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Theoretical investigations on the Energy gap, UV- Vis Spectrum and Thermochemical Properties of PVA Doped with ZnO andTiO_2

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ABSTRACT: Different polymers have attractive multiple properties due to their many uses in many fields. The synthesized polymer polyvinyl alcohol (PVA) with metal oxide nanoparticles has many applications in different approaches, such as electronics, sensors, optical, optoelectronics, and biomedical fields. The study was carried out within the framework of density functional theory with B3LYP and exchange-correlation energy functionals 6-31 G(d,p). Three compounds were PVA and PVA synthesized with Zinc oxide (ZnO) and Titanium dioxide (TiO2) nanocomposites. The results proved that using these oxides is a good way to improve the electronic properties of PVA, as the energy gap of PVA decreased from 3.8 to 3.4 and 3.3 for PVA/TiO2 and PVA/ZnO, respectively. This demonstrates the good semiconductor character of these compounds with applications related to solar cell manufacturing. The photosensitivity of both PVA/TiO2 and PVA/ZnO samples in FTIR and UV-Vis results It was indicated that TiO2 and ZnO interacted strongly with PVA.so they can be used in other applications such as energy storage capacitors. The vibrational modes were then analyzed, in terms of force constant and reduced mass, which were relatively constant hydrogen vibrations.

Keywords: Polymers, polyvinyl alcohol (PVA), density-functional theory.

1. INTRODUCTION

Polymers in general are bound together by covalent chemical bonds. Many biological systems have the fundamental idea of polymers which is the multiple assembly of basic structural elements to build a three-dimensional structure. Synthetic polymers manufactured by humans are just as numerous as natural ones, although the most significant advancements in their synthesis have only been accomplished since the Second World War [1], [2].

Due to their numerous applications, polymer nanocomposites have attracted a lot of attention and interest from researchers [3], [4]. Numerous industries, including optics, biomedical, electronics, sports, agriculture, textile, energy, healthcare, and adhesives, use polymers in one way or another. Devices, sensors, packaging materials, drug delivery systems, scaffolds for tissue engineering, and cosmetic procedures are all made with their help. Due to all of these applications and their unique flexible properties, nanocomposites have been of major interest globally. Metal oxide nanoparticles can be added to polymers to improve their characteristics and find use in optical optoelectronics, sensors, electronics, and biological industries [5], [6].

Synthetic polymers have attracted attention in many applications for several reasons. Physical and chemical properties can be achieved by using different parameters, different conversion rates of monomer units, polymerization reactions and copolymer formation.

Polyvinyl alcohol (PVA), with the formula [CH2-CH (OH)], is a polymer whose properties and uses have been extensively studied. It is often blended with other polymers to improve its thermal and mechanical properties and enhance specific functionalities [7], [8].

Adding metal oxide nanoparticles to (PVA) has many applications in medical and industrial approaches. Many studies have been conducted on polymer blends of polyvinyl alcohol (PVA) with zinc oxide (ZnO) and Titanium dioxide

(TiO_2) [9]. The doping (ZnO) and (TiO_2) particles into polyvinyl alcohol matrices can alter the mechanical, electrical, and optical characteristics of the polymer [10].

This work used the density functional theory (DFT) to calculate transmittance and UV-visible spectra. Based upon these calculations the electronic properties of Polyvinyl Alcohol can be enhanced by adding metal oxide semiconductors such as (ZnO) and (TiO_2) which can be utilized for applications in many areas.

2. COMPUTATIONAL METHODS

The calculations in this study were performed using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) a method used to study a wide range of phenomena in chemical physics, condensed matter physics, and materials science because of its computational effectiveness and conceptual simplicity. These computations were at the B3LYP/6-31G (d,p) level of theory, and were performed using Gaussian 09 and Gauss View 6.0 and the Lee-Yang-Parr correlation function (B3LYP) [11], [12]. The properties of PVA-ZnO and PVA-TiO_2 and the features of these materials will be covered in this study. Fig. 1 shows the geometries of Polyvinyl alcohol (PVA), PVA/ZnO, and PVA/TiO_2.A hydrogen atom in the polymer structure is replaced by titanium dioxide or zinc oxide.

