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Investigation of Optical properties of nano-sized lead polymeric composites

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الملخص:

يهدف البحث لدراسة الخصائص البصرية لعينات الرصاص النانوية الممزوجة بمواد بوليميرية، تم تحضير العينات بسمك 3 مم، باستخدام نسب مختلفة من الرصاص المضاف إلى المواد البوليميرية (مصلب – الإيبوكسي). تم تقييم السلوك البصري للعينات المحضرة باستخدام مطيافية الأشعة فوق البنفسجية والمرئية ضمن نطاق (250 – 800) نانومتر، دُرست الخصائص البصرية بما في ذلك الامتصاصية وطاقة الفجوة البصرية ومعامل الانكسار، كدالة لتركيز جسيمات أكسيد الرصاص النانوية، ثم استُخدمت نظرية ديفيس وموت لتحديد طاقة الفجوة لكل من الانتقالات المسموحة المباشرة وغير المباشرة باستخدام أسلوب مطابقة طيف الامتصاص تم تحديد قيم فجوة الطاقة، حيث قُدّرت قيم طاقة الفجوة بـ 1.9 إلكترون فولت للانتقال غير المباشر، بينما للانتقال المباشر، كانت القيمة 1.6 الكترون فولت، كما أظهرت الدراسة زيادة في معامل الانكسار مع زيادة نسبة أكسيد الرصاص من 1.66 عند 10% من اكسيد الرصاص إلى 1.9 عند 40%، علاوة على ذلك انخفض معامل الامتصاص بزيادة الطول الموجي. تُظهر هذه النتائج أن جسيمات أكسيد الرصاص النانوية تُعدّ مادة مائلة فعّالة لتقوية الخصائص البصرية لمركبات الإيبوكسي المُصلِّبة، مما يجعل هذه المواد مرشحة واعدة للتطبيقات في الطلاءات البصرية، والحماية من الإشعاع، والأجهزة الضوئية، وأنظمة الإلكترونيات الضوئية المتقدمة.

الكلمات المفتاحية: الايبوكسي – مصلب، بوليمر، جزيئات نانوية، مرئي، اكسيد الرصاص.

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Abstract:

This study investigates the optical properties of nano – sized lead samples mixed with polymeric materials. The 3mm thickness samples were prepared using different percentage of lead doped with polymeric materials (epoxy-hardener). The optical behavior of the prepared samples was evaluated using UV-Visible spectroscopy over an 250-800nm. The optical characteristics, including absorbance, optical gap energy and refractive index were investigated as a function of PbO nanoparticle concentration. Davis and Mott's theory was used to determine the Eg for both direct and indirect permitted transitions. Using the absorption spectrum fitting approach, the Eg values are also estimated to be 1.9ev for indirect transition (n=2), while it was 1.6ev for direct transition (n=1/2). It was also shown the increases of the refractive index by increasing the percentage of PbO from 1.66 at 10wt% to reach 1.9 at 40wt% of PbO. Moreover, the absorption index decreased by increasing the wavelength. The study of the nanostructures of the samples will be done by using SEM. In order to get information such as phase composition, morphology and spatial sharing of the heavy elements can be obtained. These findings demonstrate that nano-sized PbO is an effective reinforcing filler for tailoring the optical characteristics of epoxy hardener composites, making these materials in promising candidates for applications in optical coatings, radiation shielding, photonic devices, and advanced optoelectronic systems.

Key wards: epoxy- hardener; polymer; nano-sized; optical; lead oxide.

The Purposes:

This research aims to achieve the following points:

1- Prepare a samples of nano-sized composite of lead oxide doped to the epoxy with different weight of lead (10%, 20%, 30%, 40%).

2-Study the optical properties for these samples, including absorbance, optical gap energy and refractive index well evaluate.

3-Improve the absorbance index of nano-lead composite by increasing the percentage of PbO.

We strive for obtain high-quality materials for ion shielding with superior optical properties.

