Impact of the Zirconium Carbide Nanoparticles (ZrC NPs) on the Morphological and optical properties of Transparent Polymers

[1]Abdullah Abdulkareem Fayyadh Alalwani, [2]Sara Sadat Parhizagr
[1]The General Directorate of Education in Babil, Ministry of Education in Iraq, Iraq.
[2]Nano-Lab Plasma Research Center, Islamic Azad University, Science and Research Branch, Tehran, Iran
Email: abdullaabdulkreemlm@gmail.com

Abstract
In this paper, the (PVA/PAAm/CMC/ZrC) nanocomposites was prepared via casting process with different contented of ZrCNPs (2, 4 and 6wt.%). The morphological and opticalproperties was investigated. The optical microscope images exhibited that ZrC NPs made of continuous network inside the blend at concentration (6 wt%). The optical characteristics, such as absorbance, coefficient of absorbance, index of refraction, coefficient of extinction, dielectric constant of real and imaginary and optical conductivity, showed a growing trend with increasing ZrC NPs concentration in the experiments. However, when the concentration of ZrC NPs increased, a reduction correlation was seen between these two parameters (transmittance and indirect energy gap, both allowed and banned. Finally, from this result can be used these nanocomposites as the photodetectors application specially in the UV region.

Keywords: PVA, PAAM, CMC, ZrC, nanocomposites, optical properties

1. Introduction

Natural or synthetic polymers are used to create polymer nanocomposites, which are nanomaterials due to their nanoscale topography or composition[1]. Nanomaterials and nanocomposites may be cutting-edge in the context of materials research, yet their natural occurrence has made them familiar to scientists for decades. Nanoscale structural characterization and manipulation approaches, however, have been stimulated very recently[2].Nanocomposites follow the same structure as any other compound, with a filler and a matrix. While fibers like carbon and glass are commonly utilized as fillers in traditional composites, nanomaterials play that role in nanocomposites. Nanomaterials include things like carbon nanotubes, carbon fiber tubs, and nanoparticles of precious metals, semiconductors, and metals [3]. Polymer nanocomposites, formed by incorporating inorganic nanocomposites into an organic polymer, have attracted a lot of attention in recent years. Because of the basic and crucial part played in their applications by nanostructure control composition and shape, By successfully transferring the qualities of the original components into a single material, nanocomposites can get their new properties [4].

Since its inception in the early 1930s, the synthetic polymer known as polyvinyl alcohol (PVA) has been extensively utilized across various industrial, commercial, medical, and food-related sectors. The applications of this substance are wide-ranging and include the utilization in various fields such as resins, surgical threads, lacquers, and applications involving interaction with food [5]. PVA is a artificial polymer that is present in the form of grainy powder, with many properties including odor lessness, transparency, tastelessness, and a white or cream-colored visual appearance [6]. The favorable attribute of polycarbonate, particularly vinyl alcohol, is its resistance to solvents and oils, together with its excellent properties [7].

Polyacrylamide (PAAm) is additional watersolvable polymer that has a variedvariety of manufacturingwoollyrequests, rheology-control agents, dragtumbling polymers, and glues. PAAm and their derivatives increased attention during the past years and to the present time [8]. PAAm is often used to increase the viscosity of water, polyamides and an acrylic material solid crystal is very stable.

The presence of aggregates amine and carboxyl in the dry polymer chains lead to a severe reaction molecule when calculating the hydrogen bonds between chains and polyamides scores with very high melting relatively. Because bonded hydrogen molecular and differences in the hydrogen profile bonded poly amid and effectiveness increases strength and cohesion are used in the formation of fibers, called these kind nylons [9].

Carboxymethyl cellulose (CMC) is a linear polymer with ionic characteristics, and it is extensively employed in many international applications, surpassing the utilization of all other presently acknowledged water-soluble polymers [10].

Zirconium carbide (ZrC) is a ceramic substantial known for its amazing properties, such as excellent hardness, high melting point, substantial attireconfrontation, and chemical constancy. The aforementioned characteristics make it a material with great potential for use in applications that need extremely high temperatures [11].

