Optical and Electric Properties Study of PVA and PEG Thin Films Doped with ZnO nanocomposites After Irradiate By Gamma Ray

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By using gamma ray source to irradiate the polymers thin films samples at low-exposure rate, the polymeric characteristics were studied. The solution casting method was used to prepare a variety of pure polyvinyl alcohol (PVA), polyethylene glycol (PEG) polymers, and PVA:PEG blend composite films that had been doped with varying concentrations of zinc oxide (ZnO). Using a NaI(Th) system, the extent to which produced films were affected by gamma rays emitted by the ^{137}Cs isotope was revealed. The results of the study showed that samples with Dc conductivity measurements demonstrate how the conductivity changes in these films depending on the concentrations of ZnO present. With the aid of obtained UV-V spectra, variance in transmittance has been investigated, and the optical band gap found in these specimens has been determined.

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1. Introduction

For more than 30 years, the effect of radiation on polymeric materials quickly gained attention from many researchers when they exposed them to high-energy radiation [1], as it is very specific when used in many industries that rely on modern technologies (such as electronics) that require specialized polymers. They show a specific response when exposed to ionizing radiation. Therefore, there will be a great need to understand the effects of radiation and the physical changes that occur as a result of the radiation absorption process [2]. Hence, it was necessary to examine and evaluate many factors that enable understanding these effects that reduce the life of the polymer. So, polymer irradiation creates a new polymeric material that can be tailored in terms of their physical and optical properties through the processes of chain separation and induced crosslinking. Irradiation not only influences the occurrence of chemical changes in the studied polymer but also results in enhancements in polymer properties and increased practicality.

Due to their use in optical instruments with impressive properties such as reflection, antireflection, interference, and polarization, the investigation into the polymer's properties as electrical and optical, was given a lot of interest [3-5]. Recently, an extensive variety of doping agents, including metals, oxides, inorganic salt, and other particles, have been used to produce various composite materials [6,7]. Several studies have demonstrated that the physical characteristics of polymers depend upon a variety of factors connected to their synthesis processes and chemical structure [8]. Numerous studies have examined the interactions of polymers, and it is simple to influence the optical properties of polymers by varying the concentrations of their constituent parts [9].

The present work introduces examination and evaluation of the optical properties (absorbance, transmittance, absorption coefficient and damping coefficient), as well as the energy gap, and electrical properties (electrical conductivity, dielectric constant and electrical resistance). This study will be done before and after gamma radiation exposure, which may occur in many procedures depending on the chemical structure of the polymer and the radiation situations (i.e., radiation dose and dose rate), the response of PEG/ZnO composites thin films will investigate too. This could attest to the fact that their unique properties and features set them apart from competing materials.

2. Experimental Work

The material used for preparing the films is PVA [CH_2CHOH] has a molecular weight (Mw ≈160,000 g/mol) and viscosity of 27-33 cP was purchased from Himedia Laboratories Pvt. Ltd. (India), and PEG [$H(OCH_2CH_2)_n$] have (Mw ≈3500~4500 g/mol) and viscosity 50-55 from Sinopharm Chemical Reagent

Co. Ltd. (China). Ten films were prepared from each sample of pure PVA, PEG, and solution polymer blend based on 1g of 50% PVA and 50% PEG with three different additions (1.5, 2, and 3 wt.%) of ZnO nanoparticle. The powders were dissolved in 75°C distilled water with moderate continuous stirring for 120 minutes at room temperature, and the resulting films were left overnight. The mixture was then transferred to a petri dish to avoid contributing to air pollution. It required 10-12 days for drying after the mold was kept at 40°C.

The PEG:PVA (50/50) solutions were stirred for one hour to make the polymer blend. This led to the blend solutions being transferred to glass plates and then vacuumed, sealed for 48 hours at 45°C. The samples were removed once they reached room temperature and placed in desiccators for proper drying. The average thickness of the prepared films was 53-100 μm.

