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First Principle Computation of Polyethyleneoxide-Zno Nanocomposite: Electronic and Optical Properties

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Abstract. To format your abstract, use the Microsoft Word template style: *Abstract* or Use Times New Roman Font: 9 pt, Indent: left 0.2", Right: 0.2", Justified. Each paper *must* include an abstract. Begin the abstract with the word "Abstract" followed by a period in bold font, and then continue with a normal 9-point font. **Abstract:** The electrical characteristics of polymers, as well as the interactions between polymers and metal oxides, may be thoroughly understood via the use of molecular modeling, which is an essential technique. According to this interpretation, poly(ethylene oxide) (PEO) is represented with zinc oxide nanoparticles (ZnONP). The purpose of this computational research, which was founded on the theory of density functional analysis, was to investigate the impact that the incorporation of metal oxides, such as zinc oxide (ZnO), has on the electronic, optical and electrostatic potential (ESP) characteristics of polyethylene oxide (PEO). For the purpose of investigating the electronic characteristics of PEO, ZnONP, and PEO/ZnO nanocomposite, the DFT theory at the PBE level was used. The Grimm dispersions were applied to the PEO/ZnO nanocomposite system in order to have an accurate prediction of its optical and electrical characteristics. According to the findings of the electronic band structure, density of states, and optical functions calculations, the absorption and refractive index of the nanocomposite model structures that were investigated increased as a consequence of the incorporation of metal oxide. As a result of the interaction between metal oxide and the initial polymer matrix, the values of the energy bandgap reduced. ESP map indicated a strong interaction between PEO and ZnONP through a charge mutual accompanied with a common ESP over PEO chains and ZnONP.

Keywords: Polymer nanocomposite, Poly(ethylene oxide), ZnO nanoparticle, Metal oxide, Electronic structure, Optical properties, Electrostatic potential map.

INTRODUCTION

A polymer nanocomposites (PNC) is a composite material with a polymer matrix and a dispersed phase that is less than 100 nm in at least one dimension. The exploration of exceptional mechanistic and optoelectronic characteristics of PNC in targeted being useable, of that character flexible photonics, constitutes a vibrant field of study (Lu et al 2021, Aziz et al 2021, Ali et al 2021). Optical technologies, such as light-emitting and solar cell devices, fundamentally depend on the reciprocal action between sophisticated substances and photons. Polymer materials are described for use in semiconductor photon-emitters, light-wave processors, and detectors (Mohammed et al 2023, Abdel Moez et al 2021). This results from their appealing visual characteristics. Optimization of suitable dopant materials and their concentrations may effectively manipulate the optical properties of polymers. Theoretical and experimental document references many optical characteristics and they efficient to be used for determination (Al-Faleh and Zhilif 2011, Mohan et al 2007, Jin et al 2013). The literature indicates that the computation of the absorption coefficient and the two components of refractive index may be executed with ease (Picchi et al 2023, Ahmed et al 2024, Sadoh et al 2022). Polymers provide advantageous optical characteristics. Alterations in polymeric materials

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affect their electrical and optical characteristics, hence enabling these materials to execute many roles. In theory, structural alterations induce changes in the optical characteristics of polymers via the fabrication of nanoscale materials. This structural alteration incorporates a dopant addendum that alters the process of electron-excitations. Previous research indicates that the optical and electrical characteristics of polymers may be improved by the incorporation of metallic and semiconductor particles (Khan et al 2023, Okamoto 2023).

Polyethylene oxide (PEO) has a linear configuration with a monoclinic crystal framework in its homopolymer state (Badry et al 2021). PEO-established compounds are advantageous industrial choices due to their considerable heat constancy. It has diverse desirable attributes, including enough dimensional stability, cost efficiency, and appropriate anti-corrosion behavior (Jiang et al 2014). The advantages of polymers stem from their translucence, fading-cost, lightweight nature, simplicity of production, and strong mechanical properties. Nonetheless, the PEO is the most appropriate choice for use in the field of optics because of its comparatively faint refractive index. Many researchers developed PEO/semiconductor nanocomposites upon insertion of semiconductor nanoparticles. Several experimental investigations and theoretical studies using density functional theory (DFT) have been conducted on the physical and chemical characteristics of doped host polymer matrices (Abomostafa 2021), in addition to PEO that has been doped with Al_2O_3 (Mohammed et al 2020), NaI (Manthrammel et al 2019), Pb_3O_4 (Saeed et al 2022), NiO_n (Ruscello et al 2019), CdS (Saini et al 2013), and ZnO (Xiong et al 2001).

