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Effects of Gamma Radiation on Poly (vinyl alcohol)/ Poly (vinyl pyrrolidone)/ Nickel nanocomposite Films and Evaluation of its Dosimetric Characteristics

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A NEW medium-high dose label dosimeter film based on using gamma radiation in executing reduction for Nickel ions to Nickel-metal inside the host polymer matrix, poly (vinyl alcohol)/ poly (vinyl pyrrolidone) is prepared. The results of absorption spectra investigation reveal that the film has surface plasmon resonance (SPR) of Nickel nanoparticles (NiNPs) correlated with irradiation doses. Different techniques were used to ensure the formation of NiNPs such as XRD pattern and TEM. The size of the Ni-nanoparticles was 40 to 50 nm. Studying the dosimetric behavior for the composite film reveals a response curve ranging from 20-350 kGy covering the medium and the high dose applications such as cross-linking of polymers, polymer modifications, and others. This film can be used as a label in the chosen range as its color turns from faint green to pale gray by irradiation. PVA/PVP/Ni nanocomposites films have also excellent post stability in different environmental conditions.

Keywords: Dosimeter, Nano Nickel, PVA, PVP, Radiation.

Introduction

Ionizing radiation has wide applications such as food preservation, sterilization of medical devices, cross-linking of polymers, and others. Using gamma radiation in preparing polymer/ metal nanocomposites in one step synthesis has been recorded in several studies (Qiao et al., 1999, 2000; Jan et al., 2004; Karim et al., 2007; Abdel Maksoud et al., 2021, 2022). There is a dosimeter for each purpose to determine the absorbed dose accurately. Polymer/metal nanocomposite materials are considered a target for many researchers nowadays for their featured properties. A significant change in optical, thermal, electrical and electrochemical properties was ascertained in controlling the distribution of the nanoparticles within the chosen polymer or mixture of polymers (Saini et al., 2013). Recently, attention is paid for the nano scale materials due to their characteristic new optical properties obtained on radiation dose measurements. The new optical properties, resulting from surface plasmon resonance (SPR), appear when an electromagnetic field led the collective oscillation of free electrons from metal nanoparticle into resonance (Li et al., 2011).

This resonance can be followed in dosimetry applications. A few researches were reported on using metal nanocomposite as a dosimeter. In the following, some examples of using the nanocomposite as a dosimeter are highlighted. A gel dosimeter of gelatin/silver nanocomposite based on irradiation of silver nitrate was investigated to be utilized as a gel dosimeter in radio therapeutic gray (Gy) levels (Soliman, 2014). CeO_2 nanowires were used as a low dose aqueous-radiation dosimeter ranging from 20 µGy

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to 500 μGy (Ying-Ying et al., 2013). Moreover, copper nanoparticles (CuNPs) in polyvinyl alcohol that turns its color from faint blue to deep reddish-brown depending on metal ion concentration which cover a dose range extended from 50 to 650 kGy, indicate the possibility of using them in high dose applications (Bekhit et al., 2019). Nowadays, Nickel nanoparticles drew great attention to their distinctive properties (Chen & Hsieh, 2002; Chen et al., 2007) and their wide diversity of applications in catalysis (Wang et al., 2009), as well as conducting inks, multi-layered ceramic capacitors, micro electronics, thick-film electrode material, and solar-cells (Kim et al., 2009).

Polymers play an important role in preparing nano- metal where they are used as stabilizers, hosts or matrix (Clifford et al., 2017). Polyvinyl alcohol (PVA), is one of the most commonly reported water-soluble polymeric matrix, nontoxic, biocompatible, biodegradable, optically transparent polymer characterized by good chemical resistance and film forming ability. PVA has a wide range of potential applications in optical, pharmaceutical, medical, and membrane fields (Abou Taleb et al., 2009; Bhunia et al., 2013; Mallakpour & Dinari, 2013; Akhavan et al., 2017; Cieśla et al., 2017).

Poly (N-vinyl-2-pyrrolidone) (PVP) is a water-soluble polymer, which exhibits a series of interactions toward dissolved small molecules and ions in aqueous solutions. PVP solutions are permanently gelled when cross-linked by irradiation with gamma rays (Kaplan & Guner, 2000). PVP hydrogel has excellent transparency and biocompatibility (Benamer et al., 2006).

