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RESEARCH PAPER

Studying the Optical Properties of Nanocomposite PVA-PEG-ZrC

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ABSTRACT

In this paper, a solution casting technique has been used to investigate the nanocomposite from polyvinylalcohol (PVA) and polyethylene glycol (PEG) with additive different (1.5, 3, and 4.5) wt.% of zirconium carbide nanoparticles (ZrC NPs). The absorption spectrum between 200 and 800 nm was examined using a UV-Vis spectrophotometer. The addition of ZrC nanoparticles to the polymeric system improves the absorption of ultraviolet waves. While transmittance ratios (85-70%) are maintained allowing it to be employed for a variety of purposes, including solar radiation shields, low-cost UV protection, and drug packaging. The optical energy gap for indirect transitions (allowed and forbidden) shrank as ZrC NP content increased. Also, every optical constant has been studied, The parameters that have been experimentally studied for the nanocomposite (PVA-PEG-ZrC) have shown results that are identical to the theoretical studies and the mathematical relationships that govern these parameters.

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INTRODUCTION

Composites, which are the mixture of two or more materials with different physical and chemical properties and are distinguished by their interface, are among the most important components of contemporary technology. Consequently, unlike single materials, composite materials exhibit particular features [1]. The continuous matrix phase and the discontinuous reinforcing material are the two most common components of composite materials. Conversely, some composite materials include one or more discontinuous phases spread within a continuous phase [2]. A discontinuous phase typically possesses more sophisticated mechanical properties than a continuous phase. The discontinuous phase is referred to as "reinforcement" or reinforcing material, while the continuous phase is referred to as "matrix" [3]. Composites are frequently categorized into three basic types called macrocomposites, microcomposites, and nanocomposites based on the size of reinforcement used in the structures [4].

Nanocomposites have at least one phase with nanoscale dimensions (10–100 nm). Nanocomposites suggest superior features by the application of reinforcement in the composite below 100 nm in size phase [5]. The interaction between the matrix and reinforcement in nanocomposites is extremely strong because of the high surface-to-volume ratio [6]. The characteristics of each component, its relative proportions, and the overall shape of the nanocomposites all affect how well they perform [7]. Assorted materials

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have various qualities which when combined produce new materials with extra benefits applicable to various fields of science and industry. They are very thermally and mechanically stable, multifunctional, chemically functionalized, and have a substantial interphase zone [8]. In general, the nanocomposites exhibit improved properties, including high specific hardness and strength, low density, high toughness, thermal insulation, and corrosion resistance [9]. The limitations of many engineering materials are currently being overcome by nanocomposite composites. Nanoparticles' mechanical stability (in terms of dimension stability, strength, flexibility, toughness, Young's modulus, etc.), flame retardancy, good optical activities, low water/gas permeability, and high electro-thermal conductivity are all promoted by the integration of nanoparticles into a matrix of materials like polymer, metal, or ceramics [10]. Due to their unique properties such as optical, thermal, mechanical, electronic, and electrical capabilities, nanocomposites have received great attention at both academic and industrial levels. Therefore, for quite some time now, these materials have been the focus of academic research [11].

The current work aims to prepare PVA-PEG-ZrC nanocomposites and study their optical properties. where polymer-based electrically conductive materials have a number of advantages over their pure metal counterparts, including cost, flexibility, low weight, and the capacity to absorb shocks. This is because polymer-based composites with a conductive filler phase allow the mechanical properties of polymers to be combined and their ease of processing with electrical applications that require significant conductivity. mechanical, ability to create complex parts, wear resistance, and conductivity control [12]. Conjugated conducting polymers have been the main topic of research globally in recent years. The belief that plastic could not conduct electricity has altered since the discovery made by Shirakawa, Macdiarmid, and Heeger, who shared the 2000 Chemistry Nobel Prize. Conductive plastics, also known as conducting polymers, are now being developed for a variety of applications, including corrosion inhibitors, small capacitors, antistatic coatings, electromagnetic shielding, and smart windows, which can control how much light passes through [13]. PVA (Polyvinyl Alcohol), one of the first and best-known polymers, has been utilized in a variety of applications and is still frequently used in semiconductor applications today [14]. Visible light transmits at a relatively high rate. Additionally, when polymers are doped with noble metal nanoparticles, they exhibit innovative and unique features that result from a special fusion of the intrinsic properties of polymers with those of metal nanoparticles [15]. Additionally, PEG (polyethylene glycol) aqueous solutions have become widely used in recent years due to their low cost, low toxicity, low volatility, and biodegradability constitute significant environmentally benign properties that are particularly alluring [16]. Regarding zirconium carbide nanoparticles (ZrC), these particles are distinguished by qualities including good toughness, high strength and hardness, and resistance to oxidation at high temperatures. They also have optical characteristics like high visible light absorption, infrared reflectance, and the capacity to store a lot of energy [17].