The aim of this work is preparation of the PVA/PAAm/CMC/ZrC nanocomposite by using casting method and studying the effect of the ZrCNPs on the morphological and opticalproperties ofpolymer blend

2- Materials

Poly vinyl alcohol (PVA) polymers (partially hydrolysis, molecular wight is 160,000 $g.mol^{-1}$) could be supplied as granular form and water-soluble synthetic polymer from the Central Drug House, Ltd., Company, Indian, Poly Acrylamide (PAAm):were used in this study having the average molecular weight of (40.000), CAS No.:9003-39-8, by Chem Center 5580 la Jolla Blvd (La Jolla, CA92037), Carboxymethyl Cellulose (CMC): The material Carboxy methyl cellulose (CMC) used is a white powder, the molecular weight is 1.7×10^4 g/mol and might be got from resident marketplaces and high purity (99.97 %).Zirconium carbide (ZrC): Is an inorganic compound . It is a white powder that is insoluble in water. Its melting point 1,974 °C, a molecular weight 81.406 g mol^{-1}, the density 5.606 g cm^{-3} and the average grain size 30 nm.

3. Preparation of (PVA/PAAm/CMC/ZrC) nanocomposite

A solution was prepared by dissolving 0.6 g of polyvinyl alcohol (PVA) polymer in 50 mL of distilled water. In order to dissolve the substance completely, a magnetic stirrer was used to vigorously mix the liquid at a temperature of 70 ^{o}C for a period of 30 minutes or until complete dissolution was achieved, resulting in the production of a uniform mixture. After cooling the solution to 40 ^{o}C, it was added 0.2 g of polyacrylamide (PAAm) to synthesis the polymer until to become more homogenous and then 0.2 g of carboxymethyl cellulose (CMC) was presented into the combinationthoughupholding continuous stirring for a duration of 1 hour. The work entailed integrating ZrCNPs into the solution at concentrations of 2, 4, 6 and 8 wt.%, with the aim of producing nanocomposites as shown in Table 1. Afterwards, the casting procedure was utilized.

Table (1): **Weight percentages of PVA/PAAm/CMC/ZrC Nanocomposites.**

PVA (g)	PAAm (g)	CMC (g)	ZrC (g)
0.6	0.2	0.2	0.0
0.596	0.192	0.192	0.02
0.580	0.190	0.190	0.04
0.564	0.188	0.188	0.06

To determine the surface morphology of the films, we used an optical microscope, Olympus (Top View) type (Nikon-73346).). A Shimadzu UV-1650 PC spectrophotometer, manufactured by Phillips, a Japanese corporation, was used to examine the development of nanocomposite at wavelengths ranging from 200 to 1100 nm.

4. Result and Discussion

Figure (1)show the optical microscope (OM) images of (PVA/PAAm/CMC/ZrC) nanocomposites with different concentrations of ZrCNPsat magnification power 40x. The OM stretches the alteration of surface geomorphology of nanocomposites. Image A in fig. (1), it showshomogenous and smooth surface, which could be indicate successful method for preparing nanocomposites. Compared with pure sample images, there are many differences among this sample and nanocomposites with adding different concentrations of ZrC. In image (B, C and D) in figure (1), illustrate the addition of ZrC distributed across the polymeric blend with uniform and orderly shape and the apparent ZrC network inside. Then charge carrier in nanocomposites have pathways and charge carriers can pass through these pathways. These findings support [12].

