

Preparation and Characterization of (Biopolymer blend-PbO₂) Nanocomposites For Gamma Ray Shielding Applications

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Abstract

In the present work, nanocomposites of polyvinyl pyrrolidone (PVP), carboxymethyl cellulose (CMC) and lead oxide nanoparticles (PbO₂) have been prepared to use for gamma ray shielding applications. The nanocomposites have been prepared by casting technique. The lead oxide nanoparticles were added to the mixture of (PVP 55 wt.% and CMC 45 wt.%) with different concentrations are (0,1,5,3 and 4.5) wt.%. The D.C electrical conductivity and optical properties of nanocomposites were studied. The experimental results showed that the D.C electrical conductivity increases with increase the lead oxide nanoparticles concentrations. The absorbance and optical constants increase with the increase of PbO₂ concentrations but the energy band gap decreases with the increase of PbO₂ concentrations. The results of (polyvinyl pyrrolidone, carboxymethyl cellulose and lead oxide nanoparticles) nanocomposites application for gamma ray shielding showed that the (PVP-CMC-PbO₂) nanocomposite have high linear attenuation coefficients for Cs-137 gamma ray sources.

Keywords: nanocomposites, biopolymer, optical properties, gamma ray.

1. Introduction

Nanocomposites technology has now reached the stage where basic research is being applied towards material and process development, aimed at specific products or semi-finished materials. A number of new products are appearing on the market (automotive components, sport equipment, consumer goods); existing processes are being improved with the applications of nanocomposites technology and material [1]. Due of nanometer size of these particles, their physicochemical characteristics differ significantly from those of molecules and bulk materials. Nanoparticle reinforced polymers, synergistically combine the properties of both the host polymer matrix and the discrete nanoparticles. The approach demonstrates the potential to change characteristics of thermosetting and thermoplastic polymers fundamentally to improve their general performance".

" However, the polymer matrix must withstand high mechanical loads; it is usually reinforced with fillers" [2] Optical characteristics of polymers comprise an important aspects in study of electronic conversion and the possibility of their application as a cover in solar collection, optical filters, green house and selection surfaces [3]. Integration of macro and nanocomposites has led to the development of a new class of nanocomposite materials which find the vital approach in medicine, biology, industry and defense. 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. 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. 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" [4].

It is also cohesive in structure. " The composite materials are comprised of two major components: the matrix which is the basic material , and the additive and serving to enclose the composite and give it bulk form. Matrix surrounds other constituents and makes them more cohesive to form a "compact system". Additive are added to polymers to provide them with specific properties and improve basic properties. These constituents are added in a granular form or as small particles. Additives can increase the overall conductivity, reduce porosity, improve friction and some magnetic properties ...etc. [5].

" 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" [4] [6].

This paper deals with the results of the effect of lead oxide nanoparticles on the D.C electrical and optical properties (polyvinyl pyrrolidone- carboxymethyl cellulose -lead oxide nanoparticles) nanocomposites for gamma ray .

2. Materials and Methods

The nanocomposites films have been prepared by using of polyvinyl pyrrolidone (PVP)-carboxymethyl cellulose (CMC) as polymeric blend matrix and lead oxide nanoparticles (PbO_2) as additive. The films of (PVP-CMC- PbO_2) nanocomposites have been prepared with different weight percentages of (PVP-CMC) blend which are (PVP 55 wt.%+ CMC 45 wt.%) and PbO_2 nanoparticle was added to blend by different concentrations are (0,1.5,3 and 4.5) wt.%. The casting technique was used to prepare the (PVP-CMC- PbO_2) nanocomposites. " The D.C electrical conductivity of (PVP-CMC- PbO_2) nanocomposites" was measured by determining the electrical resistance at room temperature by using the Keithley electrometer type 2400 source meter (University of Babylon, College of Basic Education, Department of Sciences) The optical properties of (PVP-CMC- PbO_2) nanocomposites were measured by using UV/1800/ Shimadzu in range of wavelength (220-800) nm. The (PVP-CMC- PbO_2)

nanocomposites were tested for gamma ray shielding application to investigate attenuation properties of gamma rays for the (PVP-CMC-PbO₂) samples with different concentrations of PbO₂ nanoparticles. The (PVP-CMC-PbO₂) samples arranged in front of a collimated beam emerged from gamma ray source (Cs-137, 1 μ ci). The gamma ray source is positioned at distance 3 cm from the detector; the sample of (PVP-CMC-PbO₂) nanocomposites is positioned at distance 1 cm from the gamma ray source. The transmitted gamma ray fluxes through the (PVP-CMC-PbO₂) nanocomposites are measured by the Geiger counter were used to estimate the linear attenuation coefficients.

The D.C electrical conductivity (σ_v) of (PVP-CMC-PbO₂) samples calculated by using the equation [7] :

$$\sigma_v = L/RS \quad \dots\dots\dots(1)$$

Where **L** is the length of the sample, **S** is the constant area and **R** is electrical resistance.

The absorption coefficient (α) of (PVP-CMC-PbO₂) nanocomposites is given by the equation [8] :

$$\alpha = 2.303 \frac{A}{d} \quad \dots\dots\dots(2)$$

Where: d is the thickness of the sample and A is optical absorbance.