MATERIALS AND METHODS

The granular form, water-soluble synthetic polymers PVA (Mol. Wt. 18,000 g/mol, purity 99.99 percent, and melting point 230oC) and PEG (Mol. Wt. 20,000, purity 99 percent, and melting point 250oC) can be acquired from (Central Drug House, Ltd, Company), Indi. Zirconium Carbide (ZrC NPs) were used as additive materials. PVA (70 wt. %) and PEG (30 wt. %) were mixed in 30 ml of deionized water with a magnetic stirring at 70 oC to obtain a more homogenous solution. ZrC NPs were added to the solution in varying weight percent (1.5, 3 and 4.5) wt.%. To create the (PVA-PEG- ZrC) nanocomposites, the casting technique methodology was applied. A double beam spectrophotometer (Shimadzu, UV -18000A) with a wavelength range of 200-800 nm was used to investigate the optical characteristics of (PVA-PEG-ZrC) nanocomposites.

RESULTS AND DISCUSSIONS

Structural characteristics

Fig. 1 displays the field emission scanning electron microscopy (FESEM) images of PVA-PEG once as pure and in the rest images with different proportions of ZrC. The proportions of ZrC are 1.5%, 3%, and 4.5% wt respectively.

Absorbance of the nanocomposit

In order to evaluate the absorption property of prepared nanocomposites, the UV-Vis spectra of both Pure PVA-PEG and PVA-PEG-Zrc with different concentrations of Zrc have recorded in the range 200–800 nm. The results displayed in Fig. 2, amply demonstrate that while UV radiation is only marginally absorbed by pure polymers, it is significantly more absorbed by nanocomposites than by pure polymers. The observed results may be explained by the fact that the nanocomposites absorb more UV light due to the presence of Zrc nanoparticles. Other workers have also reported similar kinds of outcomes [18]. The produced nanocomposites thus demonstrate the potential for usage as UV protective materials. The Uv-Vis spectra in the figure clearly indicate that the absorption spectrum of the nanocomposite increased with the increase in the amount of zirconium carbide within the range of 1.5%-4.5% where we note that the amount of absorption reaches more than 90% when the amount of zirconium carbide is 4.5 relative to the absorption spectrum of the pure polymer (blue curve). This is in accordance with Beer-Lampard's law which states absorption is proportional to the number of absorbent molecules. We also note the widening of the absorption peak and this is due to the interaction between the polymer and zirconium carbide molecules

Effect of ZrC on transmittance of nanocomposite

In order to verify the effect of incorporating zirconium carbide nanoparticles into the PVA-PEG polymer matrix of the nanocomposite PVA-PEG-Zrc, the UV-Vis transmittance spectra were recorded within the range of 200-800 nm and for different concentrations of zirconium carbide. Where the results in Fig. 3 indicate that the nanocomposite shows a very low transmittance in the UV region by increasing the amount of zirconium carbide, which indicates that the nanoparticles of zirconium carbide absorb UV rays. The UV transmittance decreases significantly with the increase in the amount of zirconium carbide. Interestingly, the transmittance of 1.5 is higher than the transmittance of 4.5 (i.e. lower UV protection), which can be attributed to the agglomeration of zirconium carbide nanoparticles, which leads to a lower cross-sectional area exposed to UV protection. Based on the above-mentioned absorption and transmittance of the nanocomposite PVA-PEG-Zrc, it can be shown that the zirconium carbide nanoparticles show the possibility of protection from UV rays.