Zinc oxide (ZnO) is a semiconductor that is classed as having a large band gap (Ali 2023). It is an advantageous material for a wide variety of applications in the field of environmental photocatalysis and energy conversion activities. As a result, the creation of photocatalysts that are active in both ultraviolet and visible light has garnered a lot of interest. It has been shown that the incorporation of ZnO nanoparticles into polymer matrices may significantly improve the photocatalytic activity (Arya and Gupta 2023). It is the objective of this computational investigation to inspect the optoelectronic characteristics of PEO/ZnO nanocomposites. These nanocomposites were modeled and optimized at the PBE exchange functional and correlation energy level. Research was conducted with the primary objective of examining the optical functions and electrical characteristics. A theoretical model (DFT) describing a potential recommended technique of optical properties of a polymeric matrix containing zinc oxid nanoparticles (ZnONP) and a polyethylene oxide (PEO) matrix is introduced in this study.

COMPUTATION

Through the construction and execution of an adsorption simulation between a crystalline polyethylene oxide and $(ZnO)_6$, this research was able to generate the nanocarrier. Small spherical nanoparticles containing six atoms of zinc and six atoms of oxygen were used in the construction of zinc oxide. Following the modeling of the PEO and ZnONP, the structure was optimized by using the DMol3 module as part of the Materials Studio 2013 program. The optimization was performed at the PBE functional together with the numerical DNP function technique. In order to optimize the structure, the parameters are specified to 2×10^{-3} Ha/Å, 1.0×10^{-5} Ha, 5×10^{-3} and 1.0×10^{-6} Ha for the force, energy, max-displacement and SCF tolerance respectively. In order to correctly determine the configuration of the PEO/ZnONP system that would be most advantageous from a thermodynamic standpoint, an adsorption calculation was carried out with the help of the Adsorption Locator module that is included in the Materials Studio 2013 program. Through the use of the DMol3 module, a single point energy computation is utilized in order to analyze the energetic characteristics of the molecules. These attributes include quantum molecular band structure, partial density of states and electrostatic potential. However, in the meanwhile, the CASTEP software that is included in Materials Studio 2013 is used in order to compute and evaluate the optical characteristics of the molecules. These properties include absorption and refractive index. A schematic representation of the computational process that was used in this investigation may be seen in Fig. 1.

RESULTS AND DISCUSSIONS

We conducted an insertion reckoning using Adsorption Locator to determine the farthest advantageous interaction of ZnO nanoparticle into the polymer matrix. This allowed us to analyze the interaction of the ZnONP with the PEO nanocomposite. According to the most stable arrangement, the ZnONP nanocomposite has an estimated interaction energy of -311.21 kcal/mol. The average distance between Zn atom and four hydrogen atoms on two PEO chains, it may be 2.73 Å. Because of the potent interaction amidst the polymer's hydrogen atom and the nanoparticle's zinc atom, the distance of ZnONP and polymer chain level is 1.17 Å. It is possible to predict an electronic band structure using a computational method where DFT has been shown to be an effective tool. PEO, ZnONP and their composite band structures are shown in fig. 2-4 along the Brillouin zone bath (G-F-Q-Z-G) of reciprocal lattice. The PEO has a direct band gap at G-point of 5.61 eV as shown in fig. 2, which is in good endorsement with the value that have been recorded of about 5.7 eV (Arya and Gupta 2023, Telfah et al 2023), because of unsaturated bonds, which are linked to $\pi \rightarrow \pi^*$ transition. The PEO has an indirect band gap at the G-F direction of crystal, which has a value of about 5.3 eV. Fig. 3 presents the band structure of $(ZnO)_6$ which demonstrate a flat electronic band states, which indicated localized electron states, with an energy gap of 1.98 eV. After the insertion of ZnONP within PEO matrix, The interaction between PEO chains and ZnO nanoparticle made a significant changes in electronic states as a result of hydrogen bonding and electrostatic interaction. There is many electronic states initiated within PEO and ZnONP forbidden energy gap making a development for electronic and optical activity. According to fig. 4, the energy gap reduced to 0.26 eV, which referred to multilevel interactions and these will provide optoelectronic activity over a wide range of energy.