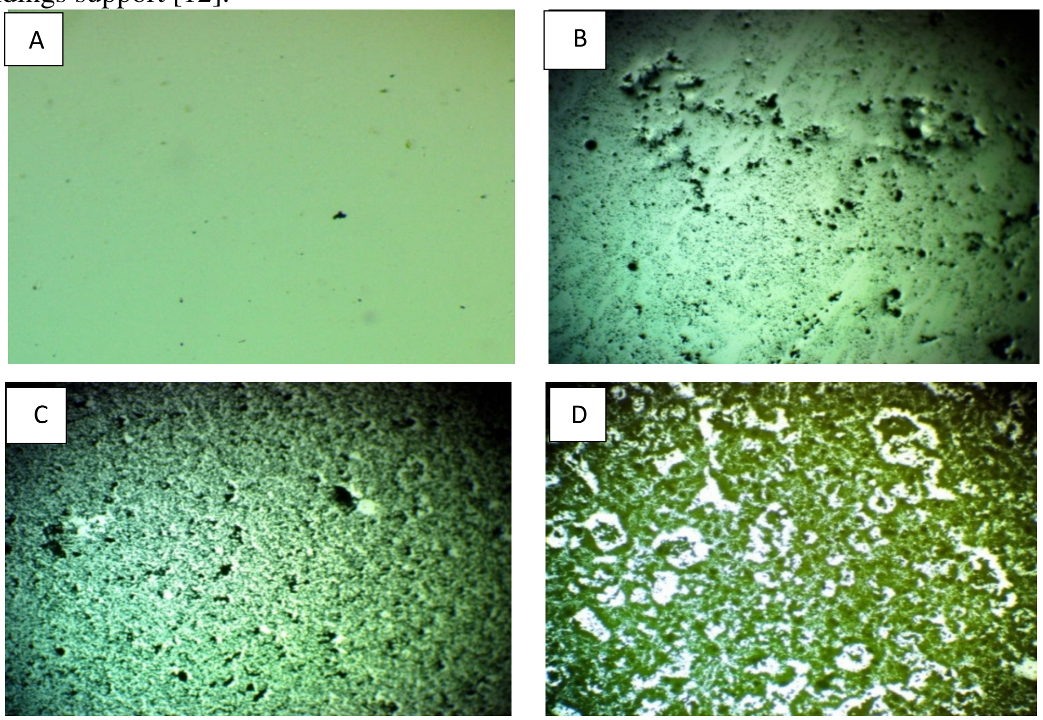
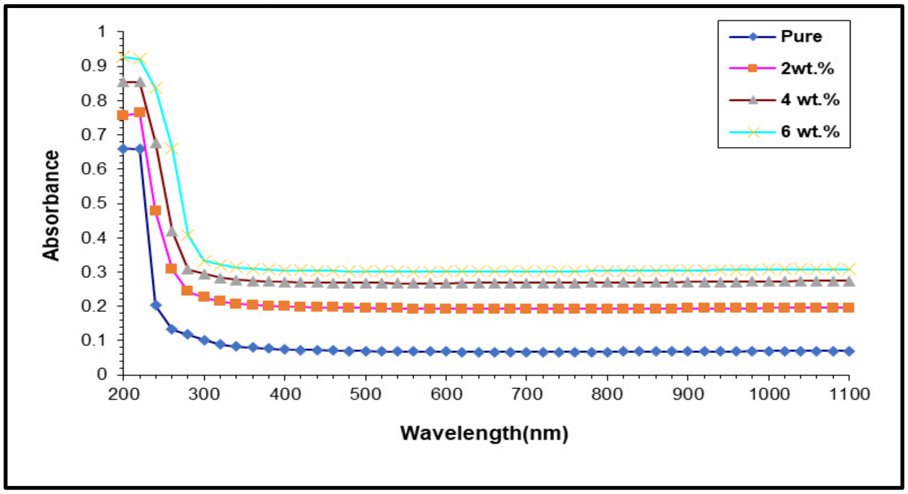


Figure (1): Photomicrographs (40x) for (PVA/PAAm/CMC/ZrC) A)(PVA/PAAm/CMC) blend, B) 2 wt% , C) 4 wt% , D) 6 wt% (ZrC)

The absorption (PVA/PAAm/CMC/ZrC) nanocomposite with various content (ZrC) nanoparticles were verified at range 200-1100 nm at RT. The optical density for (PVA/PAAm/CMC/ZrC) nanocomposite through wavelength at the occurrence light are shown in figure (2) respectively. It is observed, the absorbance rises with rising content of ZrC, while in each sample, it is descending by rising wavelength (photon with lower energy) because of the giver level electrons existence to the conduction band at high energy. Because photons have enough energy to make atoms to respond, it is possible for an electron to be stimulated from a lower to a developed energy level just by absorbing a photon that has already been established. These results agree with otherstudies[13].



Figure(2): The optical densitywiththe wavelength ofsamples

Figure(3) demonstrates the transmittance of (PVA/PAAm/CMC/ZrC) nanocomposite with wavelength. The transmittance reduces as the concentration of ZrC nanoparticles rise, also increased with increasing of wavelength, which is due to the accumulation of nanoparticles with increasing contented [14].