All samples with a 4x4 cm area (as suitable size for the irradiation process) were subjected to gamma radiation processing from ^{137}Cs irradiator source with an energy of 0.662 MeV at the temperature of the prepared films. These films located at 5 cm away from the source, which was centered on the NaI(Th) system. Using the evolution of the 600 UV eV spectrophotometer, the spectra of both unirradiated and irradiated films were recorded for absorption between 300 and 700 nm.

Before the experimental method, there is a main calculation that depend on a formula such as for the absorption coefficient [10]:

$$\alpha = 2.303\frac{A}{t} \qquad (1)$$

where A is the absorbance that defined as the ratio of absorbed intensity (I_A) to incident intensity (I_o), and t is sample thickness. It can be defined by the electronic states present in the transition, and low-frequency, whereas the absorption coefficient is defined by the underlying atomic transitions

The optical conductivity (σ_{op}) as a function of wavelength can be determined by [11]:

$$\sigma_{opt} = \frac{\alpha nc}{4\pi} \qquad (2)$$

where *n* represents the refractive index, and *c* is light speed

3. Results and Discussion

The electrical properties of a medium can be studied via the way it reacts to applied electric fields. First, the samples were subjected to a constant (d.c.) electric field. The d.c. conductivity (σ), shown in Fig. (1), varies as a function of the concentration of ZnO nanoparticles in PVA+PGE blend. Due to the charge transfer, the electrical conductivity grew as the concentration of ZnO nanoparticles is increased. A higher d.c. electrical conductivity can be related to the distribution of ZnO nanoparticles throughout the polymer matrix [12], i.e., a decrease in the degree of crystallinity is thought to be the cause of the continual increase in conductivity of polymer as ZnO concentration increase. Increasing the content of filler material has the ability for boosting the electronic charge carriers, and thus the electrical conductivity [13]. It can say that the nanocomposites have indirect energy gap when the α value less than 10^4 cm^{-1}, and the low value may be due to the low crystallinity [14].

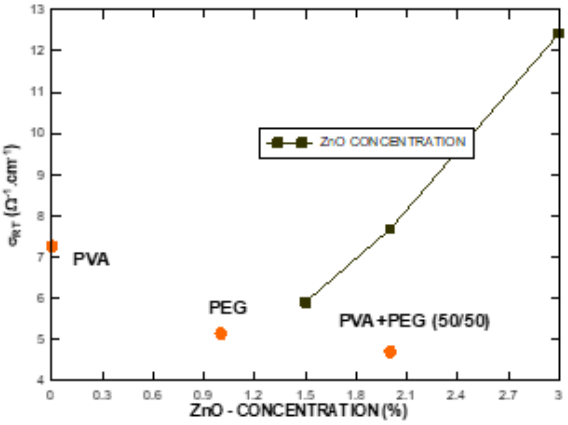

Fig. (1) DC conductivity of pure PVA, PEG, and PVE+PEG and with different concentrations of ZnO nanoparticles

From Hall measurements, it was found that the n-type charge carriers in the film samples have a negative Hall coefficient. One can see that as the concentration of ZnO nanoparticles is increased, the carrier concentration (n_H) increases while the Hall mobility (μ_H) decreases, as shown in table (1).

The temperature difference in a medium causes electrothermal flows, and this temperature gradient is caused by joule thermal effects. As shown in table (2) and Fig. (2), a temperature gradient causes local changes in conductivity, permittivity, density, and viscosity, which consequently generate net forces acting on the polymers. For instance, free bulk charges and Coulombic forces are generated by conductivity gradients, whereas dielectric forces are generated by permittivity gradients.

When the incident photon energy ($h\upsilon$) is plotted against ($\alpha h\upsilon$), the Tauc plots of both undoped and doped polymeric thin films can be obtained and the optical energy bandgap (E_g) can be determined as the average optical band gap, $h\upsilon$ is the photon energy, and *m* is the power factor that defines the type of transition. In this work, pure PVA thin films have a bandgap of 4.069 eV, which is compared to 6.28 eV in Ref. [15].