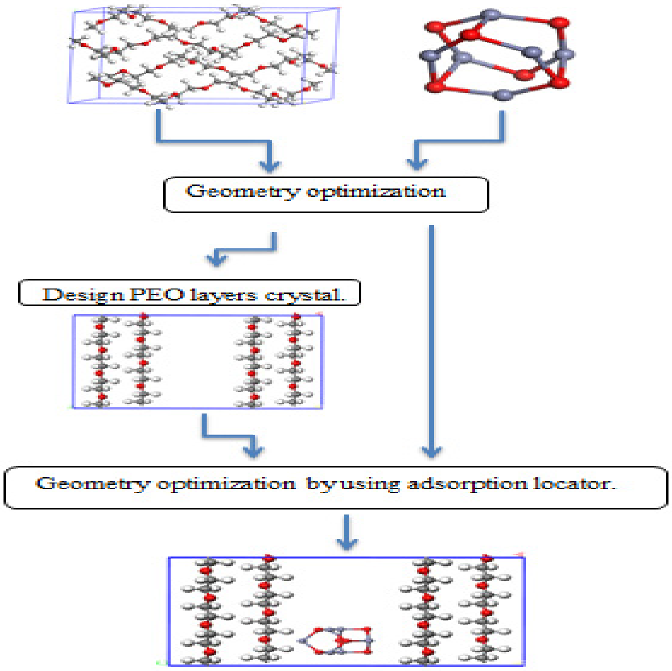

FIGURE. 1. Schematic presentation of PEO-ZnONP modeling

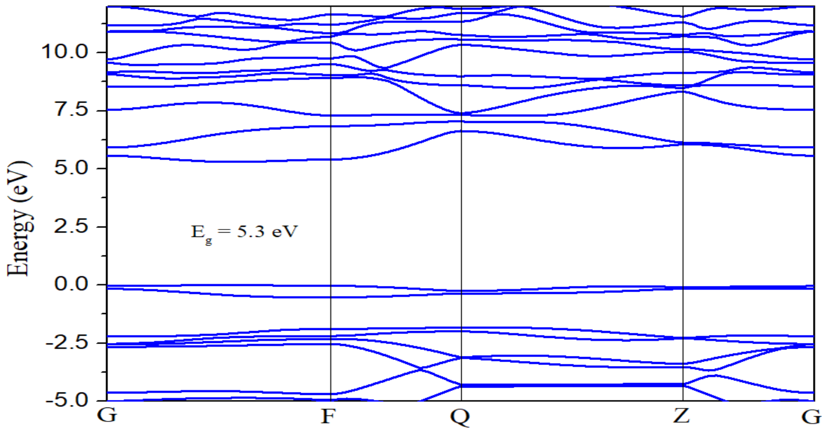

FIGURE 2. Band structure of PEO.