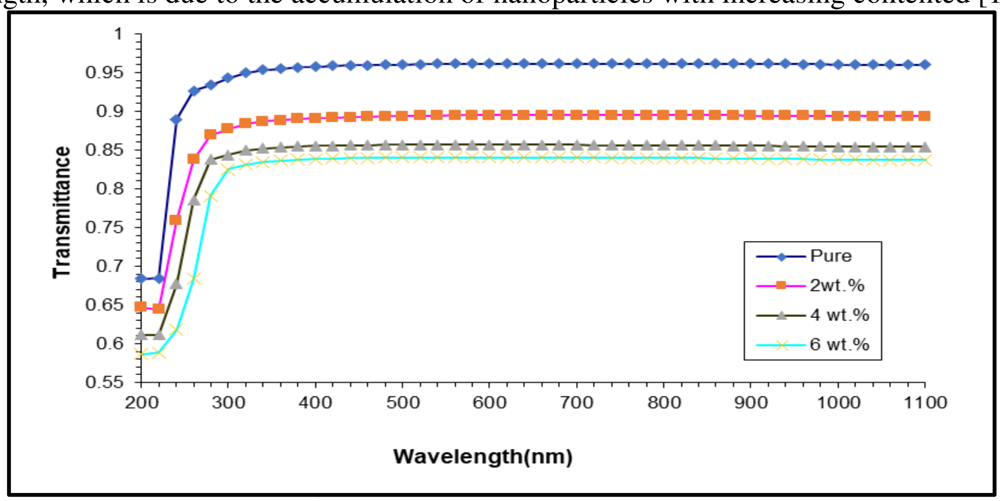


Figure (3): Change transmittance of (PVA/PAAm/CMC/ZrC) nanocompositesversus the wavelengths.

An empirical correlation was utilized to get the absorption coefficient [15].

$$\alpha = 2.303\frac{A}{t}$$

Where A is the absorbance. Figure (4) illustrates the association amid the photon energy and the α of the (PVA/PAAm/CMC/ZrC) nanocomposite. The αmight aid to figure out what kind of electron transition trade with. It is expected that direct electron transitions occur when the $\alpha$is large (>10^4 cm^{-1}). When the α is low (<10^4 cm^{-1}), an indirect transition of electrons is assumed then values of α of the (PVA/PAAm/CMC/ZrC) nanocomposite, the transition of the electron takes place in a roundabout way. Because of an rise in the total amount of charge transporters, the $\alpha$of (PVA/PAAm/CMC/ZrC) nanocomposites increased with increasing of ZrC nanoparticles. The rise in the value of nanocomposites can be attributed to this phenomenon [16].

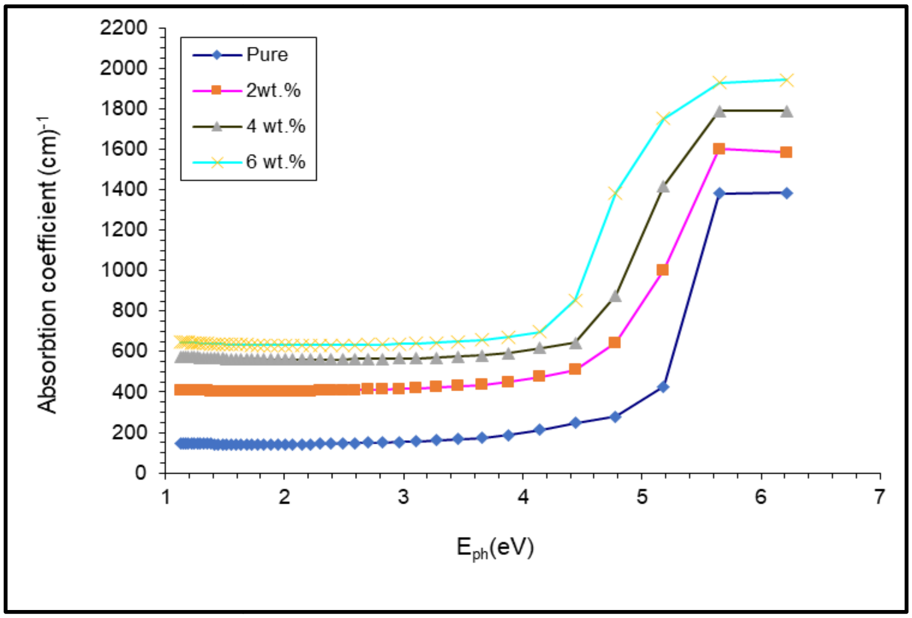


Figure (4): The distinction absorption coefficient of (PVA/PAAm/CMC/ZrC) nanocompositesversus the photon energies.