Adding 1.5, 2, or 3 wt.% of ZnO nanoparticles to the polymeric matrix causes the band gap (E_g) to drop to 4.064 eV, 4.055 eV, or 4.047 eV, respectively. After irradiation, the band gap (E_g) is slightly reduced when 2 and 3 wt.% of ZnO nanoparticles are added to the polymeric solution, suggesting some kind of charge transfer is produced between the PVA polymer and the ions of ZnO content. It has been observed that the incorporation of ZnO nanoparticles into undoped PVA:PEG results in a small narrowing

of the optical bandgap. As the concentration of ZnO nanoparticles is increased, the refractive index increases, indicating that new energy states have been formed and narrowing the energy bandgap of the PVA:PEG blend.

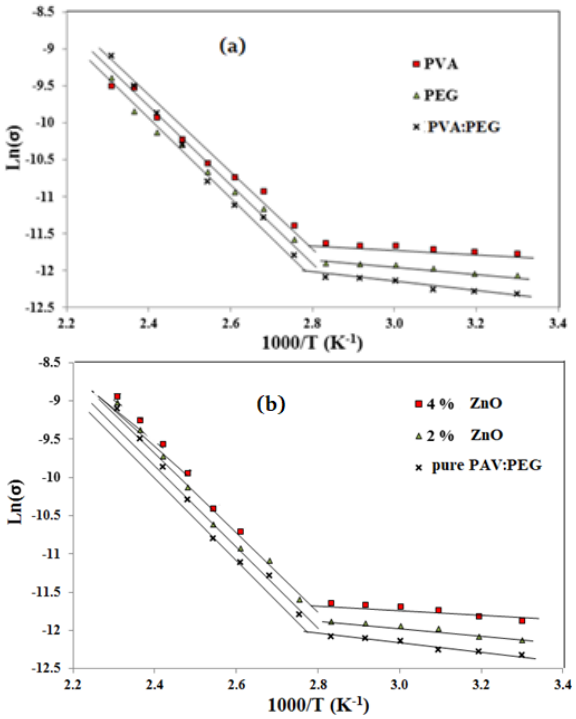

Fig.(2) ln(σ) as a function of 1000/T for (a) (PVA, PEG, and PVA:PEG composites, (b) PVA:PEG blend with different concentrations of ZnO nanoparticles

As can be seen from table (1), the increase in activation energy values before and after irradiation was decreased for pure PVA and PEG, whereas its value for PEG is higher than that for PVA in both cases (before and after irradiation). Same result was obtained for all PVA:PEG/ZnO composites due to the effect of space charge caused by the addition of ZnO nanoparticles, by which, we can create local energy levels in the forbidden energy gap that serve as traps for charge carriers, which then move by traveling between these levels [16]. The activation energy decreases as ZnO content is increased because more local centers are present. The increase and decrease in activation energy can be explained on the basis of the structure of the polymeric thin films consisting of a mixture of crystalline and amorphous regions with amorphous dominating.

A JASCO V-550 double-beam UV-visible spectrophotometer was used to record the UV-visible absorption, transmission and reflection spectra in wavelength range 190–900 nm for the prepared film samples (PVA, PEG, PVA:PEG blend nanocomposites doped with various concentrations of ZnO) before and after radiated by gamma-ray from the ^{137}Cs source.

The absorption spectra of these nanocomposites are displayed in Fig. (3). According to our findings, the transmittance of undoped PVA:PEG thin films is approximately 91.6% in the visible wavelength region. When ZnO nanoparticles are added to the polymeric solution at different concentrations (2 or 3 wt.%), the absorbance drops to 84.9% and 85.2%, respectively, of its value. The transmittance drops even further, to 83.8%, as the concentration of ZnO nanoparticles in the polymer matrix is increased to 3 wt.%. Moreover, it is found that the transmittance of PVA:PEG/ZnO nanocomposite samples with 0, 2, and 3 wt.% concentrations of ZnO nanoparticles suddenly drops in the UV region (<400nm), suggesting powerful electron transition across the bandgap. The significant absorption in this spectrum region is a defining feature.