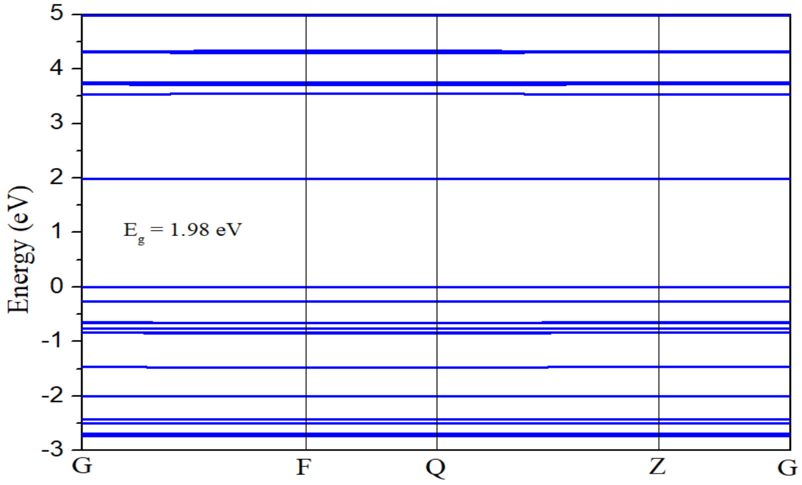

FIGURE. 3. Band structure of ZnONP.

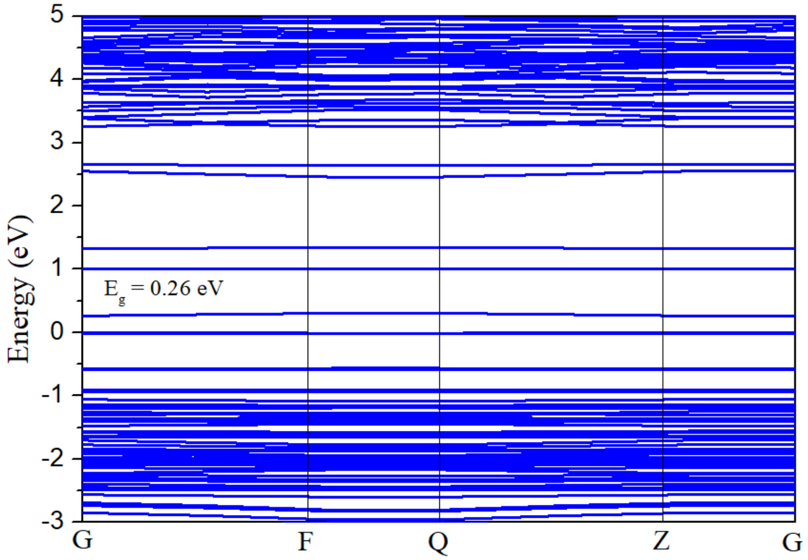

FIGURE 4. Band structure of PEO/ZnONP.

In order to study the electrical characteristics of the PEO, ZnONP, and their nanocomposite, we computed the partial density of states (PDOS). Fig. 5-7 show these outcomes and the virtual Fermi level is shown at 0.0 eV. The electronic states of PEO are consisted of s- and p-orbitals in both valance band (VB) and conduction band (CB). The valence and conduction bands in the PEO polymer's partial density of states (PDOS) are formed by s-p hybridized orbitals. In the valence band, a benevolence of oxygen atoms' 2p state is senior, and for conduction band, the contribution of hydrogen atoms' 1s orbital is equivalent to oxygen atoms' 2p. According to the results of the Partial Density of States (PDOS) analysis, as shown in Fig. 5, the HOMO is around 0.6 eV and the LUMO is around 4.8 eV. Valence bands are being formed by the energy levels below the HOMO, while a conduction band is being built by the states above the LUMO. The electronic states above the Fermi level indicate an amorphous nature of PEO chains in its crystalline structure. The electronic states of ZnONP are consisted of p- and d-orbitals in both valance band (VB) and conduction band (CB). The valence and conduction bands in the ZnONP partial density of states (PDOS) are formed by p-d hybridized orbitals. In the valence band, the contribution of zinc atoms' 4d orbital electrons is smaller, and in the conduction band, the contribution of zinc atoms' 4d orbital electrons is declined in compared to oxygen atoms' 2p. According to the results of the Partial Density of States (PDOS) analysis, as shown in Fig. 6, the HOMO is around 0.5 eV and the LUMO energy state is around 1.98 eV.

