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NOVEL LEAD OXIDE POLYMER NANOCOMPOSITES FOR NUCLEAR RADIATION SHIELDING APPLICATIONS

Polymer nanocomposites have been used in many applications such as a fabrication of protective enclosures for humans and devices at nuclear power plants and hospitals. The aim of this paper is the preparation of novel polymer nanocomposites with high linear attenuation coefficients for nuclear radiation shielding. We have produced the nanocomposites of polyvinyl alcohol, polyacrylic acid, and lead oxide nanoparticles with various concentrations of components and have studied their optical properties. As the concentration of PbO_2 nanoparticles increases, the absorbance of a polymer blend and the optical constants increase, whereas energy band gap decreases. The tests of the nanocomposite for the gamma radiation shielding showed that it has high attenuation coefficients for gamma radiation.

Keywords: lead oxide, polymer blend, absorbance, optical constants, gamma radiation.

1. Introduction

Gamma radiation and X-rays specifically are of a primary concern for the external exposure because of their high penetration power and domestic effects on humans. Accumulated doses from ionizing radiation like X-rays and gamma rays can cause cancer, DNA mutations, sterility, *etc.* With the increased usage of radioactive materials in medicine and industry, the shielding is a priority in order to protect both humans and equipments. The example of a widely used shielding material for gamma and X-rays is lead (Pb). Many dense elements can attenuate gamma and X-rays, but Pb is distinguished by its availability and low cost, as compared with other denser elements like tungsten and thorium. In addition, Pb has an advantage over various aggregate materials used to shield gamma rays such as concrete, by being more efficient and uniform in density. Some shortages of pure Pb as a nuclear shielder are its heaviness, being rigid and poorly portable, and ability to produce secondary ionizing radiation, which requires an additional shielding. Many research efforts were done to design more efficient shielding materials that are potentially capable to attenuate gamma and neutrons, possess a light weight and a low cost, and are efficient, easily portable, and flexible. Polymer composites are a suitable candidate to solve the traditional shielders' problems. The dispersion of Pb additives into high-performance hydrogen-rich polymeric material can provide a radiation shield against gamma and X-rays, as well as secondary particles and electromagnetic radiation resulting from nuclear reactions within the shield. Polymer composites are dual-purpose shielders, as they combine the hydrogen-rich polymer, which is efficient in absorbing neutrons, and metallic additives, which are efficient for the gamma shielding. Moreover, polymer composites are light, commercially available, and produce less secondary radiation, when compared with pure metallic shielders. The multifunctionality of polymer composites assigned them to be used in many applications like shielding space crafts and making protective enclosures for humans and devices at hospitals and nuclear power plants[1]. Traditionally, the polymer matrix composites have been thought as insulating materials and have been used in applications like power tool handles, cables, jackets, capacitor films, and electronic packaging materials. Especially, the electrical and optical properties of polymers have been extensively investigated due to their recent applications in optical devices. Polymeric materials have unique properties such as low density, light weight, and high flexibility and are widely used in various industrial sectors. In recent years, there has been a great progress in the understanding of polymer optical properties and in their theoretical description. Polyvinyl alcohol (PVA) is an important and interesting polymer because of its attractive physical and optical properties. Unlike most vinyl polymers, PVA is not prepared by the polymerization of the corresponding monomer. The monomer vinyl alcohol is unstable with respect to acetaldehyde. Instead, PVA is prepared, by firstly polymerizing vinyl acetate, and the resulting polyvinylacetate is converted to PVA. Other precursor polymers are sometimes used, with formate and chloroacetate groups instead of acetate. The properties of the polymer depend on the amount of residual ester groups. PVA is a colorless polymer. Because of its low cost and volume productivity, it will be one of the key materials for using instead of glass and different coatings in the optics industry. As a polymer waveguide, PVA has attracted much attention. In addition, it is found that PVA can produce a large reflective index. These materials are promising candidates as nonlinear optical elements [2]. Composites are widely used in our day-to-day life. Due to their low weight and ability to be tailored for a specific end use, they have gained a considerable ground in the high performance applications, such as the aerospace and automobile industries. The idea of connecting two or more different constituents into one substance gives almost infinite possibilities to create new engineering materials characterized by a variety of different properties. Composite materials because of these diverse properties are successfully used in almost all areas of industry and science [3-6]. One advantage of nanoparticles, as polymer additives, is that, as compared to traditional additives, the loading requirements are quite low. Microsized particles used as reinforcing agents scatter light, thus reducing light transmittance and optical clarity. The efficient nanoparticle dispersion combined with the good polymer–particle interfacial adhesion eliminates the scattering and allows the exciting possibility of developing strong yet transparent films, coatings, and membranes [7]. The optical properties of polymers constitute an important aspect in the study of electronic transitions and the possibility of their application as optical filters, a covers in solar collection, selection surfaces, and green house. The information about the electronic structure of crystalline and amorphous semiconductors has been mostly accumulated from the studies of optical properties in a wide frequency range [8].