The absorption coefficient and energy gap of nanocomposite

The definition of an absorption coefficient is the ratio of the flux of incoming ray energy to the distance unit in the direction of the incident wave length. The incident photon energy (hν) determines the absorption coefficient (α) [19].

$$\alpha = 2.303\frac{A}{d} \quad (1)$$

Where A is absorbance and is the thickness of sample. Fig. 4 shows the effect of adding zirconium carbide on the absorption coefficient as a function of the energy of the incident photon, as we note that the absorption coefficient increases with the increase in the amount of nano-zirconium carbide, and this is attributed to the increase in absorption when the number of absorbing particles increases. It can be also noted that the change in the absorption coefficient is small at low energies, while it is large at high energies, and this only indicates large electronic transitions.

The absorption coefficient is an important factor in deducing the nature of electronic transitions.

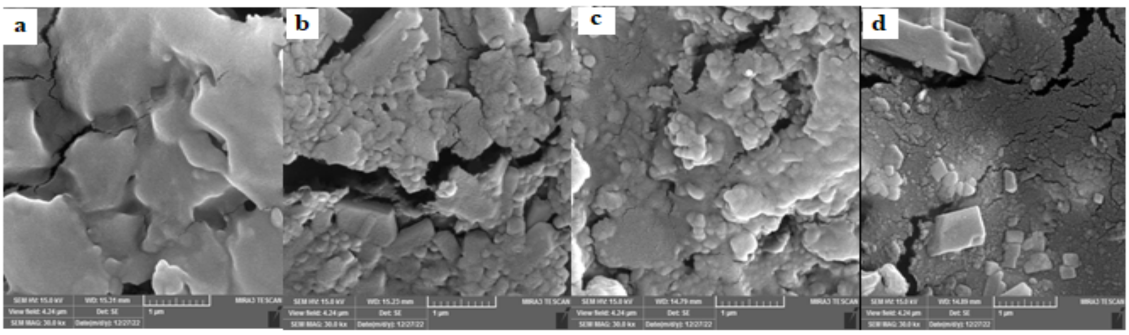

Fig. 1. The FESEM images of PVA-PEG: a- pure b- with 1.5% ZrC c- with 3% ZrC d- with 4.5% ZrC

When the value of the absorption coefficient is ($\alpha > 10^4$ cm^{-1}) at high energies, it indicates direct transitions and the energy and momentum of the electron and photon are conserved. While when the value of the absorption coefficient is ($\alpha < 10^4$ cm^{-1}) at low energies, the electronic transitions will

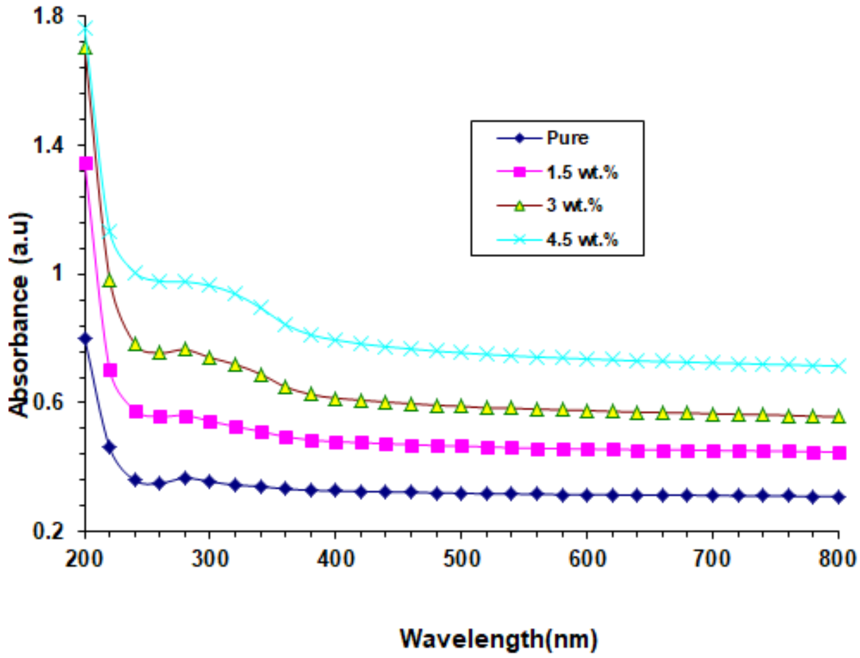

Fig. 2. The contrast of optical absorbance of nanocomposite as a function of wavelength for different ZrC concentrations.