The electronic transitions of material were defined by equation [8] :

$$ah\nu = B_0 (h\nu - E_g^{opt})^r \quad \dots\dots\dots(3)$$

Where, ν is the frequency, B_0 is a constant, h is Planck's constant, E_g^{opt} is the energy band gap between the valence band and the conduction band and r can take the values (2, 3, 1/2 or 3/2) for indirect allowed, indirect forbidden, direct allowed and direct forbidden, respectively .

The extinction coefficient (K) and (λ) wavelength of samples was calculated by using the equation [9] :

$$K = \alpha\lambda/4\pi \quad \dots\dots\dots(4)$$

The refractive index (n) of material can be calculated by using following equation [9] :

$$n = (1+R^{1/2}) / (1-R^{1/2}) \quad \dots\dots\dots(5)$$

The real and imaginary parts of the dielectric constant (ϵ_1 and ϵ_2) for nanocomposite are given by using equations [10]:

$$\epsilon_1 = n^2 - k^2 \text{ (real part)} \quad \dots\dots\dots(6)$$

$$\epsilon_2 = 2nk \text{ (imaginary part)} \quad \dots\dots\dots(7)$$

The optical conductivity of nanocomposites was calculated by using the following equation [10] :

$$\sigma = \frac{\alpha nc}{4\pi} \dots\dots\dots(8)$$

The linear attenuation coefficients (μ) of gamma ray source (Cs-137, $1\mu\text{Ci}$) can be extracted with the thicknesses of the (PVP-CMC-PbO₂) nanocomposites by the standard equation [11] :

$$I = I_0 e^{-\mu x} \dots\dots\dots(9)$$

Plotting $\ln(I_0/I)$ versus x would give straight line and μ can be obtained from the value of the slope. The correlation between the linear attenuation coefficients and the thickness of the (PVP-CMC-PbO₂) nanocomposites is used to confirm the linearity

3. Results

Figure 1: shows the effect of PbO₂ nanoparticles concentrations on D.C electrical conductivity of (PVP-CMC) blend at room temperature. As shown in the figure, electrical conductivity of (PVP-CMC) blend increases with increase of the PbO₂ nanoparticles concentrations. The increasing of electrical conductivity for (PVP-CMC-PbO₂) nanocomposites can be explained by: the PbO₂ nanoparticles " having large number of free charge carriers available for the purpose of conduction. Hence, as the concentration of PbO₂ nanoparticles increases the number of free charge carriers also increases, all together electrons from polar O²⁻ terminated PbO₂ nanoparticles surfaces and from the (PVP-CMC) chains, resulting in the improvement in the conductivity of (PVP-CMC-PbO₂) nanocomposites [12] [13] .

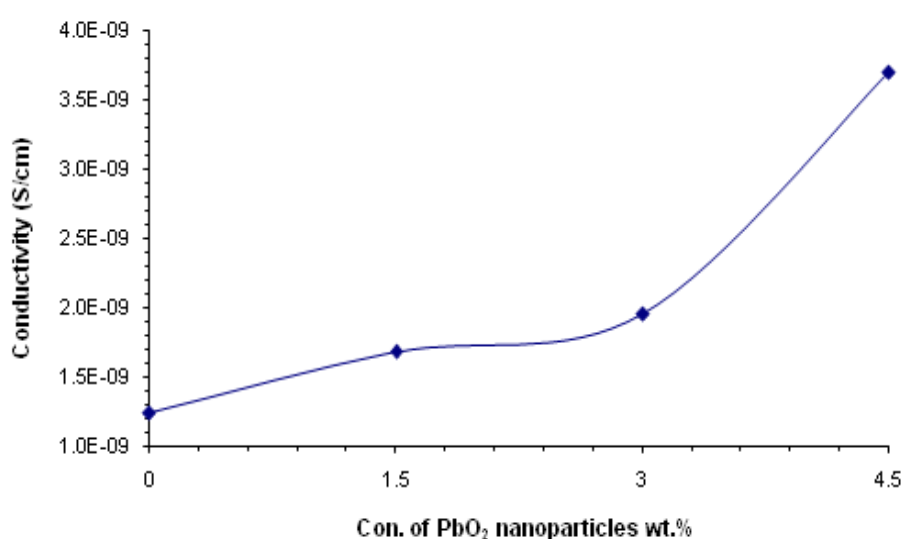


Figure 1: effect of PbO₂ nanoparticles concentrations on D.C electrical conductivity of (PVP-CMC) blend.

C)

blend (PVP-CMC-PbO₂) nanocomposites. The absorption spectrum of pure (PVP-CMC) is limited in the UV region, but it is enhanced when PbO₂ nanoparticles were added, which had a high energy gap. The curves of nanocomposites of high PbO₂ concentration showed a clear peak in the UV region and less absorption in the visible region. The peak of high absorption at around 250 nm is observed". That is due to the absorption of PbO₂ nanoparticles as shown in figure 3 which is show the variation of absorption coefficient with photon energy for (PVP-CMC-PbO₂) nanocomposites." In addition, the lower absorption in the UV and visible regions is due to the roughness of the surfaces that increased with increasing of concentration PbO₂, thus caused the scattering and then losing to incident intensity. The absorption coefficient increased with increased concentration of PbO₂ nanoparticles. Since PbO₂ nanoparticles have low transmittance and high absorbance in the UV region, the (PVP-CMC-PbO₂) nanocomposites samples show higher value of α in the UV region compared with its value in the visible region" [14]. Figure 4 and figure 5: show the values of energy band gap for allowing and forbidden indirect transition of (PVP-CMC-PbO₂) nanocomposites. It is clear that decreases with increasing PbO₂ nanoparticles content." The variation of the calculated values of optical energy gaps may reflect the role of the doping in modifying the electronic structure of the (PVP-CMC) matrix due to the appearance of various Polaroid and defect levels. The decrease in the optical energy gap on doping may be explained on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes in the host matrix. These charge transfer complexes increase the conductivity by providing additional charges, this results in a decrease of the optical energy gap" [8].