2. Experimental

The fabrication of a nanocomposite including polyvinyl alcohol (PVA), poly acrylic acid (PAA), and lead oxide (PbO_2) nanoparticles has been investigated with different concentrations of the blend of polyvinyl alcohol and poly acrylic acid and lead oxide nanoparticles, by using the casting method. The lead oxide (PbO_2) nanoparticles were added to the (PVA–PAA) blend in different concentrations: 0, 2.5, 5, and 7.5 wt.%. The optical properties of the nanocomposite were measured by using an UV/1800/Shimadzu device in a range of wavelengths (220–800) nm. The gamma radiation shielding test of the nanocomposite has been executed to investigate their attenuation properties for gamma rays for the samples with different concentrations of lead oxide nanoparticles. The samples were arranged in front of a collimated beam emerged from a gamma ray source (Co-60, 1 μCi). The gamma radiation source was positioned at a distance of 3 cm from the detector; the sample was placed at a distance of 1 cm from the gamma ray source. The transmitted gamma ray fluxes through PVA–PAA–PbO_2) nanocomposite are measured by a Geiger counter in order to estimate the linear attenuation coefficients. The absorption coefficient (α) is defined as the ability of the nanocomposite to absorb the light of a given wavelength [9]:

$$\alpha = 2.303A/t, \tag{1}$$

where A is the absorptance of the nanocomposite and t is the nanocomposite thickness in cm. The nondirect transition model for amorphous semiconductors proposed by [10] gives

$$\alpha hv = B(hv - E_g)^r, \tag{2}$$

where B is a constant related to the properties of the valence and conduction bands, hv is the photon energy, E_g is the optical energy band gap, $r = 2$ or 3 for indirect allowed and indirect forbidden transitions.

The refractive index (n) of the nanocomposite can be calculated, by using the following relation [9]:

$$n = (1 + R^{1/2})/(1 - R^{1/2}). \tag{3}$$

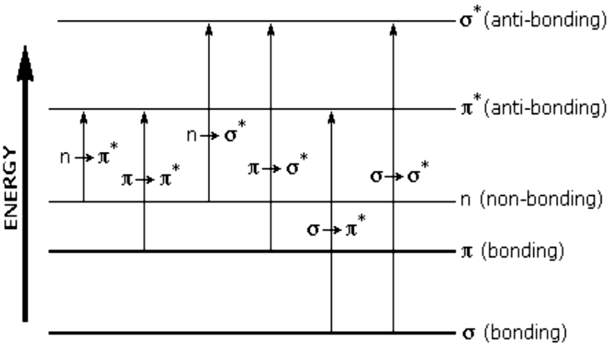

Fig. 1. Schematic of the possible electronic transitions [12]