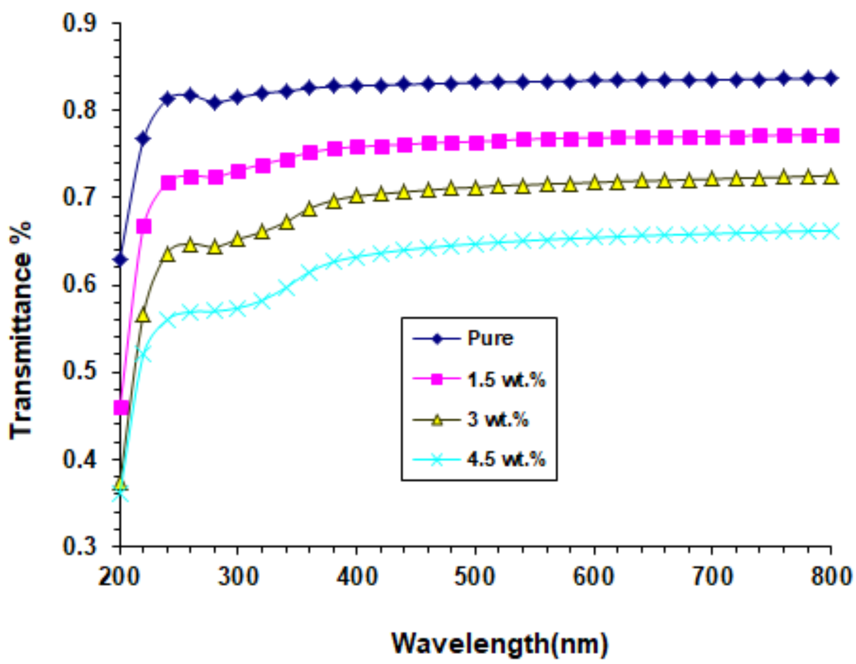

Fig. 3. the variation of optical transmittance of nanocomposite as a function of wavelength for different ZrC concentrations

be indirect. The energy gap can be calculated from

$$\alpha h\nu = B(h\nu - Eg)^{p} \quad (2)$$

Where E_g is the band gap energy, β is the constant that depends on transition probability, h is the Planck's constant, ν is the frequency of light, and p is the parameter associated with the distribution of the density of states. For the allowed direct transition and indirect transition energy gaps, the index p is equal to 1/2 and 2, respectively. For forbbiden direct transition and indirect transition energy gaps, it has a value of 3/2 and 3, respectively. Plotting a graph between $(\alpha h\nu)^{r}$ and photon energy hν and determining the value of then that produces the best linear curve is the standard approach for calculating the band gap energy [20].

According to Fig. 5 (a) the energy band gap decreases by increasing of weight percentage of ZrC nanoparticles. This results in the development of local levels in the allowed energy gap. therefore, in this instance, raising the weight ratio of the titanium nanoparticles causes the transfer of electrons to occur in two steps, first from the valence band to the local levels and then from the local levels to the conduction band [21]. Fig. 5 (b) illustrates the relationship between $(\alpha h\nu)^{1/3}$ $(eV/cm)^{1/3}$ and photon energy of nanocomposites when (p = 3) which denotes a forbidden indirect transition. The figure show that the energy band gap of PVA-PEG-ZrC nanocomposites is decreased with the increase of ZrC nanoparticles concentrations which due to increase of the localized level in energy gap. Additionally, the value of the forbidden indirect transition is less than the value of the permitted indirect transition [see to the points of intersection of the straight lines with the x-axis in Fig. 5 (a) and (b)].

Optical constants

For the creation of optoelectronic devices, factors like as refractive index, attenuation coefficient, dielectric constant, electrical susceptibility, and optical conductivity are crucial [22]. These parameters have been studied for the nanocomposite at different concentrations of nano-zirconium carbide as a function of the wavelength.