The energy gap is given by [17]:

$(\alpha h\upsilon)^{1/m}= C(h\upsilon - E_g)$

For any constant C, the photon energy is denoted as hυ, the energy gap is represented as Eg, and m can take on the values of 2 and 3 for allowed and forbidden indirect transitions, respectively.The E_g for allowed and forbidden indirect transitions of (PVA/PAAm/CMC/ZrC) nanocomposites are showed in figures (5, 6),utilizing the intercept of the expanded linear segment. A linear segment was generated by isolating a section of the depicted curve to analyze the disparity in energy. From these figures, the E_g are decrease with the rise of the ZrCnanoparticle contents, this act is owing to the creation of energy levels in the E_g and therefore, these local levels reduce the energy gap with rise of the ZrC nanoparticle contents [18]. The value of the E_g of nanocomposites are recorded in Table (2).

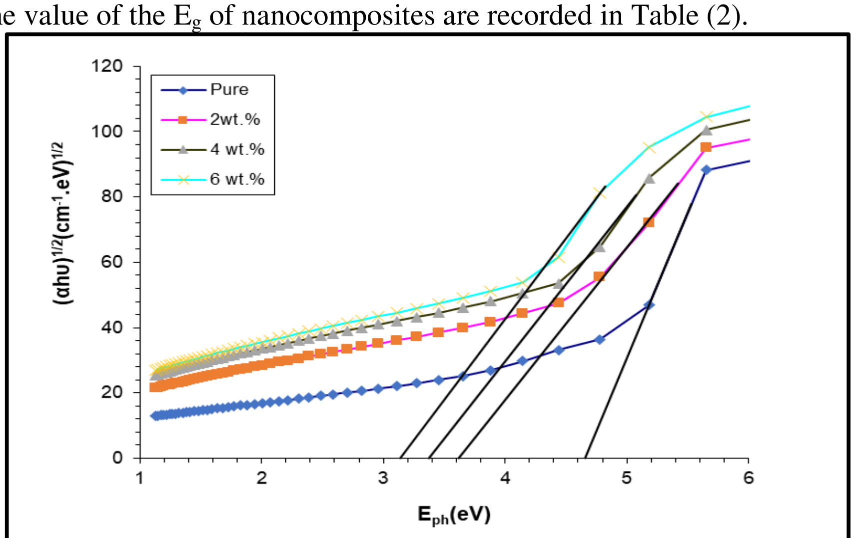
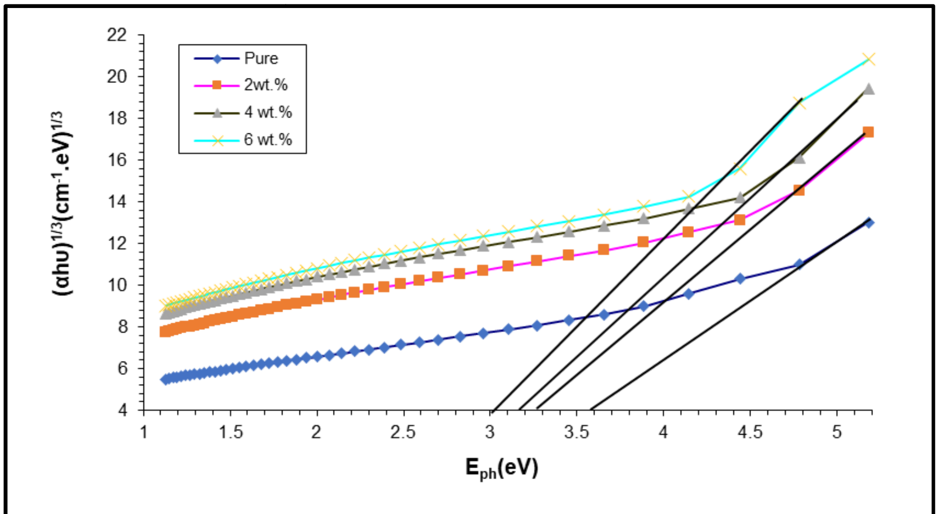


Figure (5): The $(\alpha hv)^{1/2}$ $(cm^{-1}.eV)^{1/2}$ of (PVA/PAAm/CMC/ZrC)nanocompositesversus photon energy.



Figure(6): The E_g for $(\alpha hv)^{1/3}$ $(cm^{-1}.eV)^{1/3}$ of (PVA/PAAm/CMC/ZrC)nanocompositesversus photon energy.