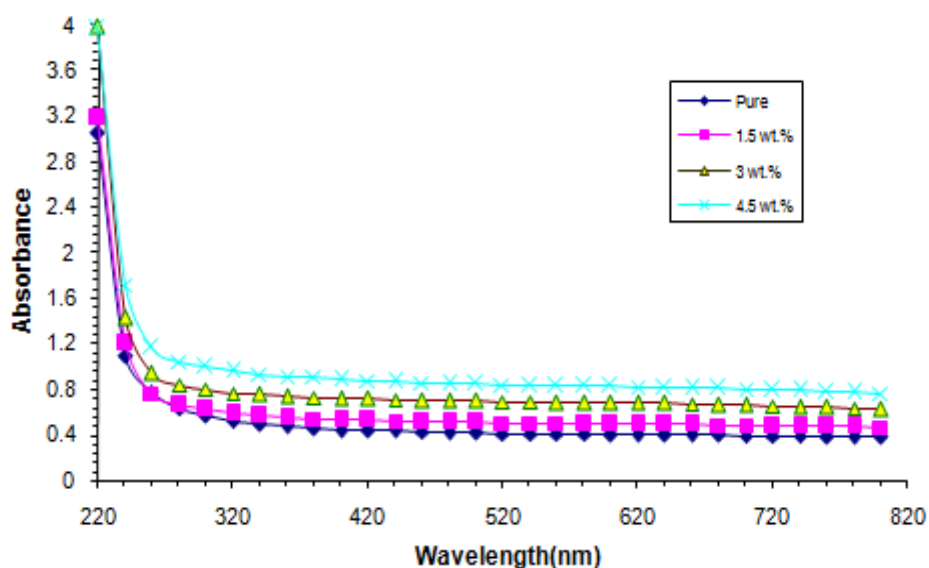


Figure 2: variation of optical absorbance (PVP-CMC-PbO₂) nanocomposites with wavelength.

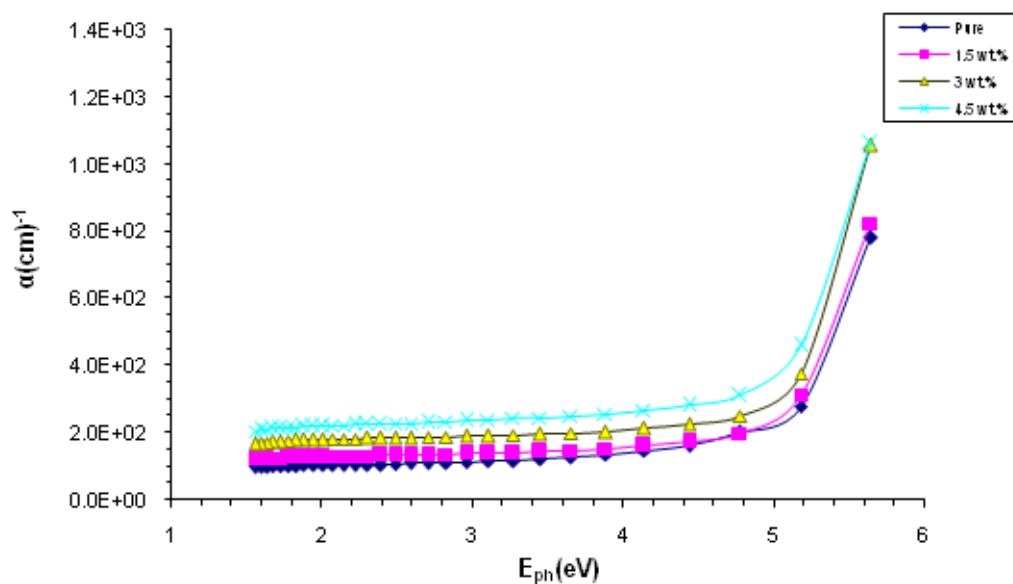


Figure 3: variation of absorption coefficient (PVP-CMC-PbO₂) nanocomposites with photon energy.