The refractive index is a measure of the propagation of light through a substance, and it is a basic physical property of the substance. Light passes through a substance more slowly the higher its refractive index. The refractive index can

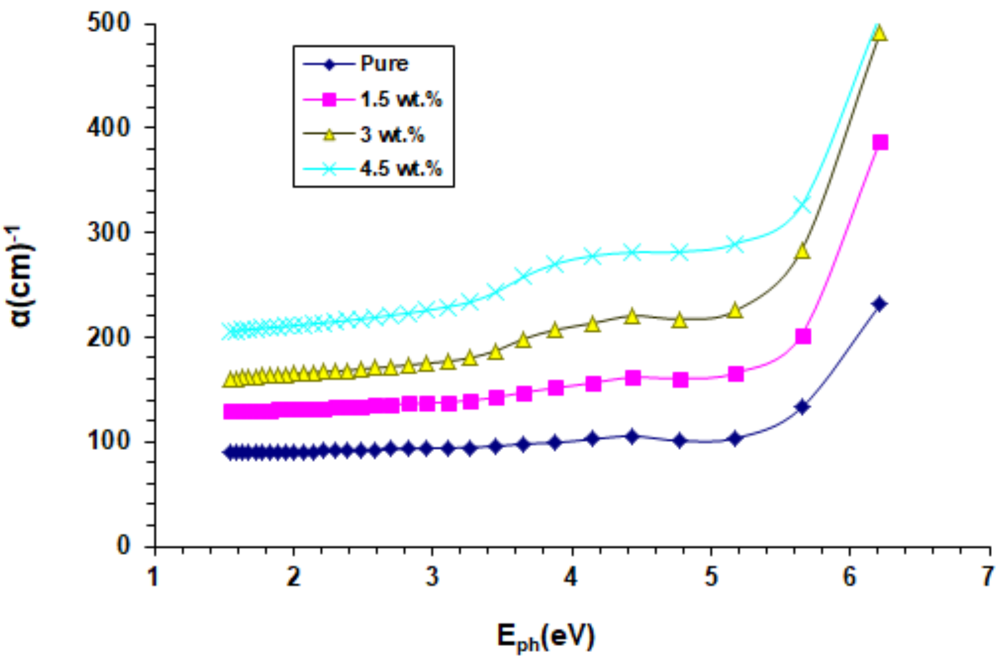

Fig. 4. Effect zirconium carbide nanoparticles concentrations on the absorption coefficient of PVA-PEG-ZrC as function of photon energy

be calculated by the relationship [23].

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (3)$$

Where R is reflectance and k is extinction coefficient. Fig. 5 shows the effect of ZrC nanoparticles concentrations on the refractive index of (PVA-PEG-ZrC) nanocomposites. It was found that the refractive index increases with the increase in the concentration of the nanomaterial, and that the refractive index of the pure polymer without the presence of the nanomaterial is the lowest, as it appears from the figure, due to the increase in the scattering of the incident light when the nanomaterial is presence.

The extinction coefficient (k) measures how strongly a material absorbs light at a specific wavelength, it is an intrinsic attribute of the material dependent on its structure. It is determined by the amount of light that is lost due