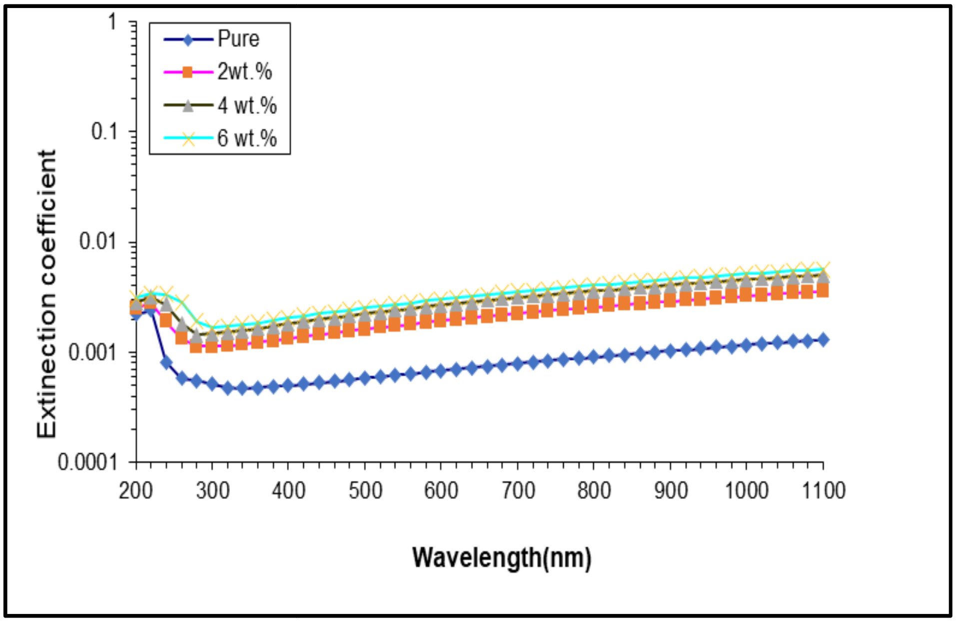
Table (2):The values of indirect optical energy gap of (PVA/PAAm/CMC/ZrC)nanocomposite

ZrC wt% NPs content	E_g allowed indirect (eV)	E_g forbidden indirect (eV)
0	**4.68**	**3.6**
2	**3.6**	**3.3**
4	**3.4**	**3.2**
6	**3.18**	**3**

The extinction coefficient (K_o)is given by the relation [19]

$k = \alpha\lambda/4\pi$

where λ is the wavelength**.** Figure (7) demonstrates thekof (PVA/PAAm/CMC/ZrC) with of wavelength. It is detected that the extinction coefficient of nanocomposites rises with the rise of the ZrC nanoparticlecontents and reduce with rising wavelength, this is owing to the rise inabsorption in the (PVA/PAAm/CMC) polymer matrix.



Figure(7): Variation of k for (PVA/PAAm/CMC/ZrC) nanocompositesversus wavelength.

The index of refractive (n) was calculated from relation [15].

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}}$$

where R is the reflectance.The n of (PVA/PAAm/CMC/ZrC) with wavelength are revealed in figure (8). It is found that the nrises with the growing of the content of ZrC nanoparticles and it decreases with the increase of the wavelength. This action is due to the rise of the density of nanocomposites [20].