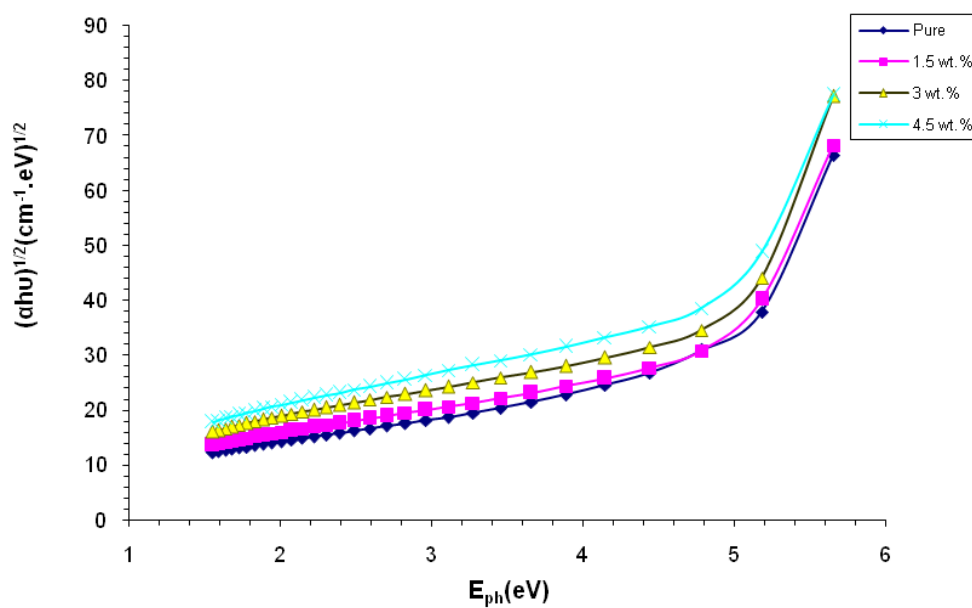


Figure 4: variation of $(\alpha h\nu)^{1/2}$ for (PVP-CMC-PbO₂) nanocomposites with photon energy.

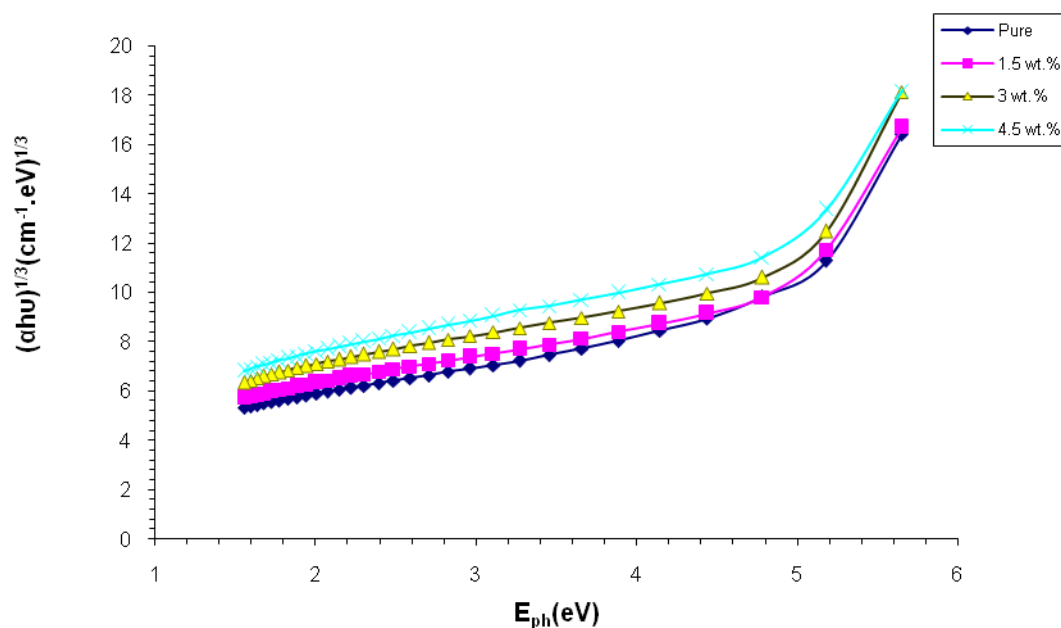


Figure 5: variation of $(\alpha h\nu)^{1/3}$ for (PVP-CMC-PbO₂) nanocomposites with photon energy.

"The most important optical properties are the refractive index and the extinction coefficient, which are generally called optical constants, are calculated using the fundamental relations of photon transmittance and absorbance. The extinction coefficient over the exponential absorption region for (PVP-CMC-PbO₂) nanocomposites samples is shown in figure 6. The low value of extinction coefficient at long wavelengths, indicating that the (PVP-CMC-PbO₂) films are highly transparent, while at low wavelength (high photon energy) the extinction coefficient

increases to a maximum value, due to the predominance of the absorption behavior. It is also evident from figure 6 that extinction coefficient increases with PbO₂ nanoparticles concentration in (PVP-CMC) films. The higher extinction coefficient value for (PVP-CMC-PbO₂) films indicates that the films dissipate more photonic energy than those of pure (PVP-CMC) when exposed to electromagnetic radiation".