In the present work, Ni/PVA/PVP/ Ni composite film was irradiated by gamma rays to create Ni nano composite of characteristics that were investigated through UV/VIS, XRD and TEM to be used in dose monitoring.

Materials and Methods

Materials

Nickel sulfate ($NiSO_4$ .5H_2O, 99.9%) was purchased from El-Goumhouria Co. Egypt. Poly (vinyl alcohol) PVA (98-99% hydrolysis, degree of polymerization 1700-1800) was purchased from LOBA Chemie, India. Poly (vinyl pyrrolidone) (PVP), 40000 g/mol was purchased from Sigma Aldrich. Deionized distilled water was used throughout the experiment.

Samples preparation

Both PVA and PVP were prepared through dissolving three grams of each polymer in 100 mL of deionized water at 80°C with continuous stirring for about 4 hrs till clear solutions were obtained. Both solutions were left to cool, then PVA solution was added to PVP solution with ratio of 70:30 respectively. 0.015M $NiSO_4$ was added to the above mixture with proper stirring for adequate homogenization then the mixture was poured on petri dish , left to dry in laboratory air under diurnal cycles of day light to execute the target film.

Irradiation processes

The PVA/PVP/Ni^{+2} films were irradiated at irradiation doses up to 350 kGy at a dose rate of about 1.4 kGy/h using Co-60 γ-cell-220 source (manufactured by the Atomic Energy Authority of India) at the National Center for Radiation Research and Technology, (NCRRT), Egyptian Atomic Energy Authority (EAEA), Nasr City, Cairo, Egypt.

Characterization techniques

UV/VIS spectrophotometer

The optical properties of PVA/PVP/Ni nanocomposites films were measured in the wavelength range of 400–900 nm using Unicam Double Beam UV–Visible Spectrophotometer (made in England).

X-ray diffraction (XRD) measurements

X-ray diffractometer (Shimadzu XRD 600), was used to investigate the PVA/PVP/ Ni nanocomposite films in the θ range between 2θ of 4° to 90° at a scan rate of 2°/ min on the diffractometer with CuK radiation source, a generator voltage of 40 KV, a generator current of 40 mA and a wavelength of 0.1546 nm at room temperature.

TEM measurements

The sample was prepared by deposition of a single drop of the PVA/PVP/Ni nanocomposite dispersion on a 300-mesh copper grid with a carbon film over a filter paper, which absorbed excess solution. The copper grid was allowed to dry at room temperature. The shape and particle size distribution of NiNPs were detected using the transmission electron microscopy (TEM) (JEOL

JSM- 100 CX, Shimadzu Co., Japan) with an acceleration voltage of 80 kV.

Results and Discussion

UV/VIS spectrophotometer of PVA/PVP/Ni nano composite film

UV- visible absorption for the unirradiated PVA/PVP/Ni^{+2} and irradiated PVA/PVP/ Ni^0 nanocomposites (0.015M) at different doses up to 350 kGy is indicated in Fig. 1. As shown in Fig. 1, there was no appearance of surface Plasmon resonance (SPR) absorption of Ni nanoparticles (NiNPs) in the unirradiated sample. Upon irradiation, there was a little peak appearing at 393 nm as shown in the inserted Figure. This peak indicated the formation of NiNPs (Meftah et al., 2014). The red shift, which occurred from 392 nm to 398 nm may be due to increase in the size of the nanoparticles (Bekhit et al., 2019). The increase in the absorbance of NiNPs may be due to the increase of the nanoparticles concentration. The recorded increase is correlated with the increase in the absorbed dose. In addition, the color of the film changed from pale green to pale grey by irradiation which indicates its possibility to be utilized as a label- dosimeter film.

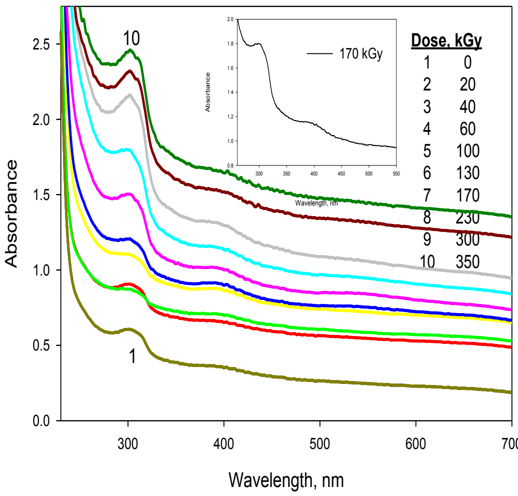

Fig. 1. UV/Visible spectra of the unirradiated and irradiated PVA/PVP/Ni composite films (0.015M) at different doses