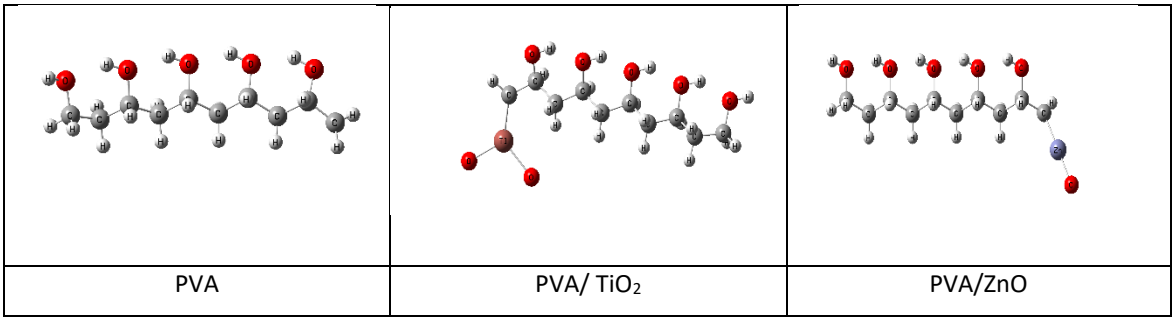

FIGURE 1. Geometry optimization of Three compounds above

3. RESULTS and DISCUSSION

3.1. TRANSMITTANCE SPECTRUM

Figure 2 shows the main peaks of all the synthesized polymer composites PVA, PVA/ZnO, and PVA TiO_2 by Fourier transform infrared spectra analysis which helped in understanding the mixing of both ZnO and TiO_2 with the polymer. In Fig. (2) it can be seen the appearance of these peaks is (2932, 1416, 1330, 1082, 915) cm^{-1} Assigned to the characteristic vibration ranges of pure PVA. The most distinctive feature of alcohol is the stretching band O–H, which appears in the range 3200 cm^{-1} and CH2 has a stretching peak located at 1327 cm^{-1}. The wagging vibration of (CH) or (C-C) stretching peaks at 1230 cm^{-1}. As for 1416 cm^{-1}, it is due to the bending of (CH3). and the bands around 2932 cm^{-1} correspond to the –CH2 asymmetric and symmetric stretching, respectively [13],[14]. The IR spectra of PVA/ZnO also indicate 435 cm^{-1} to the stretching vibration of the bond between Zn-O (metal-oxygen bond). The interaction between ZnO and PVA is responsible for the slight shift in the OH stretching position and the C-O group. [15]. In this figure, the chemical bond of PVA/TiO_2 is shown, the IR spectra analysis displays small shifts in peak positions as well as obvious changes in shape and intensity that occurred at (916, 850, and 1100) cm^{-1}. Furthermore, a broad absorption band was found for TI-O-O at 514 cm^{-1}, while the TI-O bond is responsible for the absorption peaks found between 450 and 600 cm^{-1}[16].