In the same region, the refractive index values have been calculated from a combination of reflectance and absorbance measurements at normal incidence." The variations of refractive index with wavelength of (PVP-CMC-PbO₂) nanocomposites samples is shown in figure 7. It is clear from this figure, that the refractive index decreases with increasing wavelength; while the increase with PbO₂ nanoparticles concentration can be seen. At higher wavelength, the (PVP-CMC-PbO₂) films showed non-dispersive behavior and refractive index tended to be constant. The higher refraction coefficient of (PVP-CMC-PbO₂) nanocomposites films compared to that of the pure (PVP-CMC) may be attributed to the differences in their molecular packing density. A high refractive index is preferred for some specific optoelectronic devices, such as organic solar cell. The variation of real and imaginary parts of dielectric constants with wavelength are shown in figures 8

and 9". The complex dielectric constant for a wavelength range between ultraviolet and near infrared, is important criteria for the selection of fabricated films for various applications. The real part of dielectric constant is one of the fundamental properties of a material, because it is related to the polarizability inside the material". The complex dielectric constant is a materials property depending on wavelength, temperature, conductivity, size, shape, and spatial arrangement of the constituents (the filler in the matrix). The real part is the dielectric constant which is related to the energy stored in the material, and imaginary part is dielectric loss which is proportional to the energy dissipate in material. For practical purposes, the dielectric constant play an important role in designing optical devices, especially in the field of optical communication. The general trend for all composition is decreasesing the dielectric loss factor in the investigated wavelength region, while there are a significant increase in dielectric constant with increasing the PbO_2 nanoparticles content, and finally reaches nearly a constant value in the higher wavelength. It can be seen from figures 8 and 9, that the real and imaginary parts increase with increasing PbO_2 nanoparticles concentration. The increase in the value of real dielectric constant can be ascribed to the increase of electrical polarization due to contribution of PbO_2 nanoparticles concentration in the sample, i.e., the increase in the dielectric constant represents a fractional increase in charges within the polymer blend, and hence an increase in polarization" [15].

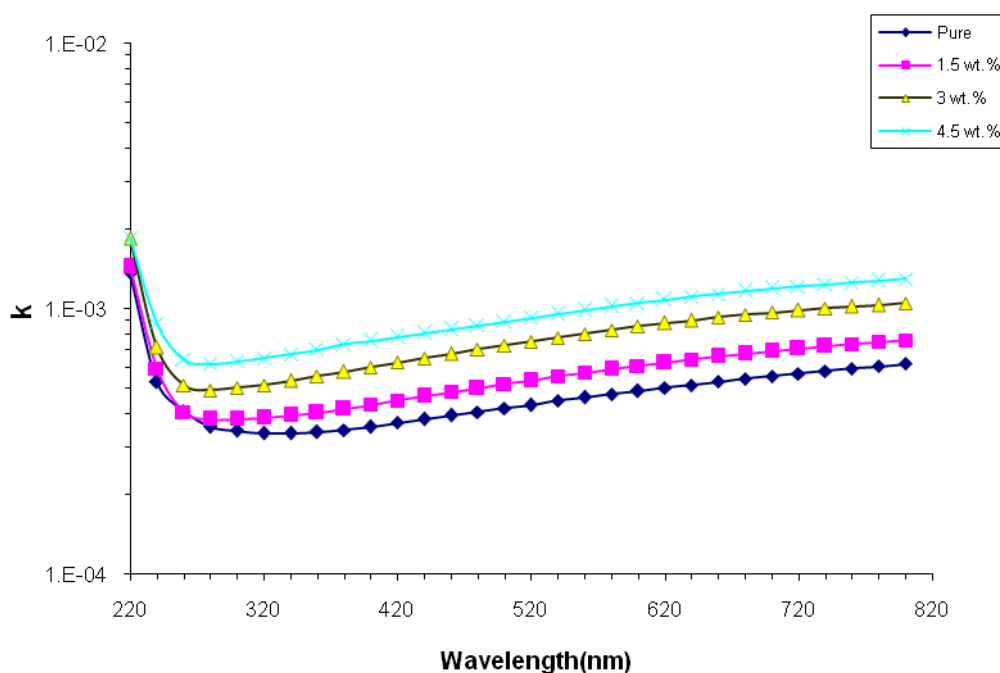


Figure 6: relationship between extinction coefficient for (PVP-CMC- PbO_2) nanocomposites and wavelength.

