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# Simulation and Preparation of an Eco-Food Container by using Bio-Additive of Beet Juice in Polyvinyl Alcohol/Polyvinylpyrrolidone Blend: Physical Application

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***Abstract***

The packaging of foods occupies a wide area of foodstuffs manufacturers' interest. Despite the subject is branched, this paper focuses on utilizing eco-friendly food container enhanced by bio-additive of beet juice contains a natural pigment (anthocyanin) to offer radiation shielding protection. The matrix used is a bio-polymeric blend of 70% polyvinyl alcohol (PVA) and 30% polyvinyl pyrrolidone (PVP) with the adding of different volumetric percentages of anthocyanin (5, 10, 15, and 20 V/V%). As all the components are naturally degradable,increasing the anthocyanin volume percentages shows improvement in the physical properties of the blend. FTIR analysis shows an interaction between the additive and the matrix due to the exchangeable proton of anthocyanin and the possibility of the interaction with the hydroxyl root of the PVA. The produced improvement and enhancement are studied through the measurement and calculation of optical properties variation. The product provides extra protection for the food from UV and visible radiation. These results were supported by the simulation of the optimized molecular structure and the representation of the electron distribution for the blend molecules, in the separated and compiled states. Additionally, the energy calculation of the neutral molecules indicates the high quality of the component compatibility.

***Keywords:*** *Bandgap, Optical Properties, Packaging of foodstuff, Polymer, UV-vis spectroscopy.*

## 1. Introduction

The motivation behind nourishment packaging is to safeguard the quality and safety of the food contains from the season of production to the time it is utilized by the purchaser. A similarly significant capacity of packaging is to shield the item from physical, chemical, or biological deterioration. Recently, environmental contamination has been one of the greatest threats to humanity. Therefore, the demand for biodegradable foodstuffs packages has been increased [1]. However, one of the innovative methods to get suitable polymeric material is the mixing of various polymers together. This is one of the key techniques to improve the exhibition of a material which permits acknowledgment of novel polymer frameworks that upgrade the performance of the parent polymer at low cost. It is a valuable method for structuring materials with a wide assortment of naturally visible properties. This technique is a consequence of adjusting the structure at the microscopic scale [2]. Polyvinyl alcohol (PVA) is a water-dissolvable polymer with high transparency and extraordinary mechanical and thermal properties. PVA has been broadly utilized in materials, paints, building materials, electronic items, cars, aviation, medication, paper making, printing, packaging, and different ventures.It is regularly mixed with different polymers to improve the properties of the mass material. The polymers, for example, cellulose (and its derivatives) and polyvinylpyrrolidone (PVP) are known to be miscible with PVA, apparently because of hydrogen-bonding between the hydroxyl groups of PVA and fitting collaborating destinations in the mixing partner (carbonyl groups of PVP and optional hydroxyl groups of cellulose) [3-6]. PVP is one of the most generally utilized polymers in medication as a result of its solubility in water and its very low cytotoxicity [6]. Whenever PVA and PVP are combined, the associations among PVA and PVP are relied upon to happen through interchain hydrogen bonding between the carbonyl group of PVP and the hydroxyl group of PVA.Subsequently, it is sensible to expect critical changes in optical properties when two polymers are mixed. Since hydroxyl radical is present in anthocyanin, as well as the exchangeable proton [7], then anthocyanin interaction being very likely to happen with the blend of PVA/PVP at the same solvent (water), as investigated by FTIR analysis. This work aims to enhance radiation shielding of PVA/PVP blend by adding natural pigment (anthocyanin) of a very specific chemical structure as an environmentally friendly packaging. The evaluation of the anthocyanin role and the mineral ions of beet juice in PVA/PVP blend protection against UV-Vis radiation transmission has been achieved through measuring the absorbance of the blend with and without adding of anthocyanin in different volumetric percentage (5, 10, 15, and 20 V/V%), in addition, bandgap calculation. The results comprise a depiction of the simulation of the molecular structures of each component of the blend as well as that of the blend and the electron density distribution. Moreover, a calculation of the considered energy of the neutral molecules was achieved.