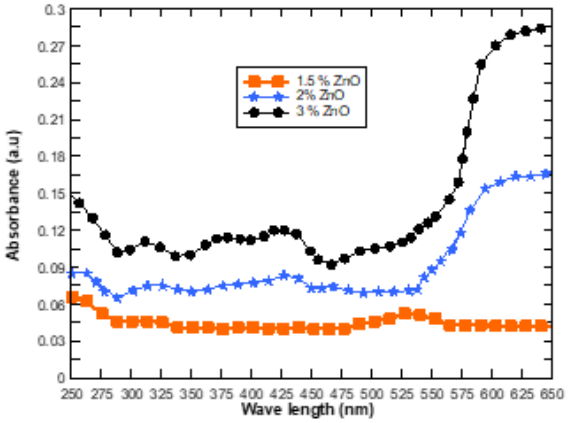

Fig. (3) UV-visible absorbance spectra for irradiated thin films PVA, PEG, and PVA:PEG/ZnO nanocomposites

Figures (4) and (5) demonstrate the room temperature absorption coefficient of PAV, PEG, and PVA:PEG/ZnO nanocomposite thin films with different concentrations of ZnO nanoparticles in the wavelength range 300-700nm before and after irradiation, respectively. The absorption coefficient of an undoped thin film in the UV region is only about 0.0118 cm^{-1}. In the visible region, however, that value drops rapidly to 0.00017 cm^{-1}. Increasing the ZnO content in the polymer solution from 1 to 2 wt.% and then to 3 wt.% leads to increase the absorption coefficient to 0.00032 and 0.000355 cm^{-1}, respectively. As the concentration of ZnO nanoparticles in the material is increased, the value of absorption coefficient remains nearly unchanged in the visible region. As a consequence, depending on the present amount of ZnO nanoparticles, all nanocomposite thin films have the potential to function as light filters across the entire visible spectrum with constant partial absorption.

Since the energy of the incident photon is insufficient to translate the electron from the valence band to the conduction band, the absorption coefficient is lowest at long wavelength and low energy. Based on the presented data, it is clear that all nanocomposites have relatively low absorption in the visible spectrum. Atomic interactions account for this

behavior, allowing the photon to be communicated. Shorter wavelengths (near the basic absorption edge) increase the likelihood of interaction between the incident photon and material, leading to increase absorbance for the photon. There is no change in peak location, but peak intensity increases [16]. As the concentration of nanomaterials in a substance is increased, the absorbance of this substance increases too. This occurs because unbound electrons soak up the light that hits them [17].

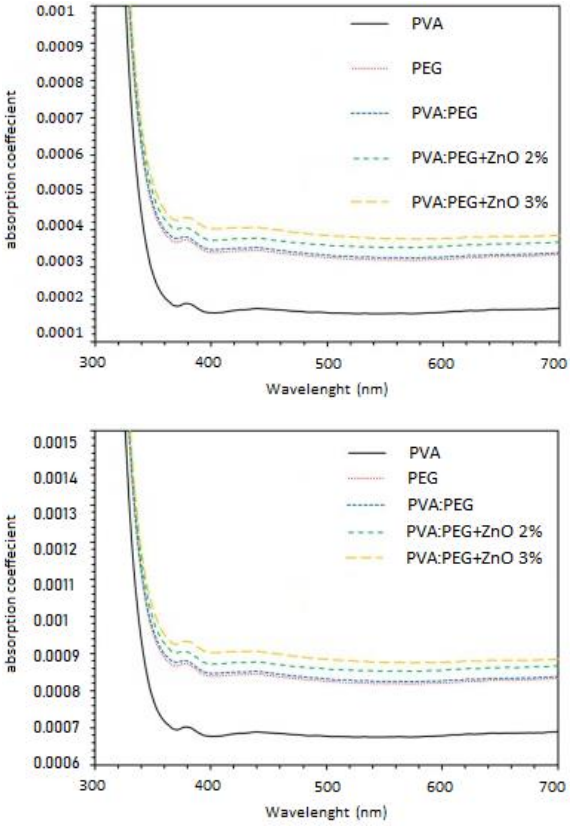

Fig. (4) Absorption coefficient of pure PVA, PEG and PVA+PEG and PVA+PEG//ZnO (a) before and (b) after exposed to radiation