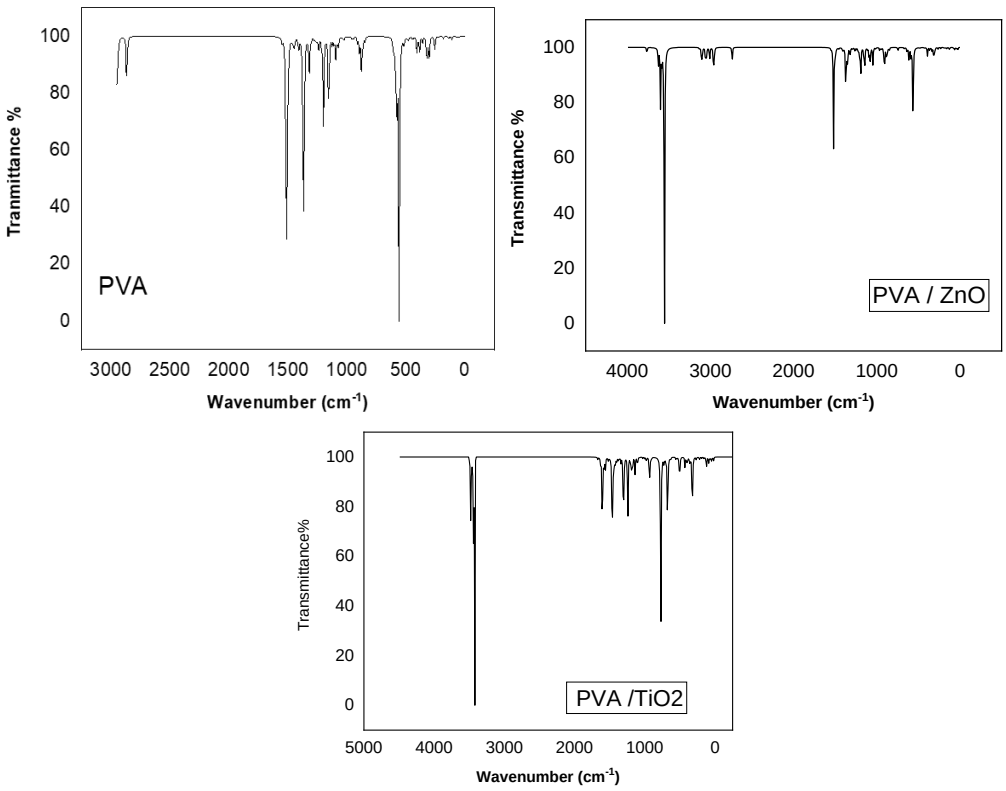

FIGURE 2. Transmittance of (a) polyvinyl alcohol (PVA), (b) PVA/ZnO and (c) PVA/TiO_2.

3.2. UV-Vis SPECTRUM

The UV-Vis spectrum of the Reaction between titanium dioxide and zinc oxide with PVA was analyzed in Fig (3). ultraviolet and visible spectrum was used to study the optical properties to compute the interaction of (ZnO) and (TiO_2) with (PVA). PVA polymer exhibited two bands at 325 and 393 nm, indicating the π-π* transition and the second band indicates the bipolaron state of the polymer as shown in Fig. (3). The absorption of UV-visible spectrum of PVA/ZnO and PVA/TiO_2 indicated a single absorption band at 500 nm and 300 nm, respectively. However, these bands demonstrate slight shifts compared to polymers, i.e. a redshift. This confirms strong interactions between (ZnO) and (TiO_2) with (PVA) that these interactions lead to the observed shift.