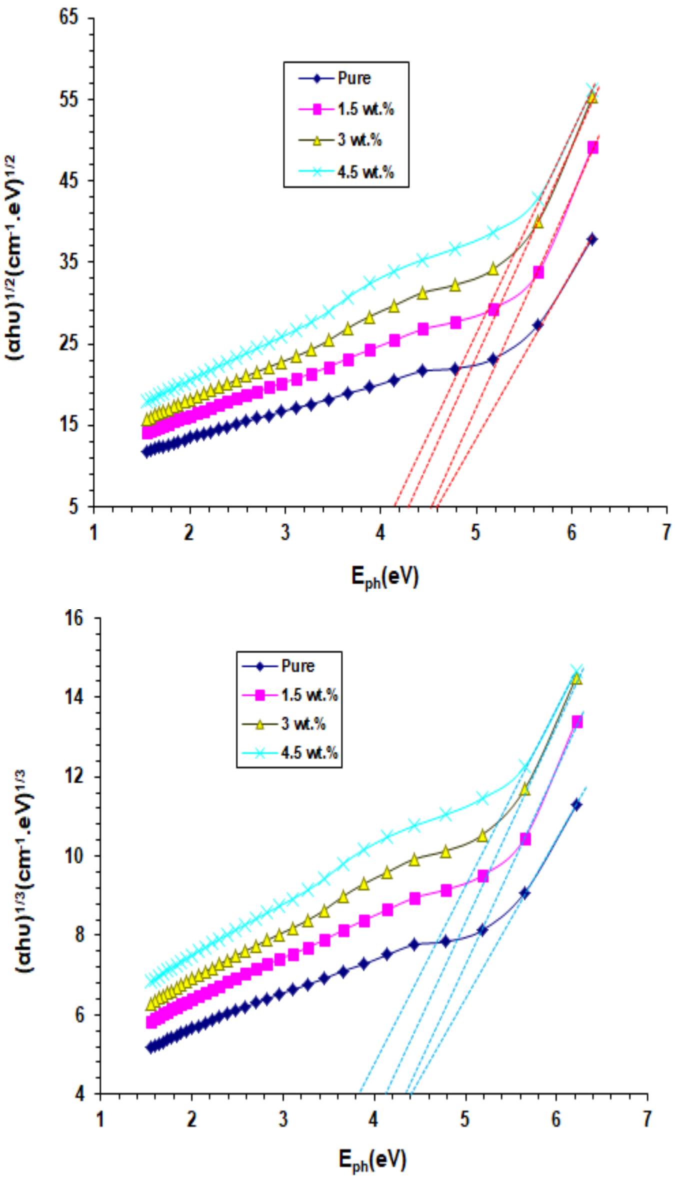

Fig. 5. The relationship between $(\alpha h\nu)^{1/3}$ $(eV/cm)^{1/3}$ and photon energy of (PVA-PEG-ZrC) nanocompsites

to scattering and absorption per unit of space in the interacting medium. By using the formula, it may be calculated. [24].

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

Fig. 6 indicates that the extinction coefficient for (PVA-PEG-ZrC) nanocomposite is lower for the pure polymer (PVA-PEG) and begins to increase with the increase in the concentration of nano-zirconium carbide, and this is an inevitable result of increasing the absorption coefficient with the

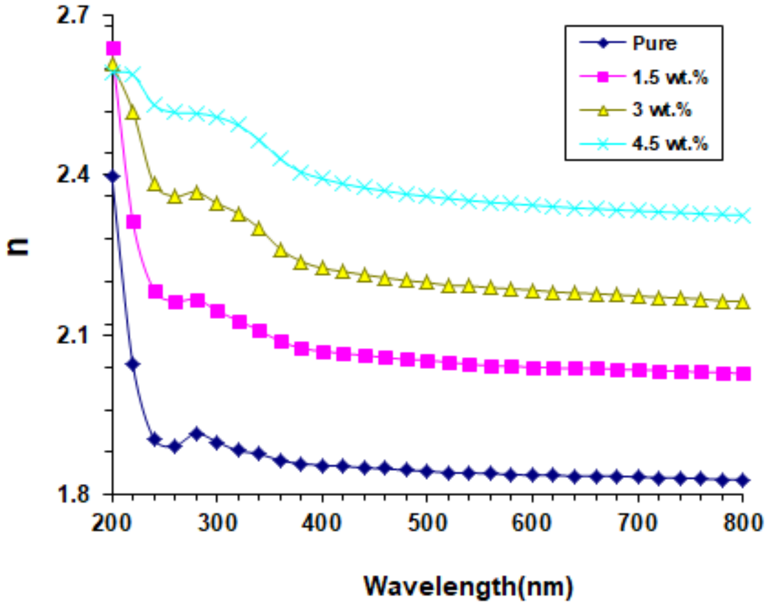

Fig. 6. The variation of refractive index of (PVA-PEG-ZrC) nanocomposie for different concentration of ZrC nanoparticles as function of wavelength