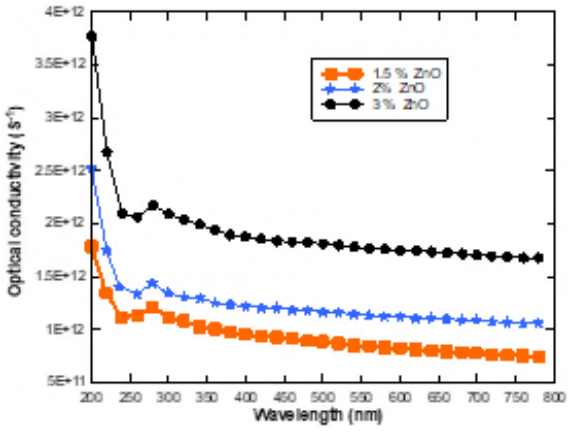

Fig. (5) Variation of optical conductivity with wavelength for ZnO nanoparticles with different concentrations

4. Conclusions

Thin films of PVA:PEG/ZnO composites were prepared and their optical and electrical properties were studied in this study. The effect of the concentration of ZnO nanoparticles on the electrical transmission of these polymeric films was studied. The electrical behavior of the films is affected by the concentration of ZnO nanoparticles where the activation energy is decreased. Increasing d.c. electrical conductivity appears due to enhancing ionic conduction in the film bulk.

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Table (1) Calculations of electrical parameters and the activation energy of thin films samples

Sample	σ_{RT} *10^{-6} ($\Omega^{-1}.cm^{-1}$)	R_H *10^5	n (cm^{-3})*10^{13}	type	μ_H (cm^2 / V.sec)	E_{a1} (eV) Before irradiating	E_{a2} (eV) After irradiate
PVA	7.25	129	0.051	p	110.54	0.026	0.366
PEG	5.12	-215	0.034	n	136.70	0.044	0.387
PVA :PEG	4.68	-46.8	0.192	n	28.91	0.046	0.394
PVA:PEG + ZnO (wt%)							
1.5 %	5.89	-26.3	0.37	n	8.39	0.047	0.485
2%	7.67	-5.6	0.94	n	5.84	0.046	0.399
3%	12.43	-0.915	1.56	n	2.61	0.043	0.371

Table (2) The main parameters result from the calculations for blend + 3 wt.% ZnO and after irradiation

T (°C)	T(K)	R (Ω)	ρ(Ω. cm)	σ=(1/ρ)	1000/T	ln (σ)
25	298	3.52E+08	3.423E-10	2.92E+09	3.355705	21.79535
30	303	4.20E+08	2.869E-10	3.49E+09	3.30033	21.97187
35	308	332602500	3.6207E-10	2.76E+09	3.246753	21.7392
40	313	3.42E+08	3.5203E-10	2.84E+09	3.194888	21.7673
45	318	2.66E+08	4.5293E-10	2.21E+09	3.144654	21.51528
50	323	1.88E+08	6.42E-10	1.56E+09	3.095975	21.16643
55	328	1.13E+08	1.0686E-09	9.36E+08	3.04878	20.65691
60	333	6.96E+07	1.7291E-09	5.78E+08	3.003003	20.17568
65	338	5.02E+07	2.4011E-09	4.16E+08	2.95858	19.84733
70	343	1.52E+07	7.9258E-09	1.26E+08	2.915452	18.65315