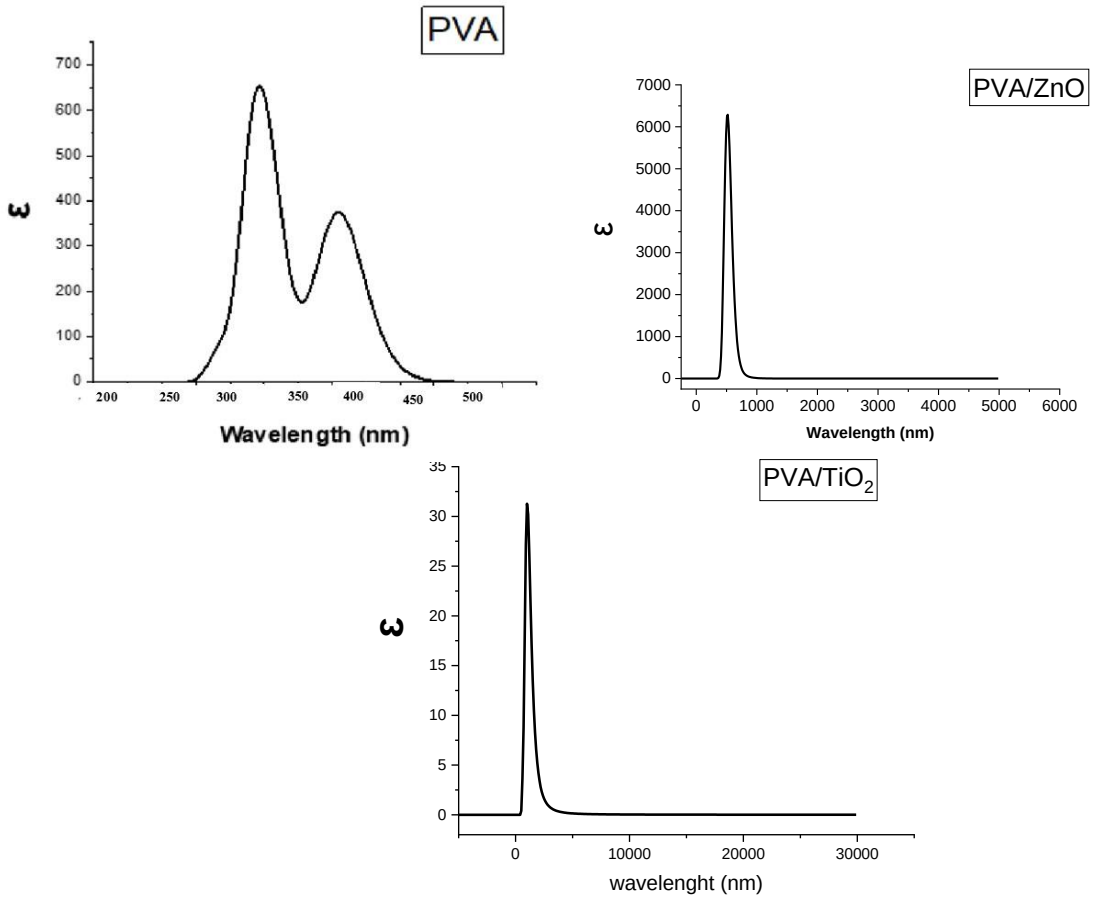

FIGURE 3. The ultraviolet and visible spectrum of the three compounds above.

3.3 HOMO–LUMO ENERGY GAP

The changes in energy gap (E_g) values are explained by the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy bands [17], [19]. Fig. 4 shows the orbital distributions of the calculating HOMO/LUMO. The energy gaps for (PVA) and for (ZnO)and (TiO_2) doping with polymer were listed in Fig (4). The addition of TiO_2 and ZnO significantly affected the energy gap which decreased sharply, due to the strong interaction of these element oxides with the polymer. Moreover, the decrease in E_g is caused by the creation of new levels in the optical bandgap, which leads to transitions of electrons from the valence band to the conduction band consequently, the doping process helped to reduce the energy gap. This behavior is in agreement with the IR and UV–Vis spectra data of the PVA PVA /TiO_2 and PVA/ZnO composite, which we obtained in the previous two sections.

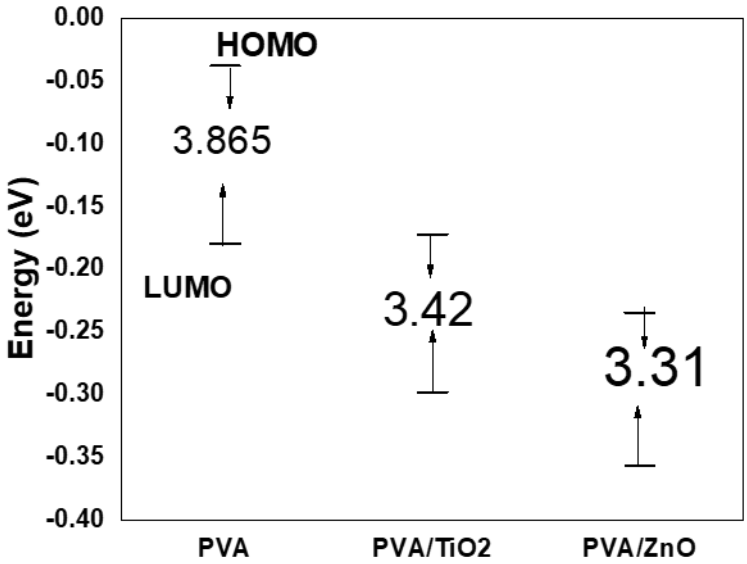

FIGURE 4. HOMO and LUMO of the three compounds above

3.4 THERMOCHEMICAL PROPERTIES

The thermochemical properties of polymers can be determined using some analytical methods. These properties such as Zero-point (ZOP), total energy (E_{tot}), Enthalpy (Hcorr), and Gibbs free energy are important for understanding the behavior and stability of polymers during synthesis. The Enthalpy (H_{corr}) was determined using equation (1- 2), all at (1.0 atmospheres and 298.15K) [20], [21]. To obtain values for thermochemical properties, theoretical methods such as quantum chemistry calculations based on density functional theory (DFT) for the PVA and PVA/ZnO and PVA/TiO_2 can be used. The enthalpy (Hcorr) measures the system's heat content at constant pressure and temperature. When the polymer is formed or transformed, the Gibbs energy (G) combines the enthalpy and entropy of the system and gives information about its stability [22], [23]. Tables 1,2 show how these results can generate various chemical properties for (PVA/ZnO, PVA and ZnO) and (PVA TiO_2, PVA and TiO_2). The equations (1- 2) imply that the reactants are stable and the products of the reaction are unstable when ($\Delta G < 0$) While the products of the reaction are stable and the reactants are unstable when ($\Delta G > 0$) This also indicates whether something is thermodynamically stable or unstable. This shows whether something is stable or unstable from a thermodynamic perspective. If the value of (ΔG) is negative, it means that the product is spontaneously generated, and is stable. If the value of (ΔG) is positive, it indicates that the system requires energy to form the product and is unstable. In addition, the enthalpies of our doped compounds are all negative, which makes it possible to conclude that they are thermodynamically stable. Similar behavior has been observed for the total energy values.