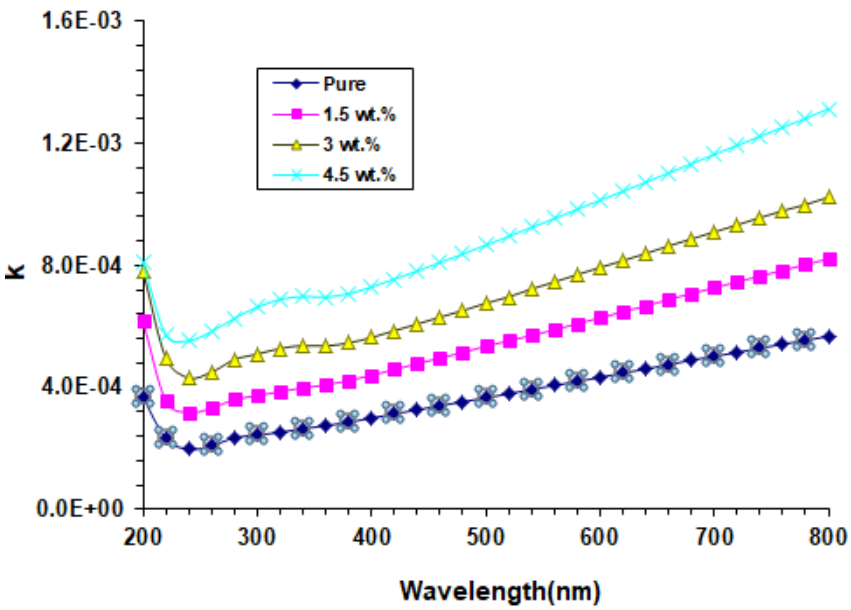

Fig. 7. The variation of extinction coefficient of (PVA-PEG-ZrC) nanocomposie for different concentration of ZrC nanoparticles as function of wavelength

increase in the concentration of the nanomaterial.

A refractive index with a complex value can be used to describe how light moves through absorbent materials. Attenuation is taken care of by the imaginary part, k, whereas refraction is handled by the real part, n. The complex dielectric constant has a relationship with the real part n and imaginary part k. The imaginary component of the dielectric constant indicates how much a material will absorb energy from an electric field due to the motion of its dipoles, but the real part indicates how much it will slow down light speed in the material [25].

The other parameter is the dielectric constant and is obtained from the relationship $\varepsilon=\varepsilon_1-\varepsilon_2$ where the real and imaginary parts are related to the refraction index and extinction coefficient as follows [26].