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1. Introduction:

Recently, the use of regular, macro or nano polymer compounds as nuclear shielding materials have attracted the attention of many researchers due to their importance, the development of radiation shielding materials has extended beyond conventional protection purposes to include optical applications [1, 2]. Modern shielding materials are required not only to provide effective attenuation ionizing radiation but also to maintain desirable optical properties such as high transparency, controlled refractive index, and optimized light transmission. These characteristics are particularly important in medical imaging systems, optical protective windows, LED encapsulation, and photonic devices. Therefore, investigating the optical behavior of lead –polymeric composites is essential for understanding their multifunctional performance and expanding their practical applications [3,4, 5].

Epoxy- hardeners are chemical substances that help epoxy resins cross-link; they are often referred to as curing agents or catalysts. These hardeners start the curing process when combined with liquid epoxy resins, forming a robust, cross-linked network that turns the resin into a solid, long-lasting substance. Epoxy- hardener systems are among the most widely used thermosetting polymeric materiel due to their excellent mechanical strength, chemical resistance, thermal stability, and ease of processing [4, 6]. The addition of lead oxide PbO nanoparticles to the epoxy- hardener matrix has attracted considerable attention because of their high density, large surface area, and high electronic polarizability. To study properties such as modulus of elasticity and tensile strength of the polymer matrix the Scanning electron microscopy (SEM) has been used. The incorporation of PbO nanoparticles can significantly modify the microstructure and electronic behavior of the polymer composite, leading to changes include variation in the refractive index, optical band gap, absorption coefficient, making epoxy-hardener –PbO nanocomposites promising material for optical coatings, optoelectronic devices, radiation shielding, and advanced photonic application [7].

2. Experimental

2.1 Samples preparation

The samples prepared by three steps, which are:

1. The nano-sized composite of heavy elements of lead oxide added to the epoxy with the hardener with different weight of lead (10%, 20%, 30%, 40%); using 50ml of

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deionized water which added to C8H12O8Pb (11.08)" lead Acetate". Also the NaOH added to 50ml of deionized water to prepare the lead oxide.

2. Then the materials mixed together in room temperature using a mixture machine for 30-45min, and then the lead oxide filtered and dried before mixed with the hardener.
3. The hardened motley in the epoxy resin by 2:1. After that the mixture was placed in a silicon mold of silicon rubber with 3mm thickness for ten hours.
4. The four samples have prepared with specific percentage as shown in table 1 below:

%	PbO	Epoxy	Hardener	Total 'g'
10%	1	6	3	10
20%	2.4	6.4	3.2	12
30%	4.5	7	3.5	15
40%	7.2	7.2	3.6	18

Table 1: shows the percentages of the components and the total weight

2.2 Optical measurement

The optical properties of the studied lead oxide –epoxy- hardener composites were investigated by UV–Visible–NIR Spectrophotometer (JASCO model V770) to determine the optical transition in the range 190–2000 nm through absorption spectra with a resolution of 2 nm. We have used the software (Original 8.6) for absorption spectroscopy, the optical properties of the samples were calculated**.** The absorbance has calculated using the formula:

$$A = -\log T \qquad (1)$$

Whereas: A = is the absorption, T = the transmission. The mathematical formula correlating the optical absorption coefficient (α) with the photon energy ($h\upsilon$) was deduced by Davis and Mott [8] as follows:

$$(\alpha h\upsilon)^n = B(h\upsilon - E_g) \qquad (2)$$

where B is a constant called band tailing parameter, hυ is the incident photon energy, and n Is the index which can have different values, viz. 1/2, 2, 1/3 and 3 corresponding to direct allowed, indirect allowed, direct forbidden and indirect forbidden, respectively. For amorphous materials, the indirect transitions i.e. n = 2 and n = 3 are valid according to

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the Tauc's relations. The Tauc's plots for n = 1\2 and n = 2 are shown in Figure. 2(a and b), respectively. The value of Eg can be estimated from the above relation by extrapolating the linear region of the curves to zero absorbance. The absorption coefficient α is estimated from the optical absorbance A through the relation [9],

$$\alpha(cm)^{-1}=2.303(A/d) \qquad (3)$$

where d is the sample thickness. In Eq. (2), m takes the following values 1/2 and 2 for direct and indirect transition, respectively. Generally, for composite, indirect allowed transitions (n = 2) are valid which result from electromagnetic interaction of photons with electrons present in the valence band. The linear refractive index no for composite has been correlated with the optical band gap by Dimitrov and Sakka as [10].

$$\frac{n_0^2-1}{n_0^2-2}=1-\sqrt{\frac{E_g}{20}} \qquad (4)$$

This relation allows getting *n*o values by using *E*g data.