XRD analysis

XRD analysis was performed to examine the crystalline structure formation of NiNPs. Figure 2 shows the XRD patterns of the unirradiated and irradiated PVA/PVP/Ni composite films at 170 kGy. The diffraction pattern displays one abroad diffraction peak for PVA/PVP blend at 2θ= 20°. On the other hand, for the 170 kGy irradiated PVA/PVP/Ni there are three diffraction peaks located at 2θ values of 30.2°, 45.6° and 56.2° which correspond to (111), (200) and (222) crystal planes of nickel with a face-centered cubic (FCC) phase structure, respectively (Meftah et al., 2009, 2014). The resulting peak at 2θ value of 26 ^{O} may be attributed to the Ni oxide.

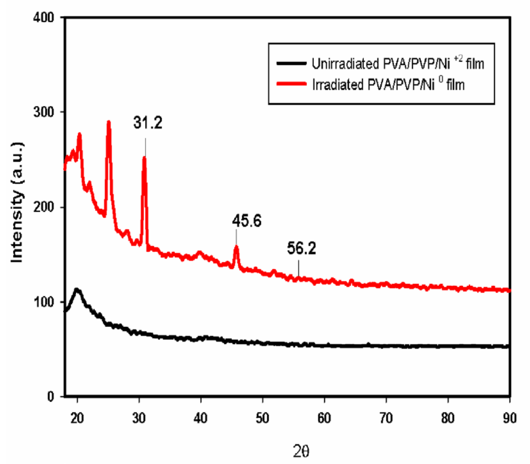

Fig. 2. XRD pattern of the unirradiated and irradiated PVA/PVP/Ni composite films, at 170 kGy

TEM analysis

Figure 3 reveals that the particles distribution is almost homogeneous and their morphology is spherical in shape. No agglomeration occurred and obviously separated particles were observed. The average particle size of NiNPs (0.015M & 170 kGy) was determined to be 50 nm.

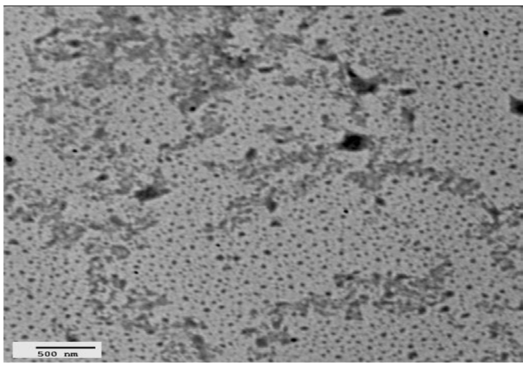

Fig. 3. The TEM image of PVA/PVP/ Ni nanocomposite films (0.015M &170 kGy)

Reduction mechanism of Ni^{+2} ions in polymer matrix

In this work, gamma rays were used as a source of ionizing radiation. Gamma photons interact with the hydrated electrons in the film matrix through photoelectric absorption, Compton scattering, and pair production. These diversity interactions lead to the formation of secondary electrons, mainly by Compton scattering that induces among other hydrated electrons ($e^{-}aq$), hydroxyl radical ($OH^{.}$), and hydrogen radical ($H^{.}$) by radiolysis of water according to Equation 1: (Meftah et al., 2014):

$$H_2O+^{\gamma\text{-rays}} \rightarrow 2e^{-}_{aq}, H^{+}, H_3O^{-}, H\cdot, OH^{.}, H_2, H_2O_2 \quad \text{(radiolysis of water)} \quad (1)$$

The formation of Ni nanoparticles can be described by the following reactions (Naghavi et al., 2010) :

$$Ni^{2+} + 2e_{aq} \rightarrow Ni^{0} \quad (2)$$

$$nNi^{0} \rightarrow NiNPs \quad (3)$$

The hydrated electrons reduce Ni^{+2} into zero valent Ni atoms (Ni^{0}) by the nucleation process (Equation 3). A number of Ni^{0} atoms can agglomerate to form Ni nanoparticles. The function of PVP in the PVA/PVP/Ni composites is not only as a binder, but it prevents the process of agglomeration of Ni nanoparticles (Bogle et al., 2006; Kang et al., 2006). PVP has been used because it is a reducing agent, which leads to the rapid formation of Ni nanoparticles and due to its hydrophilic nature that protects the surface of the Ni nanoparticles.