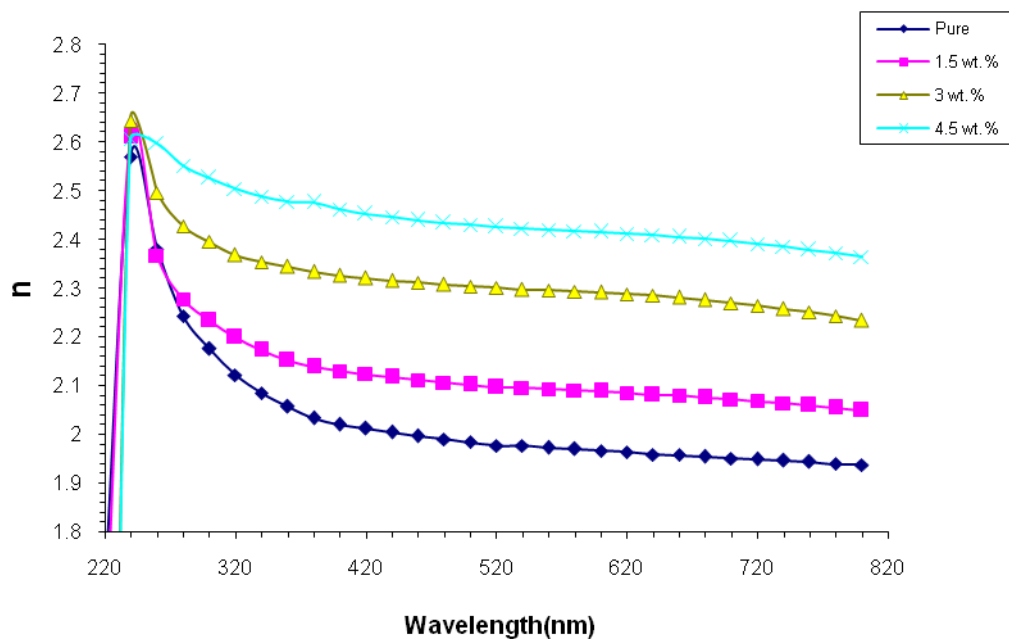


Figure 7: relationship between refractive index for (PVP-CMC-PbO₂) nanocomposites and wavelength.

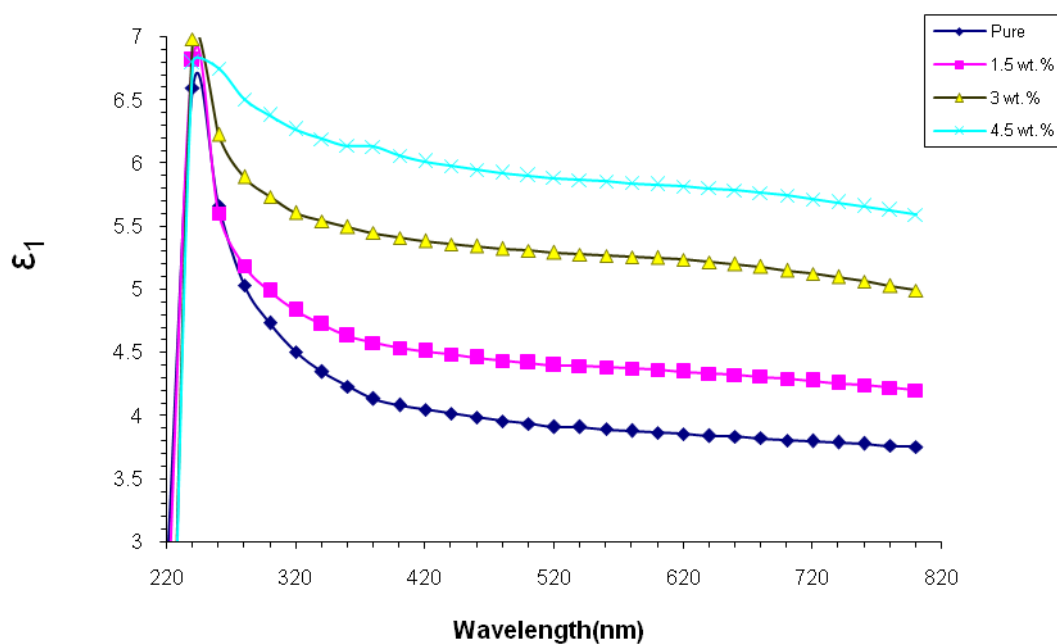


Figure 8: variation of real part of dielectric constant for (PVP-CMC-PbO₂) nanocomposites with wavelength.

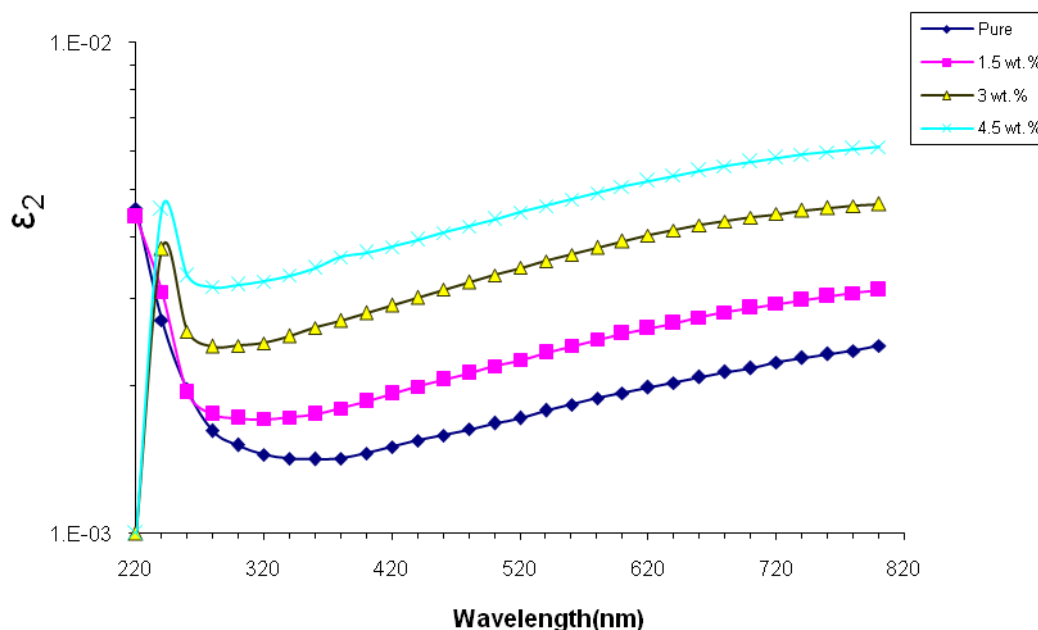


Figure 9: variation of imaginary part of dielectric constant for (PVP-CMC-PbO₂) nanocomposites with wavelength.