3. Result and Discussion

Figure1, illustrates the UV–V absorption spectra of the produced PbO-doped by Epoxy resin for the samples of PbO weight of (10%, 20%, 30%, 40%) are plotted in Y-axis against the wavelength(nm) in X-axis. As it is shown, absorption increases progressively with increasing PbO content to observed to be high at around 300nm, inducting enhanced interaction between the incident photons and the composite material. The incorporation of PbO nanoparticles introduces additional localized electronic states and increases the intensity of optical transition centers, leading to higher light absorption. At the highest concentration (40wt%PbO), the absorbance increases again at longer wavelengths of (700nm), which may be attributed to nanoparticle aggregation and enhanced light scattering. These observations are consistent with a decrease in the optical band gap and an increase in the refractive index in lead oxide-epoxy composite materials a topic we will examine later.

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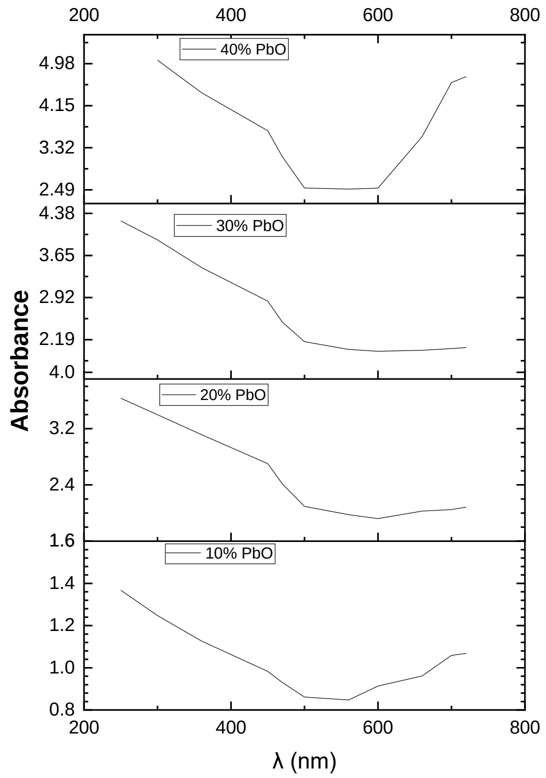

Figure 1: shows the variation in the absorption spectra of nano-PbO doped by Epoxy resin with respect to λ (nm).

The direct and indirect optical band gaps of epoxy hardener lead oxide nanocomposites have been studied using the Tauc plots and the results were presented in figure 2. The optical band gap energy (Eg) is described as the simplest way between the valence and conduction band. It also represents the energy of the electron transition between these two bands. There are different types of optical transitions that may occur through these two bands. the optical band gap was estimated by extrapolating the linear portion of the curves to the photon- energy axis. It was observed that the slope and intercept of the linear region vary with increasing PbO concentration, indicating that PbO nanoparticles significantly modify the electronic band structure of the epoxy matrix. if the calculated band gap values decrease with increasing PbO content. This can be observed in Figure (2), where the estimated energy gap values are (1.8, 1.7, 1.7,1.6) eV for direct transitions upon the addition of lead oxide at molar percentages of 10%, 20%, 30%, and 40%, respectively;

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regarding indirect transitions, the energy gap is (2.2, 2.1, 2, 1.9) eV. These values are consistent with previous studies for Ahmed, S.M. et el, (
2021) [11]. This behavior can be attributed to the formation of localized defect states and enhanced electronic interactions, which facilitate electronic transitions and reduce the energy required for excitation.

