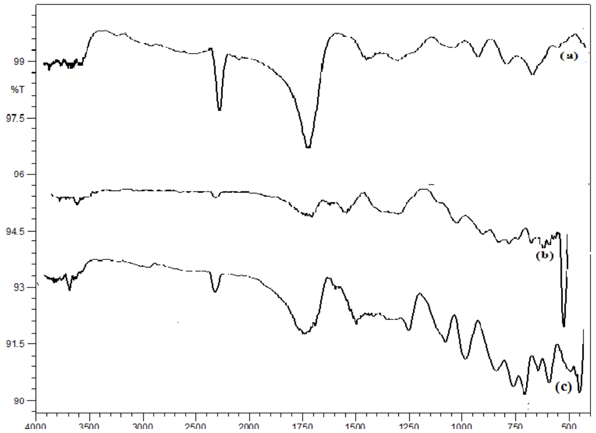

Fig. 4. Effect of varying dose of gamma radiation on spectral pattern of 4.32 mM PPy containg nanocomposites (a) 0.25 Mrad, (b) 5Mrad, and (c) 10 Mrad.

The results show that from 0.72 to 1.29 mM content of PPy, the number of absorption peaks increases while for 4.32 mM of PPy content, both the number and intensity of the spectral peaks decreases. The observed results may be explained by the fact that from 0.72 to 1.29 mM content of PPy, the gamma radiation causes greater scission of the polymer chains while beyond 1.29 mM i.e. at 4.32 mM of PPy, the fragmented chains may again undergo crosslinking by recombination of macroradical chains to form a greatly crosslinked network which consequently results in restrained mobility of chains. This clearly reduces both the number of peaks and peak intensities.

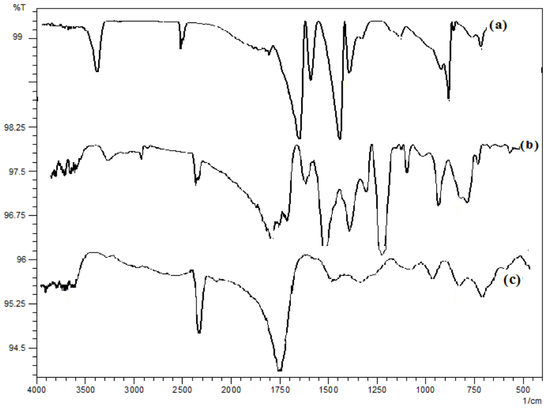

Fig. 5. Effect of varying amounts of PPy contain in the nanocomposite on spectral pattern at fixed dose of gamma radiation of 0.25 Mrad. (a) 0.72 mM PPy, (b) 1.29 mM PPy, and (c) 4.32 mM PPy.

Effect of irradiation on morphology

An internal structural change in the bulk of a matrix is always accompanied by a change in morphology of the material. The interaction of matter with gamma radiation is also expected to produce a change in morphology of material that can be best investigates by SEM technique as discussed in the forthcoming text.

Effect of varying radiation doses at low PPy content

The influence of varying doses of gamma radiation on morphology of the nanocomposite has been investigated by varying the radiation in the range 0.25 to 10.0 Mrad, when the PPy content in the nanocomposite was 0.72 mM only. The obtained SEM images are shown in **Fig. 6 (a)**, **(b)** and **(c)**, which represent morphologies of the irradiated nanocomposite surfaces at 0.5, 5 and 10 Mrad doses, respectively. It is clear from the observed SEM images that as the radiation dose increases the images show increasing fragmentation of polymer chains which is evident from the enhanced ruptured surfaces of the nanocomposites. The observed results may be attributed to the fact that increasing dose of the gamma radiation causes scission of the polymer chains which results in an enhanced heterogeneity of the nanocomposite surfaces.

Effect of varying radiation doses at high PPy content

The effect of increasing doses of gamma radiation on morphology of irradiated nanocomposites with higher PPy content has been studied by irradiating 4.32 mM PPy containing matrix with gamma radiation of doses varying in the range 0.5 to 10 Mrad. The results are shown in **Fig. 7 (a)**, **(b)**, and **(c)**, which exhibit morphological changes in the surface of the nanocomposite when irradiated with 0.5, 5 and 10 Mrad doses, respectively. It is clear from the observed images that with increasing dose of radiation, the heterogeneity in the morphology increases. The observed changes may be attributed to the fact that enhanced radiation doses produces greater scission of the polymer chains and generate heterogeneity which is evident from the obtained images.