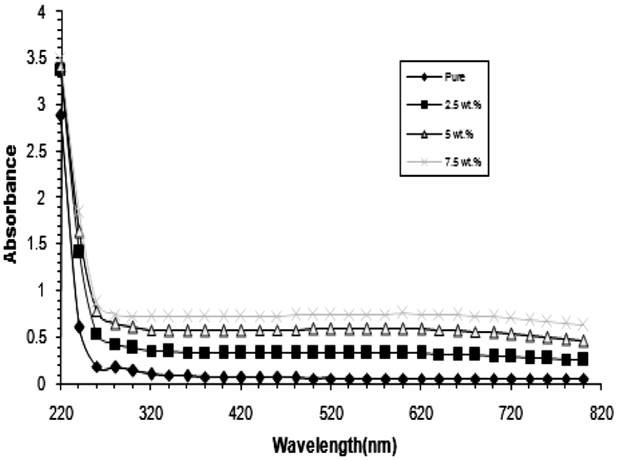

Fig. 2. Absorbance versus the wavelength for a (PVA–PAA) blend with different concentrations of PbO_2 nanoparticles

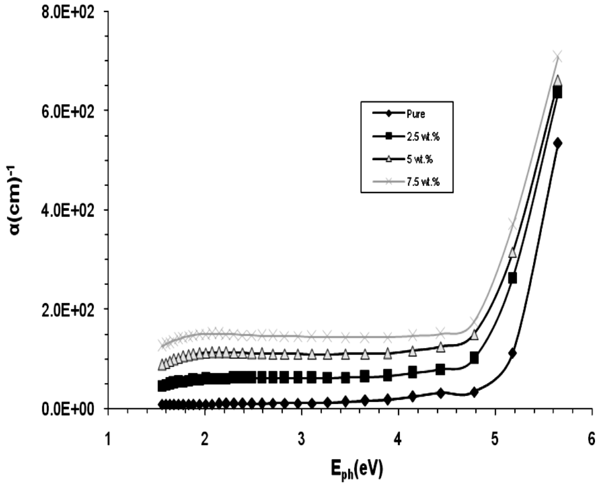

Fig. 3. Relationship between the absorption coefficient of the (PVA–PAA) blend for different weight percentages of PbO_2 nanoparticles and the photon energy

The extinction coefficient (k) was calculated, by using the relation [10]:

$$K = \alpha\lambda/4\pi. \tag{4}$$

The real and imaginary parts of the dielectric constant (ε_1 and ε_2) for the nanocomposite can be calculated by the relations [9]

$$\varepsilon_1 = n^2 - k^2 \quad \text{(real part)}, \tag{5}$$

$$\varepsilon_2 = 2nk \quad \text{(imaginary part)}. \tag{6}$$

The optical conductivity was calculated, by using the following relation [11]:

$$\sigma = \frac{\alpha n c}{4\pi}. \tag{7}$$

3. Results and Discussion

The absorption of Uv-vis radiation corresponds to the excitation of outer electrons. There are three types of electronic transitions, which can be considered: (1) Transitions involving π, σ, and n electrons; (2) Transitions involving charge-transfer electrons; and (3) Transitions involving d and f electrons [12] as shown in Fig. 1.

Figure 2 shows a variation of the absorbance with the wavelength for a (PVA–PAA) blend with different concentrations of PbO_2 nanoparticles. As is seen in the figure, the absorption increases at the UV region. This is due to the excitations of donor level electrons to the conduction band at these energies. The high absorbance of nanocomposites at the UV region is attributed to the energy of photons enough to interact with atoms; the electron is excited from a lower level to a higher energy one by absorbing a photon of the known energy. The changes in the absorbed and transmitted radiation can indicate the types of possible electron transitions. The fundamental absorption of absorbance spectra refers to the band-to-band or excitation transition [13]. In addition, the figure shows that the absorbance increases with the concentration of PbO_2 nanoparticles. This behavior is attributed to the agglomeration of nanoparticles with increasing the concentration and the number of charge carriers [14].