## 2. Materials and methods

### 2.1Computational detail of the working mechanism for the eco-container

Through the usage of the density functional theory (DFT) and executing some suitable methods of Gaussian 09 program group, the ground-state Hamiltonian of each molecule has been obtained and its optimized geometry as well. It was helpful to identify the compounds by knowing their computable molecular properties by using simultaneously both the Lee, Yang and Parr correlation functional [8], and Becke's three-parameter exchange functional B3LYP [9]. The construction of an idea about the structure of the eco-food container at the lowest energy invokes to perform a conformational analysis for the molecules. The same basis sets have been used in the performance of the geometry optimization at the B3LYP density functional theory. At the same level of theory, the harmonic vibrational frequencies were computed. Usage of the hybrid functional B3LYP appeared highly successful in calculating the electronic properties like the electronic states and ionization potentials [10].

The DFT divisions the electronic energy as $E= E_v + E_t + E_j + E_{xc}$, where $E_v$, $E_t$, and $E_j$ are the electron-nuclear attraction, electronic kinetic energy, and the electron-electron repulsion terms, respectively. The electron correlation is considered in DFT via the term of the exchange-correlation $E_{xc}$, which involves the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motion of individual electrons, it keeps DFT dominant over the conventional HF procedure [11].

### 2.2Anthocyanin pigment extraction

Anthocyanin pigment was extracted by clearing the red beets with distilled water. Then cut them into slices. After that, the slices have been crushed, squeezed and then filtered completely by mechanical ways.

### 2.3Preparation of PVA/PVP blend and the specimens

The blend of PVA/PVP was prepared by mixing a weight percent ratio of 70% PVA with 30% PVP of the total weight. The used PVA and PVP were of average molecular weight 7000 and 1300,000 respectively from SIGMA, Aldrich. Polymers have been dissolved by using double distilled water. The dissolving ratio of the used polymers to the distilled water volume is 1/20 (g/ml). The diversity of samples depends on the adding volumetric percentage of the beet juice to the solved polymers, the ratios were (5, 10, 15, and 20 V/V%). The components of films specimens are mixed by a magnetic stirrer for about one an hour to get a high homogeneity. The solution casting in glass Petri dishes is the used technique to form the films. Drying of specimens is important to get dehydrated blends; therefore, the samples were left for ten days at about 40°C.

The specimens spectra by FTIR are gained within the wavenumber range of 4000-400 cm-1. The instrument used for this measurement is an FTIR spectrometer (BRUKER). While, the absorbance spectra of the blend films are measured within region 200-800 nm by UV-VIS spectrophotometer 1800 (Shimadzu Corporation).

## 3. Results and discussion

### 3.1 Molecular simulations

Figure 1 shows the symmetrical distribution of positive and negative charges for PVA, PVP, and Anthocyanin pigment, whereas the distribution differs definitively when handling the mixture. Where we notice the increase in the density of electronic distribution and that the charges went to the side of Anthocyanin and this is a sign of the high physical-chemical compatibility of the mixture.

Anthocyanin pigment works to protect the sensitive ingredients within your plastic packaging. And therefore help you reduce field failures and returns, improve weather resistance and outdoor durability, and protect against premature color fading. This confirms the transformation of the bond from the double covalent bond to a single bond for C-O, Which is working on mitigating the harmful effects of UV radiation on the polymers you use in your products, This is consistent with FTIR results and refractive index.