$$\varepsilon_1 = n^2 - k^2 \quad (5)$$

$$\varepsilon_2 = 2nk \quad (6)$$

Due to low values of k^2, the variation of ε_1 is

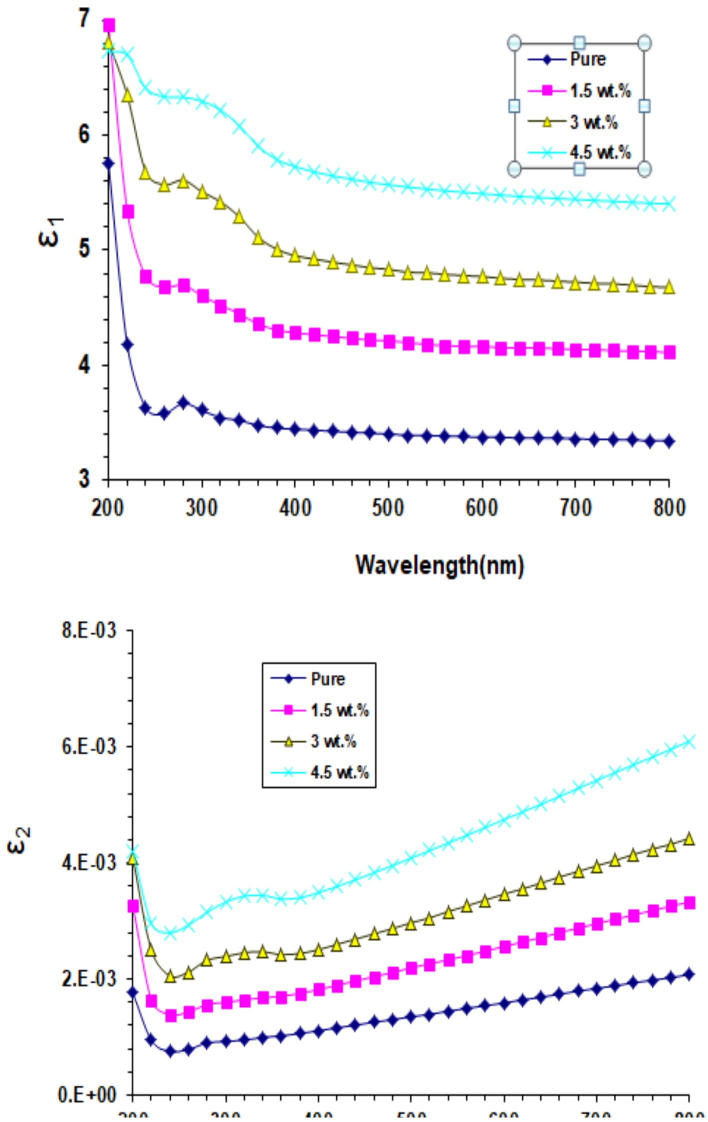

Fig. 8. variation of real part ($\varepsilon_{1)}$ and imaginary part ($\varepsilon_{2)}$ of dielectric constant with wavelength of different concentrations of ZrC-nanoparticles

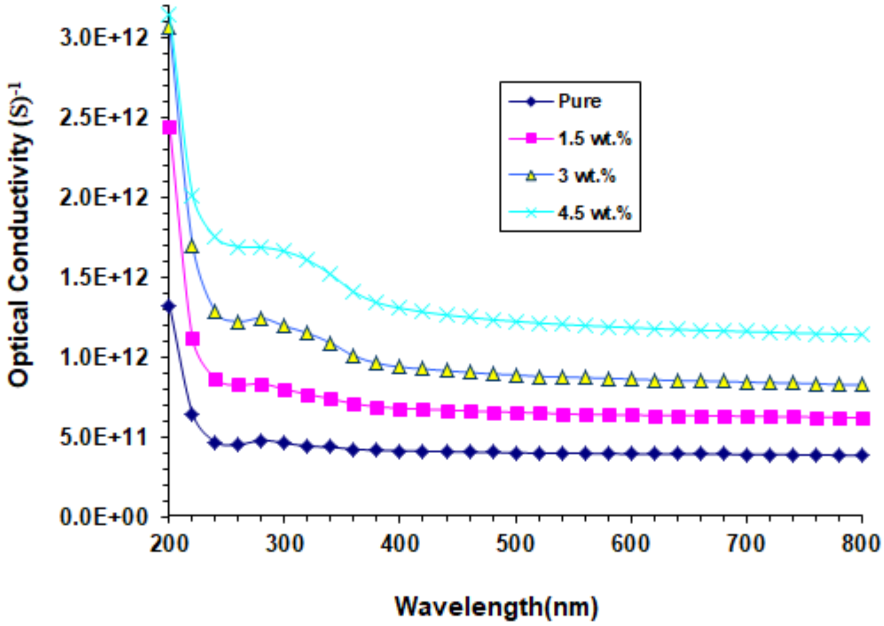

Fig. 9. variation of optical conductivity as function wavelength with different concentrations of ZrC-nanoparticles

mostly dependent on n^2, whereas the variation of ε_2 is primarily dependent on k values, which are related to the variation of absorption coefficients [27]. Fig. 8 The connection between the real and imaginary components of the dielectric constant for various ZrC-nanoparticle concentrations. It is noticed from the figure that the real part and the imaginary part of the dielectric constant increase with the increase in the concentration of the nanomaterial. But the interesting thing is that the real part of the dielectric constant decreases very little with increasing wavelength, while the imaginary part of the dielectric constant increases significantly with increasing wavelength.

The last parameter that will be discussed in this article is the optical conductivity which directly depends on the absorption coefficient and refractive index according to the following relationship [28].

$$\sigma = \frac{\alpha n c}{4\pi} \quad (7)$$

Where c is the velocity of light. Fig. 9 shows that the optical conductivity increases with the increase in the concentration of zirconium carbide nanoparticles, and this is due to the increase in the absorption coefficient that we referred to from the beginning.

CONCLUSION

The parameters that have been experimentally studied for the nanocomposite (PVA-PEG-ZrC) have shown results that are identical to the theoretical studies and the mathematical relationships that govern these parameters, and we summarize below the most important results:

1. The absorbance increases while the transmittance decreases for all nanocomposites with increasing concentrations of nanoparticles.
2. The absorption coefficient of the nanocomposite increases with the number of absorbent molecules
3. As for the energy gap of the indirect transition (forbidden and allowed), it decreases with the increase in the concentration of the nanomaterial.
4. With increasing nanoparticle concentration in the nanocomposite, other parameters like refractive index, extinction coefficient, dielectric constant, and optical conductivity rise as well.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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