Figure 3 shows the relationship between the absorption coefficient of the (PVA–PAA) blend for different weight percentages of PbO_2 nanoparticles and the photon energy. The gradient of the absorption coefficient is from high to low photon energies. This means that the possibility of the electron transition is small, because the energy is not sufficient to move the electron from the valence band to the conduction band ($h\upsilon < E_g$). It was observed that, at high energies, the absorption is high and the forbidden energy gap is less, which indicates the large probability of electronic transitions [15]. The energy band gap of the (PVA–PAA) blend for different concentrations of PbO_2 nanoparticles is shown in Fig. 4. It is seen that the indirect energy band gap of blend decreases with increasing the concentration of PbO_2 nanoparticles, which may be due to charge transfer transitions [16].

The variation of the refractive index and extinction coefficient of the (PVA–PAA) blend for different concentrations of PbO_2 nanoparticles with the photon wavelength are shown in Figs. 5 and 6. The figures show that the refractive index and extinction coefficient increase with the concentration of PbO_2 nanoparticles, which is related to the increase in the scattering and the number of charge carriers as a result of the increase in the absorption coefficient and reflectance [9, 17].

The real and imaginary parts of the dielectric constant of the (PVA–PAA–PbO_2) nanocomposite shown in Figs. 7 and 8 increase with the concentration of PbO_2 nanoparticles, which is due to the increase in the refractive index and absorption coefficient (Eq. 5 and Eq. 6).

Figure 9 shows the optical conductivity of the (PVA–PAA–PbO_2) nanocomposite for different concentrations of PbO_2 nanoparticles, which increases with the concentration of PbO_2 nanoparticles due to the increase in the absorption coefficient and refractive index (Eq. 7).

Figure 10 shows the relationship of the gamma ray (Co-60) transmission through the (PVA–PAA–PbO_2) nanocomposite. Figure 11 represents a variation of the linear attenuation coefficients of the (PVA–PAA–PbO_2) nanocomposite for gamma rays (Co-60). It is most important to understand the manner, in which radiation interacts with matter and transfers its energy. The radiation energy is transferred to matter in two ways: ionization and excitation. Ionization is the process of removal of an electron from an atom leaving the atom with a net positive charge. In the excitation, the energy of incoming radiation raises an outer electron to a higher energy state, from which it returns

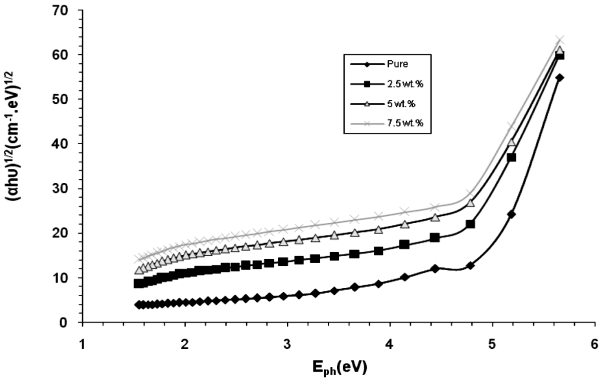

Fig. 4. Energy band gap of the (PVA–PAA) blend for different concentrations of PbO_2 nanoparticles

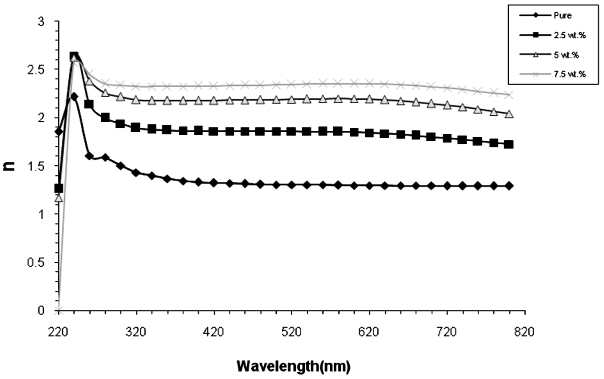

Fig. 5. Refractive index of the (PVA–PAA) blend for different concentrations of PbO_2 nanoparticles versus the photon wavelength