Table 1 represents the results of the ground state total energy and electronic states (LUMO and HOMO), energy gaps and softness of the studied

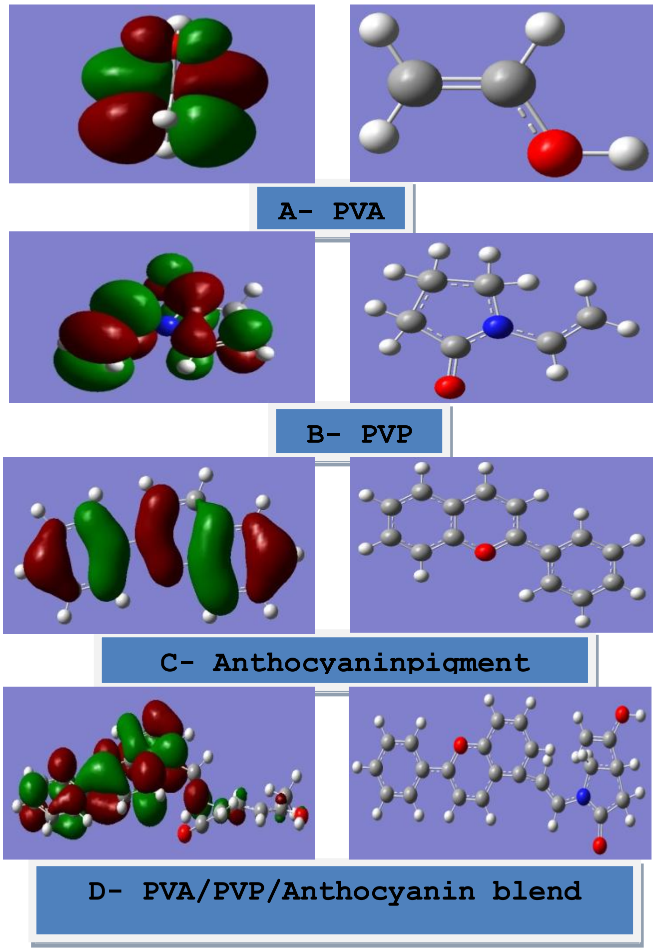


Figure 1: For the considered molecules, (Right): Optimized structures. (Left): HOMO and LUMO shapes.

molecules. It is obvious that from Table 1, the total energy depends on the number of side groups adding to the ring. The total energy is decreasing with the increase of the anthocyanin pigment number as a linear relationship, this indicates that the addition gives the molecule more stability. On the other hand, the total energy is independent of the position of the anthocyanin pigment in the ring, as we see in figure 1. We note that the elasticity of the eco-food containers very high and this is an indication of the increased preservation of the samples confirms this severe decrease in the value of the energy gap for the mixture, Thus, the possibility of making the eco-friendly container with high-efficiency specifications.

Table 1: The calculated energies of study neutral molecules.

| Molecule | Total Energy (a.u) | Electronic States | | Softness (eV) | Bond Length (nm) |
|---|---|---|---|---|---|
| | | HOMO (eV) | LUMO (eV) | | |
| PVA | -153.7594 | -0.2271 | 3.805 | 0.0357 | C-C :14.321<br>C=O :12.358<br>C=N :13.857<br>C-H :11.0131<br>O-H :9.7124 |
| PVP | -363.8709 | -0.2124 | 5.186 | -0.0195 | |
| Anthocyanin pigment | -653.2616 | -0.1469 | 8.684 | -0.0318 | |
| PVA / PVP/ Anthocyanin blend (Eco-Food Container) | -1168.4939 | -0.1397 | 12.079 | -0.0569 | |

### 3.2 Fourier transforms infrared radiation analysis (FTIR analysis)

To identify the changes of the chemical species and the structure of the PVA/PVP blend due to adding Anthocyanin pigment, FTIR analysis has been achieved for all the specimens in figure 2. It is helpful to recall with the wavenumber of some important molecular bonds in each of PVA and PVP as well as that of the blend to show the interaction effect of anthocyanin pigment with the blend. It is found [12] O-H stretching in the PVA at wavenumber ~3444 $cm^{-1}$. In figure 1.a, there is a broadband of IR absorption at 3274.88 $cm^{-1}$. This may refer to dimer O-H are bonded by H-bond.