Figure 10 shows the variation of optical conductivity with the incident photon wave-length. The optical conductivity is constant up to 400 nm of photon wavelength after that it increases with decrease in photon wavelength. The increased optical conductivity at high photon energies is due to high absorbance of (PVP-CMC-PbO₂) nanocomposites film in that region. The optical conductance spectra indicated that the (PVP-CMC-PbO₂) nanocomposites films are transmittance within the visible range. Figure 11 shows the relationship of gamma ray Cs-137 transmitted through nanocomposites with PbO₂ nanoparticles concentration.

From the figure, the gamma ray transmitted decreases with increase the PbO₂ nanoparticles concentration. " One of the most interaction mechanisms is an interaction in which an incident gamma photon loses enough energy to an atomic electron to cause its ejection, with the remainder of the original photon's energy being emitted as a new and lower energy gamma photon with an emission direction different from that of the incident gamma photon, it is termed Compton scattering". The probability of Compton scatters decreases with increasing photon energy. The variation of linear attenuation coefficients with PbO₂ nanoparticles concentration is shown in figure 12. As shown in figure, the linear attenuation coefficients increases with increasing of PbO₂ nanoparticles concentration which is due to complete cross-linking of the polymer blend and PbO₂ nanoparticles [16].

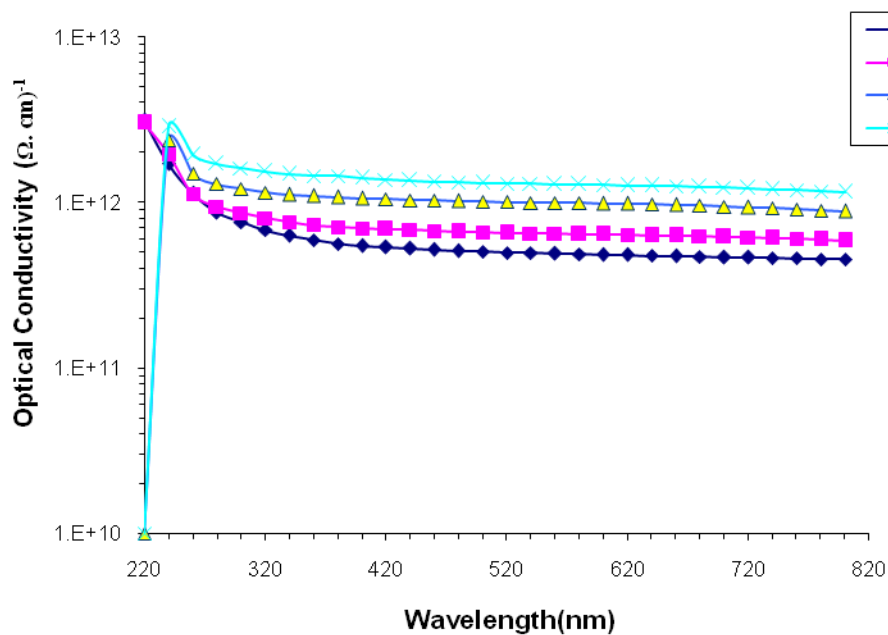


Figure 10: variation of optical conductivity for (PVP-CMC-PbO₂) nanocomposites with wavelength.

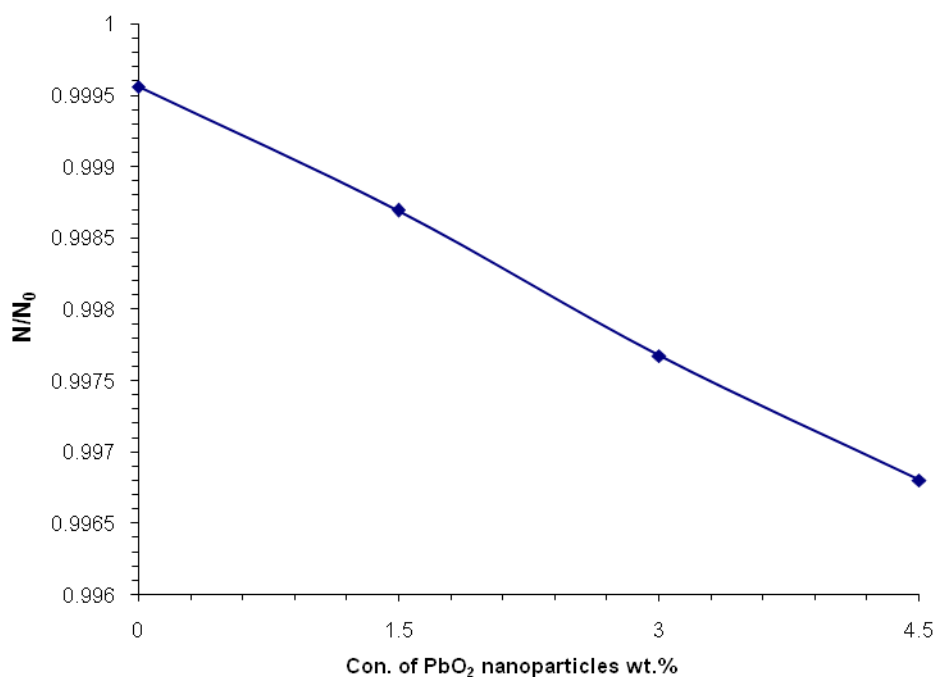


Figure 11: relationship of gamma ray (Cs-137) transmitted through (PVP-CMC PbO₂) nanocomposites with PbO₂ nanoparticles concentrations.