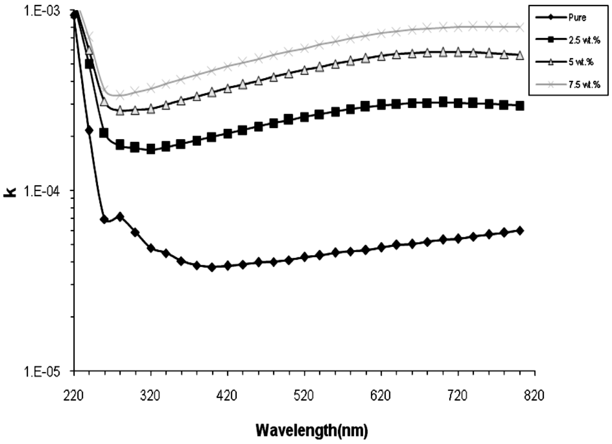

Fig. 6. Variation of the extinction coefficient of the (PVA–PAA) blend for different concentrations of PbO_2 nanoparticles versus the photon wavelength

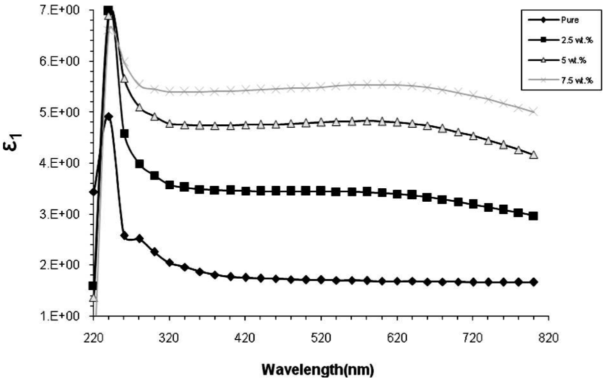

Fig. 7. Real part of the dielectric constant of the (PVA–PAA–PbO_2) nanocomposite

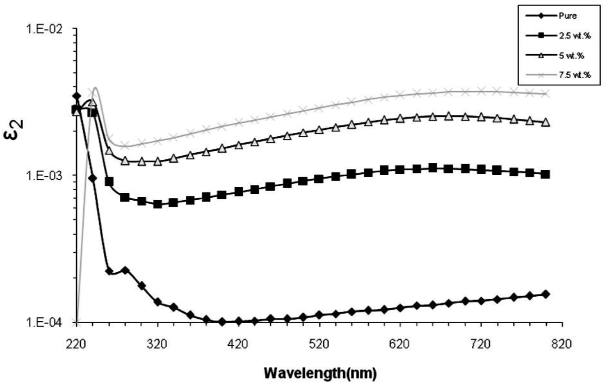

Fig. 8. Imaginary part of the dielectric constant of the (PVA–PAA–PbO_2) nanocomposites

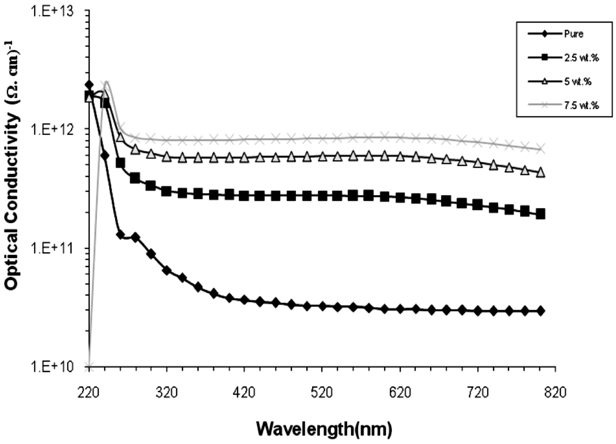

Fig. 9. Optical conductivity of the (PVA–PAA–PbO_2) nanocomposite for different concentrations of PbO_2 nanoparticles