As this type of bond covers the wavenumber domain of 2800-3400 $cm^{-1}$. By increasing the volumetric percentage of anthocyanin, there is some a little rise in the wavenumber can be noted for the same region reaches to 3275.4 $cm^{-1}$. This may indicate to higher attractive strength belongs to the creation of a higher number of hydrogen-bond, as the increment of anthocyanin gives higher interaction due to its ability to liberate a free proton. The latter plays role of the interactive tool and that interprets the shifting of wavenumber toward greater numbers or in other words stronger bonding. Moreover, the other notable IR absorption is located at 1652.22 $cm^{-1}$ of the PVA/PVP blend, which refers to the C = O stretching. While for pure PVA and PVP the IR absorption of this species equals 1647 $cm^{-1}$ and 1681 $cm^{-1}$ respectively (12,13). In this case, the obvious thing is the decreasing in the bond energy of the carbonyl by the progression of anthocyanin volume fractions. It is expectable, the effect of anthocyanin adding causes changes in the blend structure of higher saturated construction due to the effect of the exchangeable proton which is supplied by anthocyanin pigment [7]. This interaction works on saturating the chemical structure of the polymeric blend. That is why the clear lowering in IR radiation absorption, which can be noted through the changes in the transmittance percent, from about 75% of the PVA/PVP blend to 85% for blend of 20V/V% anthocyanin. The notable point which supports the former deduction is the peak of 1088.39 $cm^{-1}$, which belongs to the C-O stretch species of the PVA/PVP blend. It grows with anthocyanin ratio accretion in the blend from the transmittance ratio of 65% to about 20% as well as the decline in the energy of the bond, as the wavenumber comes up to 1003.38 $cm^{-1}$.

### 3.3UV-vis spectroscopy analysis

The key behavior of the proposedsample is it's withstanding against the physical environment influences, especially the shielding which should be presented for the packaged foodstuff.Subsequently, keeping them for a longer time without degradation. Therefore, the effect of anthocyanin upon the absorbance of the PVA/PVP blend is tested in a wavelength field of 220-800 nm, figure 3.The attenuation ability of the blend

(a)

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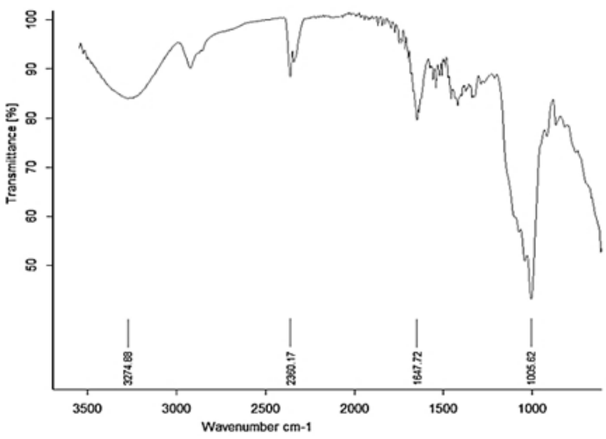