Table 1. shows how these results can be used to analyze various chemical profiles (PVA, ZnO, and PVA/ZnO)

System	ZOE (Hartree)	E_{tot} (Hartree)	H_{corr} (Hartree)	G_{corr} (Hartree)
PVA	-769.418746	-769.400849	-769.3999	-769.4661
ZnO	-138.939907	-138.936425	-138.9354	-138.9637
PVA / ZnO	-4542.919822	-4542.897855	-4542.8969	-4542.9762

Table 2. Shows how these results can be used to generate various physicochemical data

for PVA, TiO_2 and PPy/TiO_2 composites.

System	ZOE (Hartree)	E_{tot} (Hartree)	H_{corr} (Hartree)	G_{corr} (Hartree)
PVA	-769.4187	-769.4008	-769.3999	-769.4661
TiO_2	-0.2286	-0.2241	-0.2232	-0.24821
PVA / TiO_2	-2835.1746	-2835.1505	-2835.1496	-2835.2336

$\Delta_r H°(289K) = (\Delta_f H° products) - (\Delta_f H° reactant)$ …… (1)

$\Delta_r H°(289K) = [(PVA/ZnO) - [(PVA + ZnO)]]$ = -3634.5616 *627.51

= - 2279415.30 Kcal / mol

$\Delta_r G°(289K) = (\Delta_f G° products) - (\Delta_f G° reactant)$ ……. (2)

$\Delta_r G°(289K) = [(PVA/ZnO) - [(PVA + ZnO)]]$ = - 3634.5464 *627.51

= - 2280714.211 Kcal / mol

$\Delta_r H°(289K) = [(PVA/TiO2) - [(PVA + TiO2)]]$ = -2065.5265*627.51

= - 1296138.534 Kcal / mol

$\Delta_r G°(289K) = [(PVA/TiO2) - [(PVA + TiO2)]]$ = - 2065.5192 * 627.51

= - 1296134.01 Kcal / mol

Endothermic reactions are reactions in which substances absorb energy from their surroundings, which means they have a positive enthalpy. In contrast, exothermic reactions are reactions that release heat into the surroundings, and they have a negative enthalpy. We can see from these calculations that the enthalpy is negative for all three compounds mentioned, i.e. the reactions are exothermic. This means that an exothermic reaction is one in which the area energy is greater than the energy absorbed.

3.5 REDUCED MASS

Although the figures are related to the vibrational spectra of the three above compounds, we observe the highest reduced mass mode (HRMM) in Fig. (5) and the highest constant force mode (HFCM) in Fig. (6). If m_1 and m_2 are masses of two particles, then the reduced mass (μ) is given by the following equation: [24], [25].

$$\mu = \frac{m_1 * m_2}{m_1 + m_2} \quad \ldots (3)$$

The reduced mass of PVA is approximately (8) atomic mass units (amu) close between two Oxygen atoms, which shows that some vibrations involve one type of atom and exclude the other. In PVA/TiO_2 the reduced mass is approximately (17 amu) between Titanium and two oxygen atoms. As for PVA/ZnO the reduced mass is (8 amu) and it is also between two oxygen atoms. It can be observed at a frequency of 1600 cm^{-1} for the three compounds that the reduced mass becomes equal to one, which is due to the hydrogen atoms, while in Figure (9) at the same frequency it increases because the vibrational frequency (υ) is proportional to the square root of the force constant [26], [27].

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \qquad \ldots\ldots (4)$$

Where K is the force constant in (mDyne/ Å), the force constant is (1.8 mDyne/ Å), (2.4 mDyne/ Å) and (1.7 mDyne/ Å) for PVA, PVA/TiO_2 and PVA/ZnO respectively. It was observed that the force constants of (PVA) and (PVA/ZnO) are almost equal because they have the same reduced mass. While (PVA/TiO_2) has a large reduced mass compared to the rest, it has a small force constant. PVA/TiO_2 has a higher force constant, enhancing the chemical and physical stability and improving the overall performance and Optical active material i.e. improving optical properties.