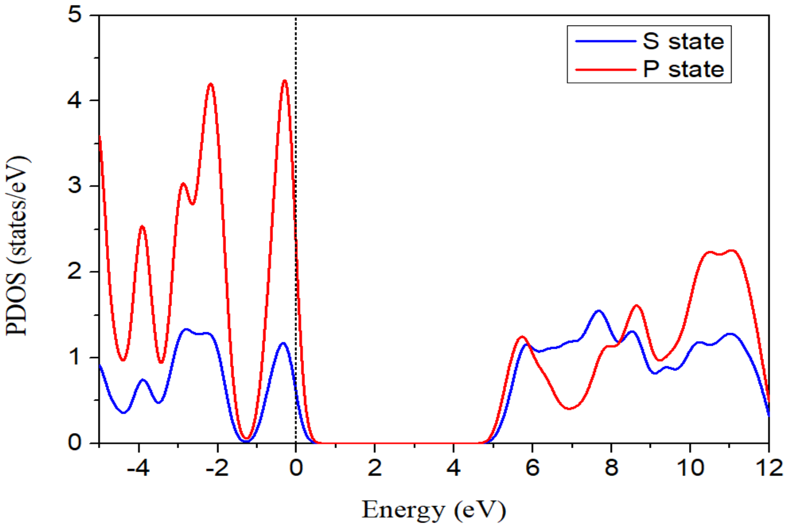

FIGURE 5. Density of states of PEO.

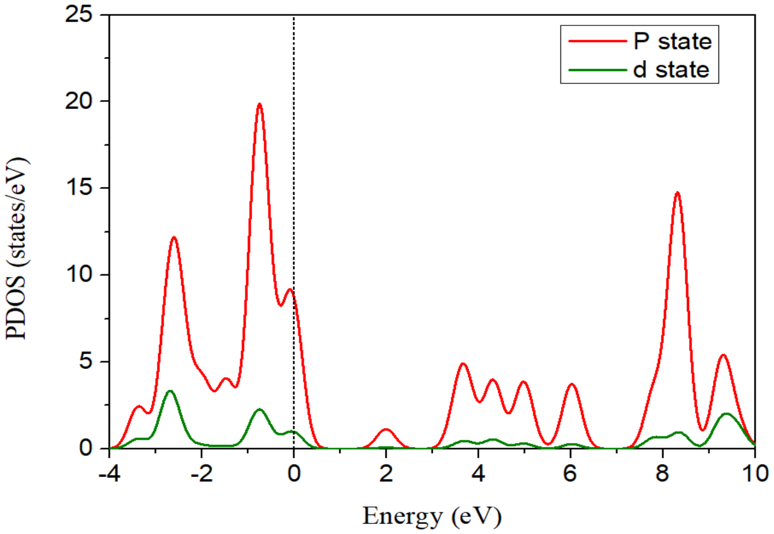

FIGURE 6. Density of states of ZnONP.

Fig. 7 illustrates significant d-s and d-p overlapping amidst zinc and hydrogen/oxygen atoms in PEO, resulting in the formation of limited energy states inside the forbidden energy gap next to the HOMO and LUMO, from this diminishing the prohibitive energy. The contribution of the electrons from the 4p orbital of Zn in PEO-ZnONP exceeds that of the other atomic orbitals. The donation of electrons by zinc atoms facilitates their conversion into cations, hence augmenting the condensation of cations, which is a allowed the p orbitals to form HOMO and LUMO states. The support of 2p states in O-atom is substantial in the occupied band and the unoccupied conduction band.

The UV–Vis absorption spectra were analyzed to examine the absorption bands of PEO-ZnONP complex composites (Fig. 8). The integration of PEO with ZnONP results in a reduction of bandgap energy, with a shift towards the red region of the absorption bands and the emergence of a new sub-band at 150 nm, 188 nm, and a subsequent redshift to 280 nm. The absorbance spectra for PEO display three transition bands with maxima at 225, 165, and 105 nm. According to molecular orbital theory, three potential electronic transitions for PEO are identified: at 225 nm (5.51 nm), corresponding to the $\pi \rightarrow \pi*$ transition from unsaturated bonds. The experimental absorption curve is in good agreement with the theoretical one, where the onset electron excitation near 275 nm as predicted theoretically and the absorption raised 233 nm which come to an agreement with PEO computed energy gap (5.3 eV). In the absorbance spectra of ZnONP in PEO, there are four bands that can be seen about 170, 188, 230, and 280 nm. These bands are attributed to the absorption of complex formation between ZnONP and PEO, respectively.