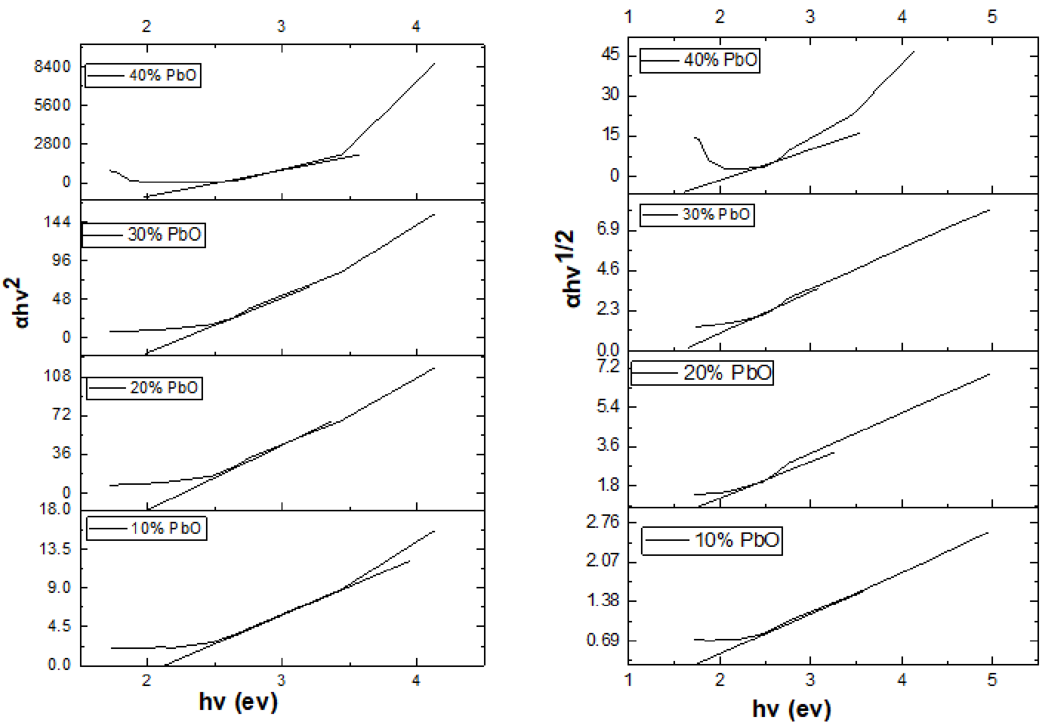

Figure2 shows the direct and indirect energy band gab transition.

Figure 3 shows the variation of the refractive index of lead oxide mixed with epoxy-hardener composite as a function of PbO concentration. It is clearly observed that the refractive index increases progressively with increasing PbO content, rising from approximately 1.66 at 10 wt% to about 1.9 at 40 wt%. The linear fitting demonstrates as strong positive correlation and the refractive index. This increase could be attributed to the high refractive index, high density, and high electronic polarizability of PbO particles compared with the epoxy matrix, all of these factors contribute to enhancement of the refractive index. The incorporation of PbO also reduces the free volume within the polymer matrix and improves the packing density.

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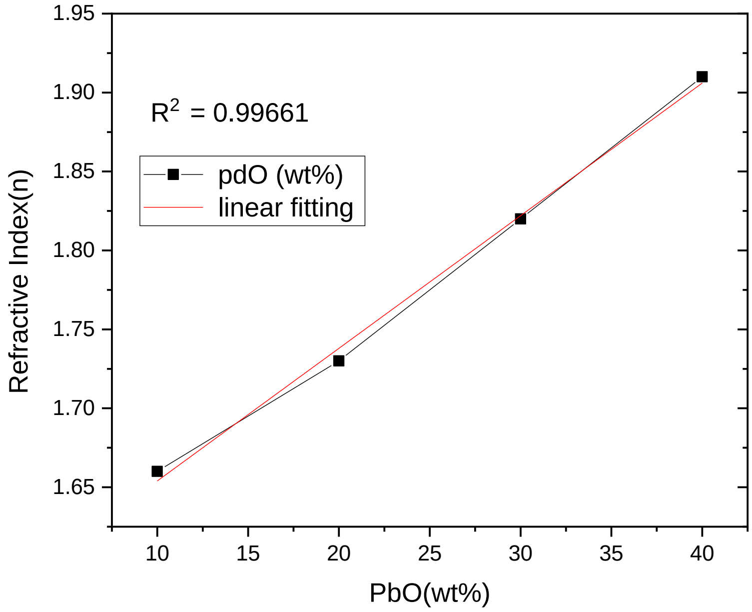