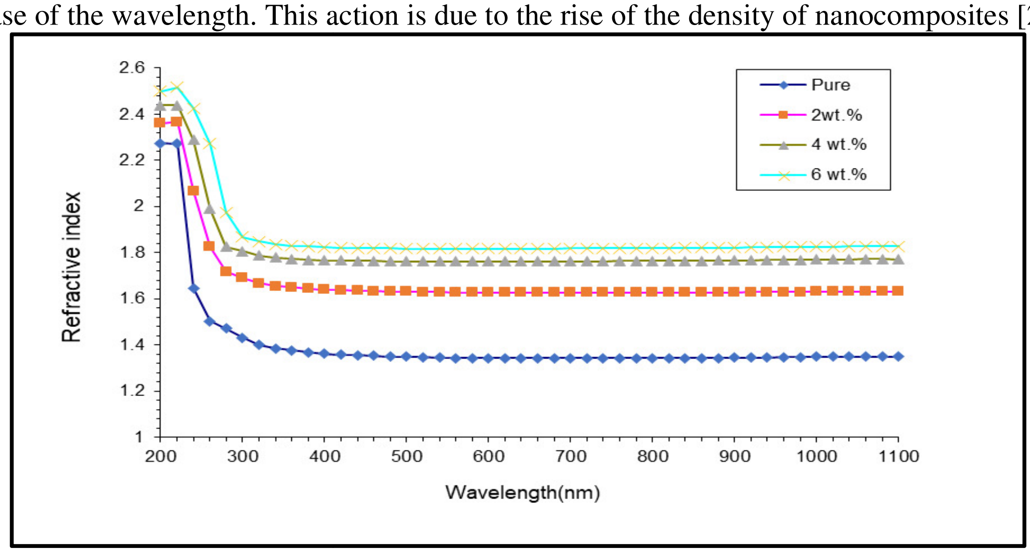


Fig. (8): Differenceof nfor (PVA/PAAm/CMC/ZrC) nanocompositesversus wavelength

The dielectric constant is composed of two parts: the real part (ε_1) and the imaginary part (ε_2) [21]:

$\varepsilon_1 = n^2 - k^2$

$\varepsilon_2 = 2nk$

Theε_1 and ε_2 part of insulator constantwith the wavelength for (PVA/PAAm/CMC/ZrC) are demonstrates in fig. (9) and (10) respectively. The data presented indicates that the insulator constant of PVA/PAAm/CMC/ZrC nanocomposites has greater values for both the real and imaginary components at shorter wavelengths, and diminishes as the wavelength increases. The nanocomposite films display a prominent increase in both the real and imaginary values as the wavelength decreases. The observed resemblance can be elucidated by the fact that the effective dielectric constant is predominantly influenced by the magnitudes of (n) rather than (k), considering that the latter values are considerably less than the refractive index, particularly when squared [22, 23]

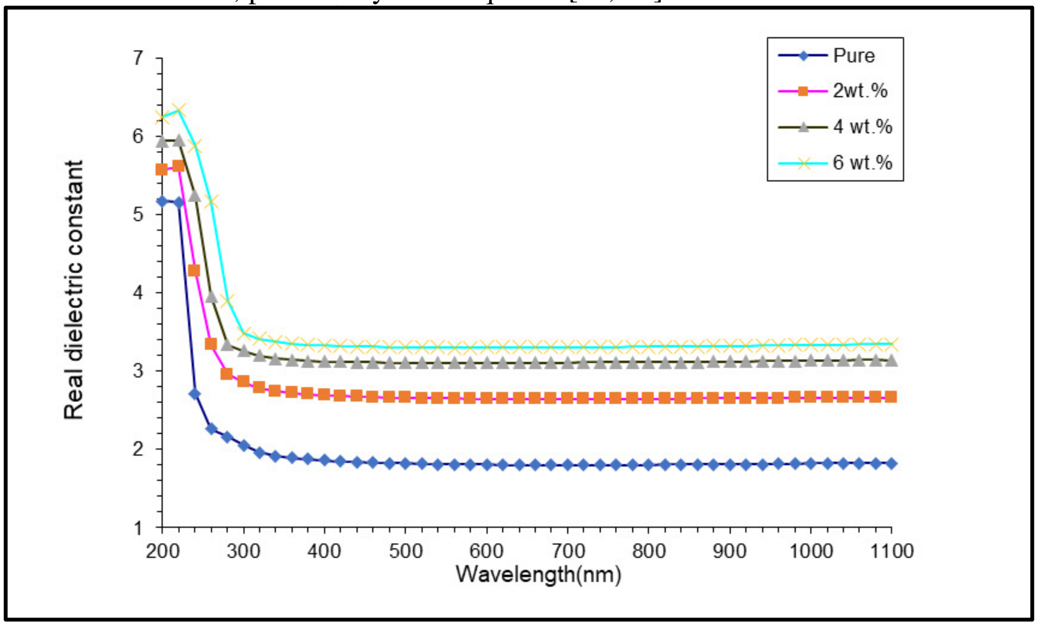
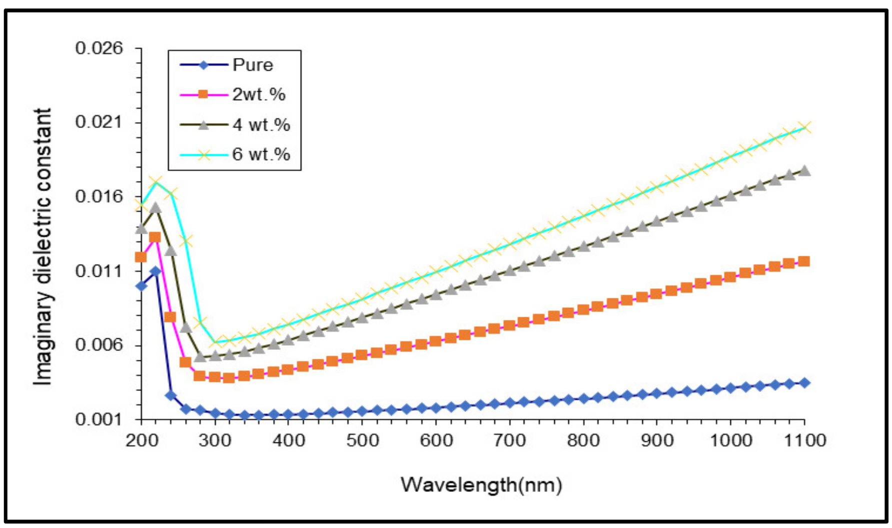