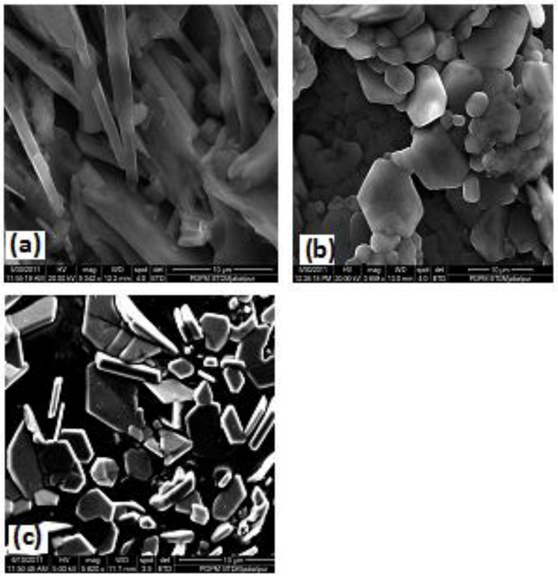

Fig. 6. Effect of varying doses of gamma radiations on morphology of 0.72 mM PPy containing nanocomposites (a) 0.5 Mrad, (b) 5 Mrad, and (c) 10 Mrad.

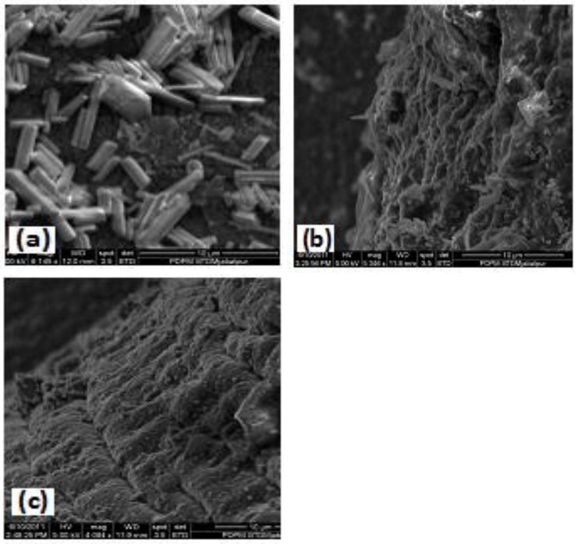

Fig. 7. Effect of varying doses of gamma radiations on morphology of 4.32 mM PPy containing nanocomposites (a) 0.5 Mrad, (b) 5 Mrad, and (c) 10 Mrad.

Effect of PPy content on irradiation behavior

The effect of PPy content of the nanocomposite on morphology of irradiated sample has been investigated by varying the amount of PPy in the range 0.72 to 4.32 mM and irradiating the materials with 5 Mrad gamma radiations.

The observed results are shown in **Fig. 8 (a)**, **(b)** and **(c)** which depict morphologies of the irradiated samples containing 0.72 to 4.32 mM of PPy content. The results clearly reveal that increasing amount of PPy present in the nanocomposite tends to reduce the heterogeneity of the surface. The reason for the observed changes in SEM images may be attributed to the fact that increasing PPy content of the nanocomposite shows a greater tendency to absorb gamma radiations and thus show a radiation shielding potential.

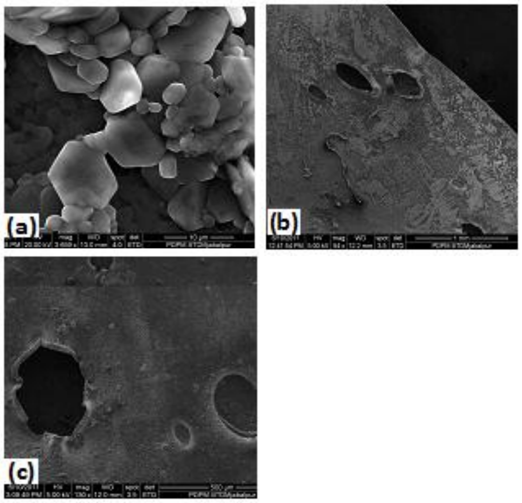

Fig. 8. Effect of varying amounts of PPy on the morphology of nanocomposites at fixed gamma radiation of 5 Mrad (a) 0.72 mM PPy, (b) 1.29 mM PPy, and (c) 4.32 mM PPy.

Conclusion

The impregnation of PPy into polymer matrix results in a nanocomposite material with radiation shielding property. It is noticed that exposure of nanocomposite to gamma radiation causes structural and morphological changes in the matrix. The nanocomposite with increasing PPy content shows an enhanced radiation shielding behaviour.

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