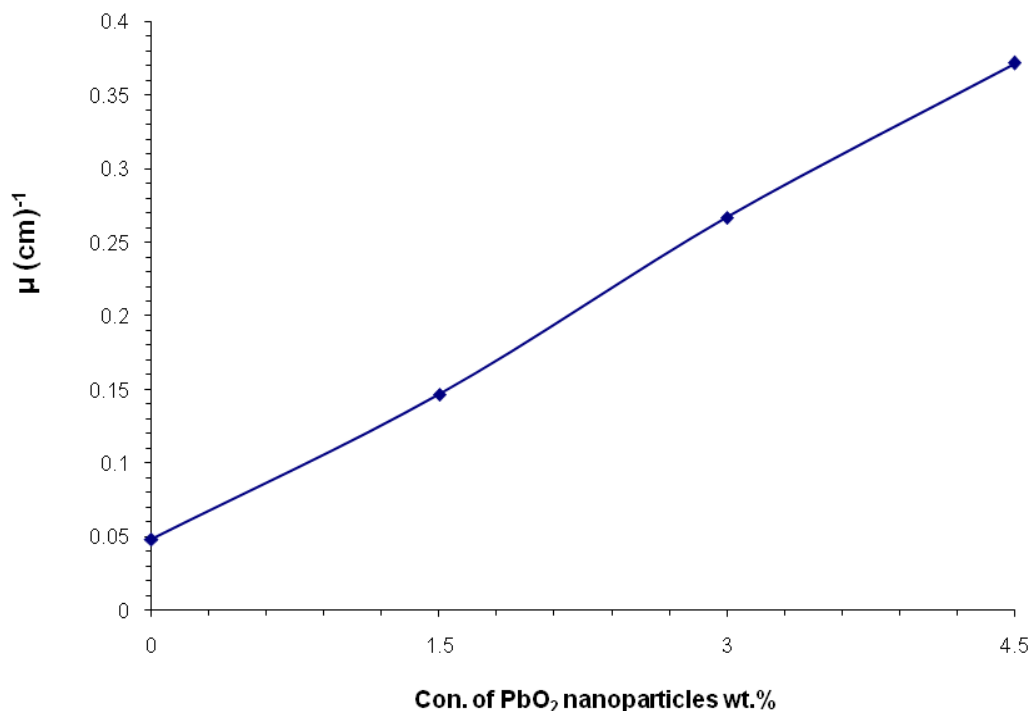


Figure 12: variation of linear attenuation coefficients for (PVP-CMC PbO_2) nanocomposites with PbO_2 nanoparticles concentrations.

4. Conclusions

The D.C electrical conductivity of (polyvinyl pyrrolidone (PVP), carboxymethyl cellulose (CMC) and lead oxide nanoparticles (PbO_2)) nanocomposites increases with an increase in PbO_2 nanoparticles concentrations. The absorbance and optical constants (refractive index, extinction coefficient, real and imaginary parts of dielectric constant, optical conductivity) increase with the increase of PbO_2 concentrations but the energy band gap decreases with the increase of PbO_2 concentrations. The (PVP-CMC- PbO_2) nanocomposite have high linear attenuation coefficients for Cs-137 gamma ray sources.

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تحضير ودراسة خصائص متراكبات (خليط بوليمري حيائي - PbO_2) النانوية

لتطبيقات تدريع اشعة كاما

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الخلاصة

في العمل الحالي، حضرت متراكبات نانوية من بولي فاينيل بيروليدون (PVP) - كاربوكسي مثيل سيليلوز (CMC) - اوكسيد الرصاص النانوي (PbO_2) لاستعمالها في تطبيقات تدريع اشعة كاما. المتراكبات النانوية حضرت بتقنية الصب. اوكسيد الرصاص النانوي اضيف الى المزيج (PVP 55 wt.% and CMC 45 wt.%) بتركيز مختلفة هي (0,1.5,3 and 4.5) wt.%. درست التوصيلية الكهربائية المستمرة والخواص البصرية للمتراكبات النانوية. النتائج العملية بينت ان التوصيلية الكهربائية المستمرة تزداد مع زيادة تركيز PbO_2 النانوي. الامتصاصية والثابت البصري تزداد مع زيادة تركيز PbO_2 النانوي لكن فجوة الطاقة البصرية تقل مع زيادة تركيز PbO_2 النانوي. نتائج تطبيق متراكبات (بولي فاينيل بيروليدون - كاربوكسي مثيل سيليلوز - اوكسيد الرصاص النانوي) النانوية كدروع اشعة كاما بينت ان متراكبات (PVP-CMC- PbO_2) النانوية تمتلك معاملات توهين خطية عالية لمصدر اشعة كاما Cs-137.

الكلمات المفتاحية: متراكبات نانوية، بوليمر حيائي، الخواص البصرية، اشعة كاما.