Figure (9): Difference of ε_1 of (PVA/PAAm/CMC/ZrC)) with the wavelength



Figure(10): Distinction ε_2 of (PVA/PAAm/CMC/ZrC) with wavelength.

The optical conductivity (σ_{op}) is definite by [24, 25]:

$$\sigma_{op} = \alpha nc/4\pi$$

where c is the speed of light**.** The $\sigma_{op}$of the of (PVA/PAAm/CMC/ZrC) with a wavelength is shown in figure (11). The PVA/PAAm/CMC/ZrCnanocomposites demonstrate a notable enhancement in optical conductivity at shorter wavelengths, followed by a reduction at longer wavelengths. This behavior can be explained by the concurrent increase in the absorption coefficient. The relationship between the concentration of ZrC nanoparticles and the observed optical conductivity is found to be directly proportional[25].

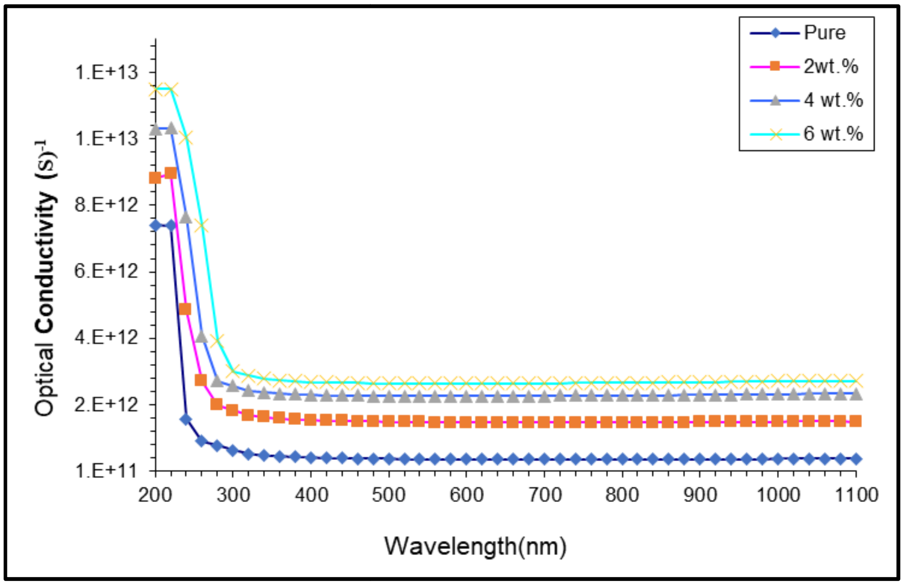


Figure (11): Variation σ_{op} of (PVA/PAAm/CMC/ZrC) nanocomposites with the wavelength.

5- Conclusion

From these results can be concluded from the OM images that ZrC NPs made of continuous network inside the blend at concentration (6 wt. %).The experimental results revealed that as the concentration of ZrC NPs increased, various optical properties such as absorbance, absorption coefficient, refractive index, extinction coefficient, real and imaginary dielectric constant, and optical conductivity also increased. Conversely, the transmittance and indirect energy gap reduced with growing concentration of ZrC NPs.Finally, from this result can be used these nanocomposites as the photodetector application specially in the UV region.

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