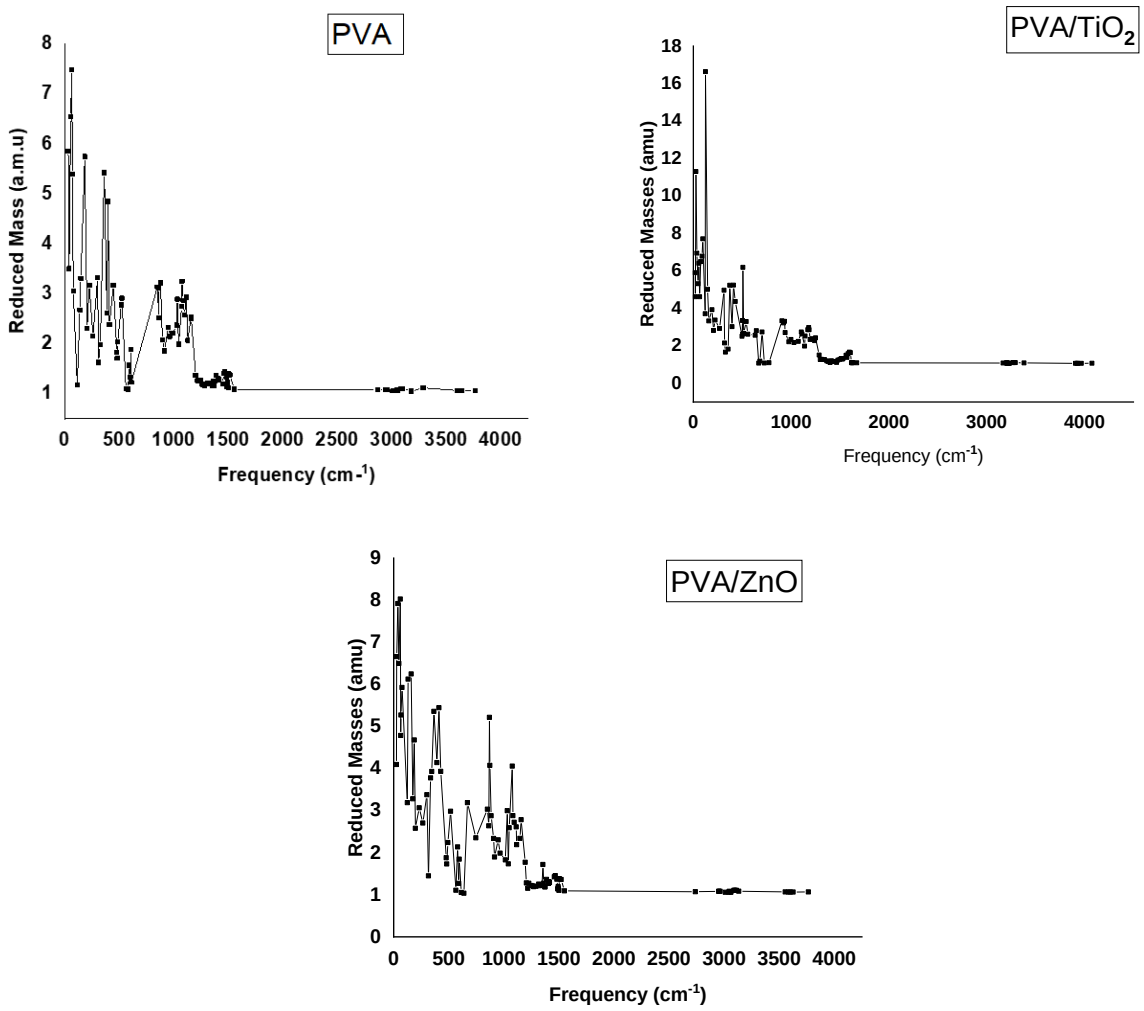

FIGURE 5. Reduced masses of three compounds

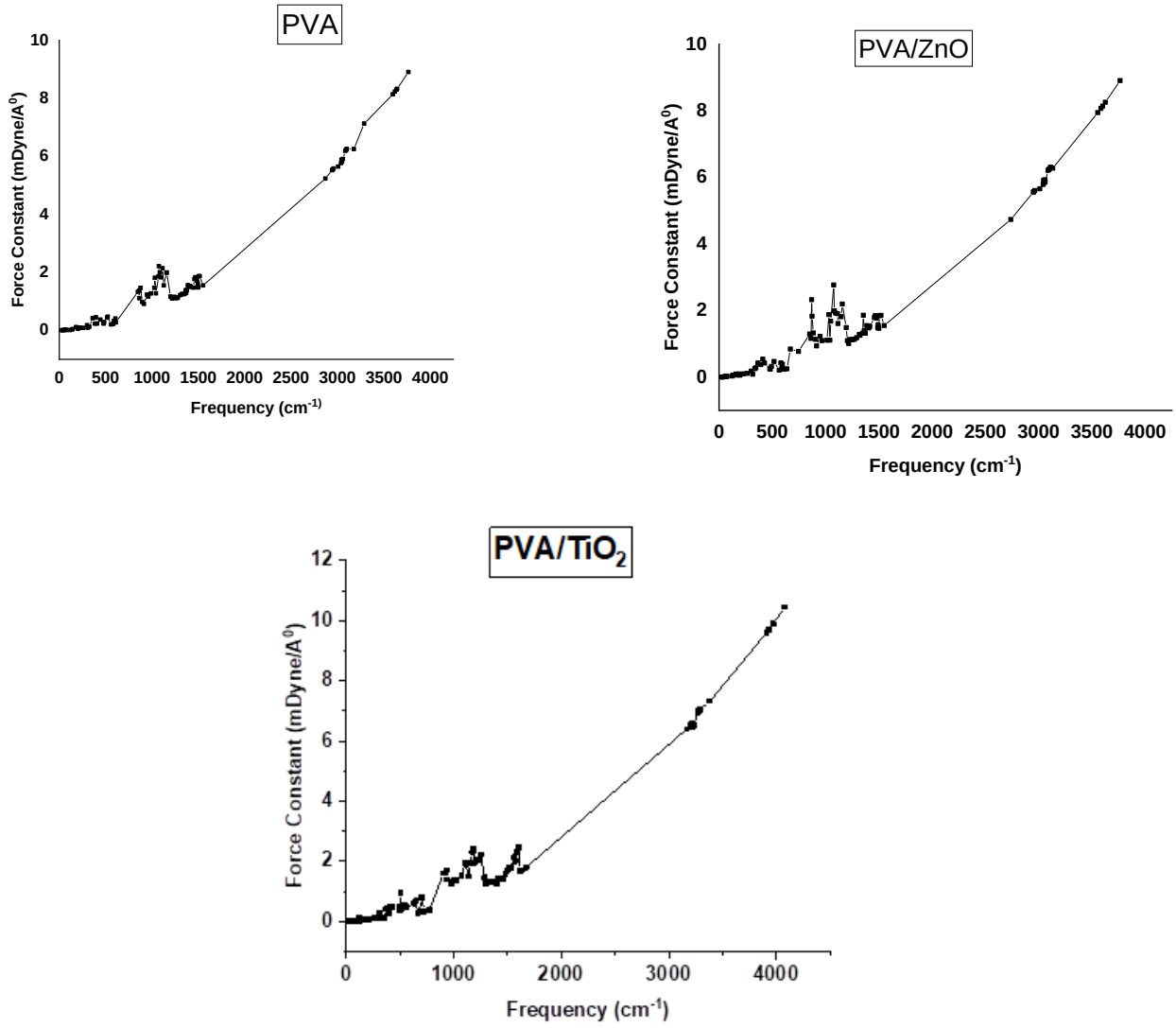

FIGURE 6. The force constant of three compounds.

CONCLUSIONS

In this work, the DFT method was used to investigate the structural, electrical, spectral and thermodynamic properties of the PVA polymer doped with ZnO and TiO_2. The determination of the thermodynamic properties revealed thermodynamically stable compounds with high reactivity and suitable for interactions with other compounds. The results of the geometry optimization indicate that the doping reduces the energy gap but does not change the molecular structure of the PVA under study. In addition, the analysis revealed electronic properties. The electronic properties of the compounds resulting from doping are further enhanced. FTIR and UV-Vis studies revealed substantial interactions between TiO_2 and ZnO with PVA and thus they can be used in other applications such as energy storage capacitors.

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