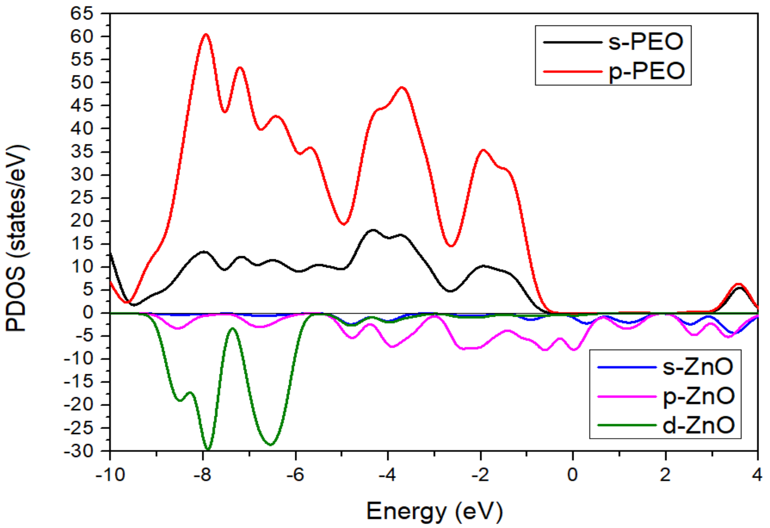

FIGURE 7. Density ofstates of PEO/ZnONP conposite.

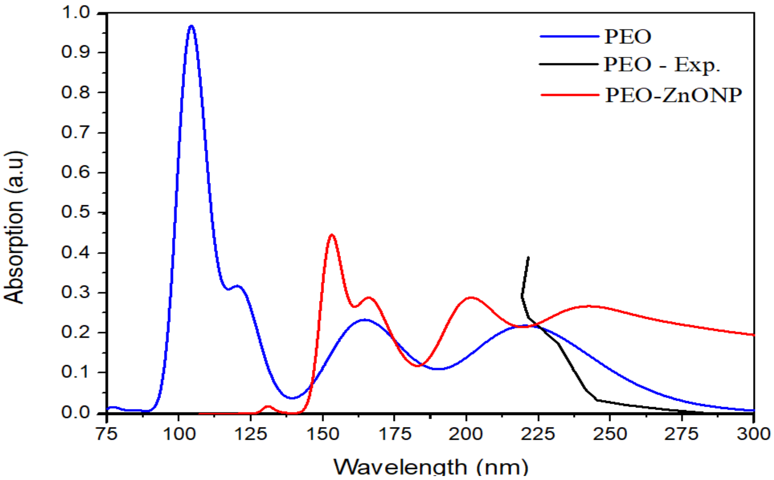

FIGURE 8. Absorption spectra of PEO and PEO/ZnONP.

The refractive index of the resultant materials often rose with the addition of ZnONP to the PEO as shown in Fig. 9. The crystalline constituents in the nanocomposites exhibiting the greatest refractive indices included ZnONP. It was noticed that the refractive index of nanocomposite did not undergo a considerable change during the course of the wavelength intervals. According to the results of several experimental investigations, the refractive index of the PEO may vary anywhere from 1.6 to 2.0. The refractive index demonstrates that PEO-ZnONP has well-formed crystalline structures, despite the fact that it possesses a phase that is more amorphous.

Fig. 10 illustrate the electrostatic potential (ESP) map of PEO, ZnONP and PEO-ZnONP composite. The ESP map of PEO has a neutral characteristic because of a uniform charge distribution over the whole PEO chains. The ZnONP has a distinct ESP map according to the positive and negative charge of zinc and oxygen atoms respectively. While adding the zinc oxide nanoparticle to PEO matrix, the interaction forces made a dramatic changes in the electrostatic potential map. The charge distribution over PEO will changed because of charge exchange with ZnO nanoparticle, thus the ESP map will altered and there is a distinct positive and negative electrostatic potential over the whole nanocomposite (PEO and ZnONP).