Figure 3 Refractive index (n)of epoxy- hardener as function of PbO (wt%) with linear fitting.

When lead oxide (PbO) particles are incorporated into the epoxy – hardener system, they become dispersed throughout the polymer matrix and microstructure and electronic characteristic. this incorporation increases the electronic density and polarizability of the composite, leading to enhanced optical properties, including higher reflective index [9,12]. Meanwhile, the value in the optical band gap may be associated whit the improved structural homogeneity of the composite and the reduction of localized defect states, resulting in fewer electronic transitions within the forbidden energy region. these findings suggest that the incorporation of PbO modifies the optical characteristics of the epoxy-hardener composite and enhances its suitability for optical and photonic applications.

5. The Scanning Electron Microscopy analysis:

The morphological property of lead oxide was studied using scanning electron microscope. The SEM images revealed the shapes and distributions of the lead oxide nanoparticles. Lead oxide has a spherical shape and the molecules are evenly distribution as fig 4 shows. It is clear to see that when the wavelength was increased to 600 nm, the particle sizes ranges between 17.7 nm to 31,2 nm.

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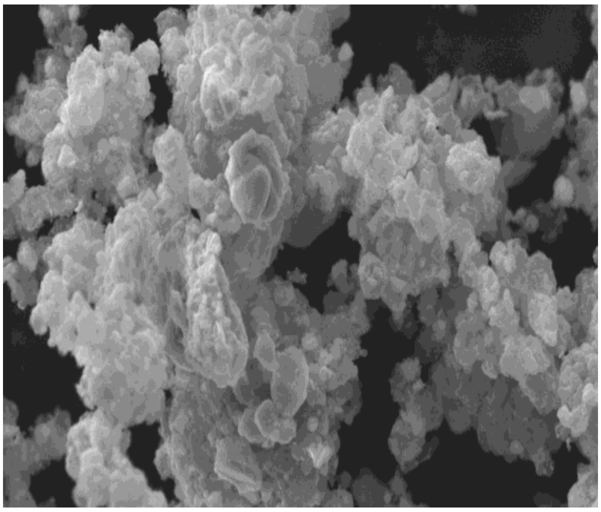

Figure 4: shows the SEM image for nano-lead oxide composite with 10Kv

5. Conclusion

By incorporating lead oxide (PbO) particles the epoxy – hardener system, they become dispersed throughout the polymer matrix and nanostructure and electronic characteristic. As a result shows that:

1- The electronic density and polarizability of the composite increased, hence the optical properties such as reflective index and the optical band gap increased to 1.9 and 1.6 eV respectively.
2- The scanning electron microscope (SEM) results revealed that nano-lead oxide composite has spherical shape; the wavelength has an effect on the particle sizes of lead oxide.
3- However, localized defect states reduced. These findings suggest that the incorporation of PbO modifies the optical characteristics of the epoxy-hardener composite and enhances its suitability for optical and photonic applications.
4- This project offered a new approach for the design of the shielding of protection from the rays ionized using nanostructured of lead polymeric materials, optical coatings, optoelectronic devices, and advanced photonic application.
5- Its ability to increase the refractive index and lower melting points makes it ideal for optical lenses and.

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6. Recommendation:

1. Further study including the elemental distribution of PbO could be carried out experimentally using the microstructural instruments such as TEM, and XPS and simple model using percolation theory could be suggested.
2. Study of the electrical properties of nano- lead oxide doped with epoxy
3. Study of other types of metal oxide films using different techniques.

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