Irradiation dose response

The irradiation dose response curve shown in Fig. 4 reveals a relation between the change in optical density for the target film PVA/PVP/Ni at a fixed concentration of Nickel sulfate (0.015 mol/L) through $\Delta A = A_i - A_0$ (where A_i and A_0 are values of optical densities for the irradiated and unirradiated films) and the absorbed irradiation dose. By exposure of PVA/PVP/Ni film to ascending doses of gamma ray, the yield of the Ni nanoparticles increased and led to the increase in the recorded optical density correlated with the absorbed doses. The useful dose range extent is up to 350 kGy. In addition to the significant color change from pale green to pale grey correlated with the absorbed doses, this PVA/PVP/Ni nanocomposite film is a strong candidate to cover many applications in medium and high dose ranges.

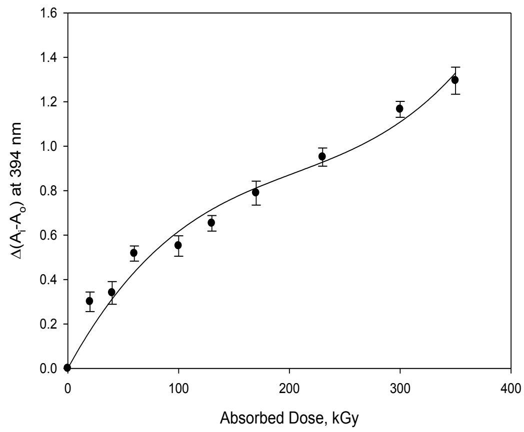

Fig. 4. Change of response as a function of absorbed dose for PVA/PVP/Ni nanocomposites film (0.015 M)

Post-irradiation stability

The measurements of the stability of the dosimeter after irradiation are one of the most important characteristics in dosimetry science. Post-irradiation stability study was carried out using PVA/PVP/Ni nanocomposite film (0.015 M) irradiated at a dose of 170 kGy. The irradiated dosimeter was stored in dark and under laboratory fluorescent light at room temperature over a period of 60 days. The optical absorbance was carried out at 394 nm using UV-Vis spectrophotometer after irradiation at room temperature and at different intervals of time as shown in Fig. 5. It is noticed that there is a slight increase in the absorbance that does not exceed 1.5 % and 2% for dark and light, respectively until the end of the storage time. This slight increase in the optical absorbance as a result of the post irradiation storage at different intervals ensures that PVA/PVP/Ni nanocomposite film has an excellent post irradiation stability.

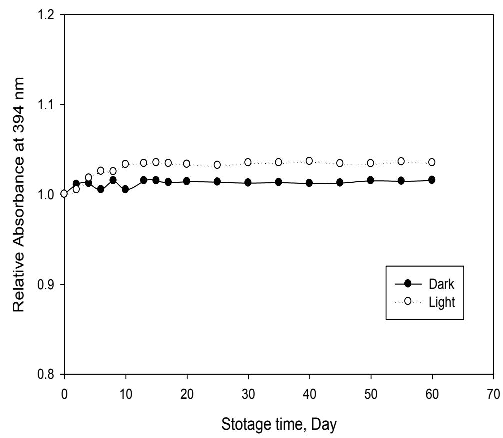

Fig. 5. Post-irradiation stability of PVA/PVP/Ni^{0} nanocomposite in the dark and light at room temperature

Conclusion

Nickel nanoparticles dispersed in PVA/PVP matrix film were synthesized by gamma radiolytic technique to be used as high dose dosimeters. UV-visible absorption spectra showed the presence of SPR band of Ni-nanoparticles at 393 nm, which is congruent by the previous researches. The absorbance of the SPR band increased by increasing the irradiation dose due to the increase in the yield of Ni nanoparticles. The formation of Ni nanoparticle in PVA/PVP is confirmed by XRD and TEM. The size of Ni nanoparticles ranges from 40 to 50 nm. The color of the film changes from pale green to pale grey in the dose range up to 350 kGy. PVA/PVP/Ni nanocomposite shows a good stability in dark and light until the end of the storage period. Thus, this film is suggested to be used as a label-dosimeter in medium and high dose applications.

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