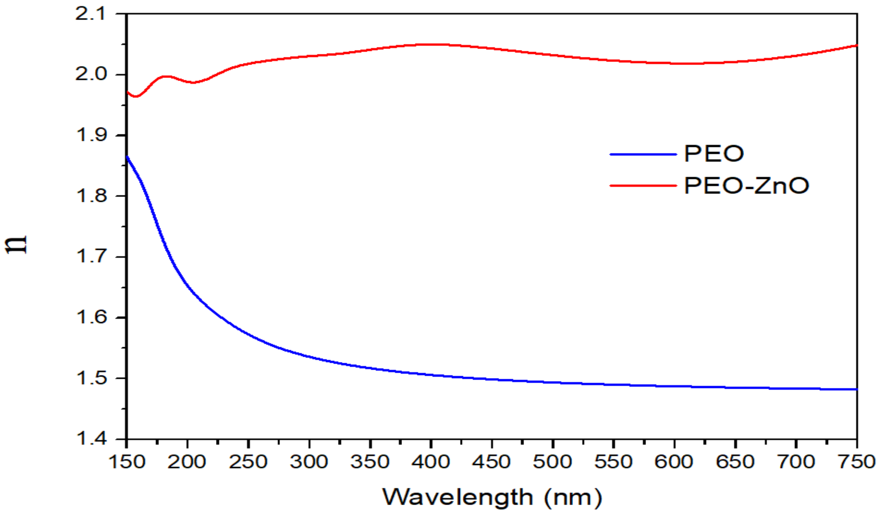

FIGURE 9. Refractive index of PEO and PEO/ZnONP.

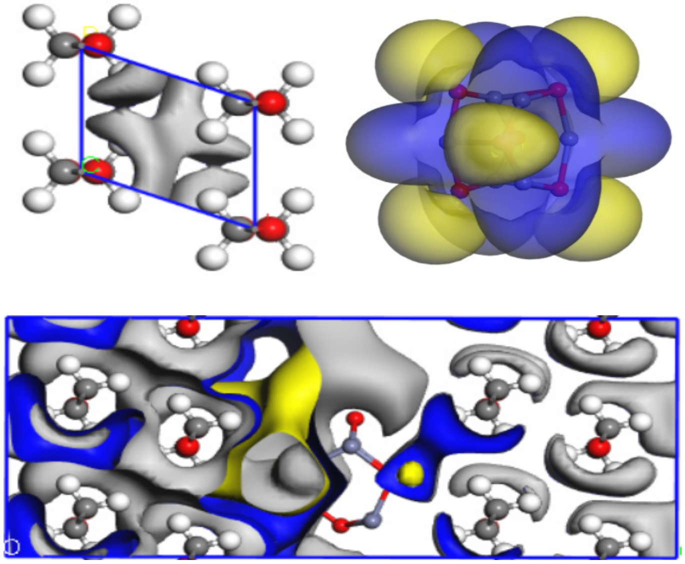

FIGURE 10. Electrostatic potential map of PEO, ZnONP and PEO/ZnONP nanocomposites.

CONCLUSIONS

This interpretation depicts poly(ethylene oxide) (PEO) in conjunction with zinc oxide nanoparticles (ZnONP). This computational research, based on density functional theory, aimed to examine the effects of incorporating metal oxides, such as zinc oxide (ZnO), on the electronic, optical, and electrostatic potential (ESP) properties of polyethylene oxide (PEO). The DFT theory at the PBE level was used to investigate the electronic properties of PEO, ZnONP, and the PEO/ZnO nanocomposite. The Grimm dispersions were used in the PEO/ZnO nanocomposite system to get precise predictions of its optical and electrical properties. The computations of the electronic band structure, density of states, and optical functions indicate that the absorption and refractive index of the examined nanocomposite model structures increased due to the addition of metal oxide. The interaction between the metal oxide and the original polymer matrix resulted in a reduction of the energy bandgap values. The ESP map revealed a significant interaction between PEO and ZnONP, characterized by charge mutuality and a shared ESP between the PEO chains and ZnONP.

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