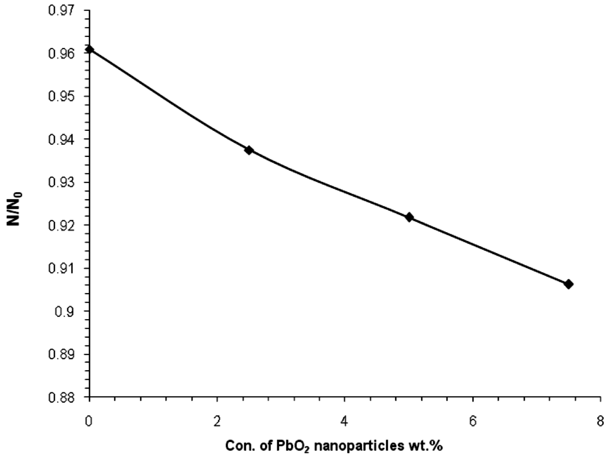

Fig. 10. Relationship of the gamma ray (Co-60) transmission through the (PVA–PAA–PbO_2) nanocomposite

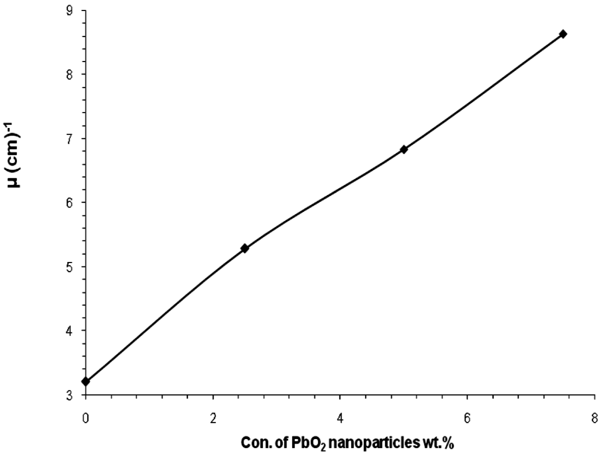

Fig. 11. Variation of the linear attenuation coefficients of (PVA–PAA–PbO_2) nanocomposite for gamma rays (Co-60)

very rapidly (10^{-8} s) to its original state emitting a photon of light in the process. Gamma-radiation is an electromagnetic wave, which interacts with matter via the photoelectric effect, Compton scattering, and pair production. The most important reactions occurring during the radiolysis of polymers are those that lead to permanent changes in their molecular weight. The reactions leading to either an increase or a decrease in the molecular weight are referred to as the cross-linking and chain scission, respectively. In general, the cross-linking and scission processes can occur simultaneously in any irradiated material; however, it is often observed that one tends to dominate over the other, and, thus, the polymers can be broadly placed into the categories of cross-linking or degrading [9]. The (PVA–PAA–PbO_2) nanocomposite has high attenuation coefficients, which is due to the high atomic number of PbO_2 nanoparticles.

4. Conclusions

The absorbance of the (PVA–PAA) blend increases with the concentration of PbO_2 nanoparticles. The nanocomposite has high absorbance in the UV-region. The energy band gap of the (PVA–PAA) blend decreases with increasing the concentration of PbO_2 nanoparticles. The absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of the dielectric constant, and optical conductivity of the (PVA–PAA) blend increase with the concentration of PbO_2 nanoparticles. The (PVA–PAA–PbO_2) nanocomposite has high linear attenuation coefficients for gamma radiation.

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НОВІ НАНОКОМПОЗИТИ ПОЛІМЕР–ОКИС СВИНЦЮ ДЛЯ ЗАСТОСУВАННЯ В РАДІАЦІЙНОМУ ЗАХИСТУ

Резюме

Полімерні нанокомпозити застосовуються в багатьох випадках для захисних покриттів для приладів і захисту людей на АЕС і в лікарнях. Мета даної роботи – створення і дослідження нових полімерних нанокомпозитів з великими коефіцієнтами лінійного ослаблення з наночастинок оксиду свинцю і полівінілового спирту та поліакрилової кислоти з різними концентраціями для екранування радіації. Вивчено оптичні властивості наночастинок. З ростом концентрації PbO_2 наночастинок поглинання нанокомпозиту і оптичні константи збільшуються, а ширина забороненої зони зменшується. Випробування нанокомпозиту показало, що він володіє хорошими захисними властивостями в умовах гамма-радіації.