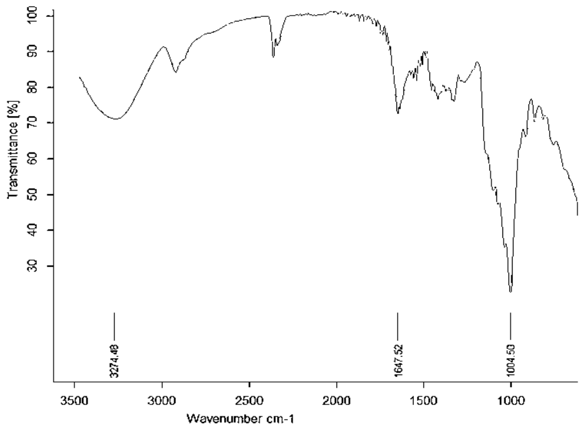


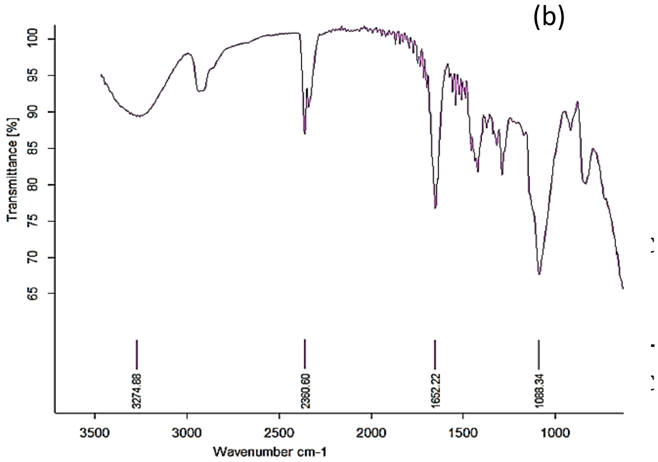


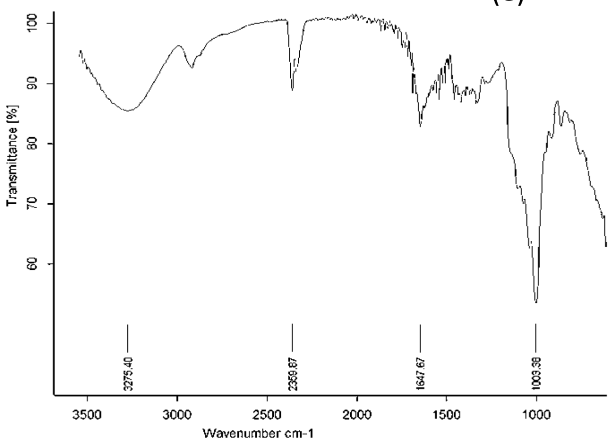


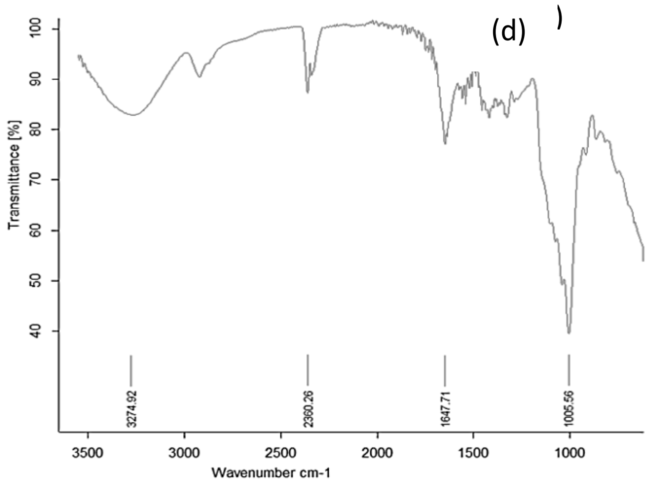


Figure 2:FTIR analysis A of the PVP blend (70:30) and shows the physical interaction of anthocyanin adding of different volumetric percentage 5, 10, 15, 20%V/V in B, C, D, and E respectively with the matrix blend.

The visible light has a lower effect because of its lesser energy. In general, the blend of 20 V/V% anthocyanin adding enhanced the absorbance of the blend for about 200%, see figure 3, along the entire wavelength field. This good protection for the virtue of anthocyanin may belong to its good solubility in the blend and high molecular weight by the presence of phenols in the chemical structure of anthocyanin [7]. Despite anthocyanin has a density (1.35 g/cm$^3$) a little higher than that of each one of PVA (1.19–1.31 g/cm$^3$) and PVP (1.2 g/cm$^3$) (14-16), the beet juice has high mineral content (Ca, Na, Mg, K, P, Fe, Zn, Cu, Ni) [17]. This thing gives it higher absorbance and meet with results of others [18]. There is a characteristic shoulder can be observed at a wavelength of 274 nm, due to the transition of $n \to \pi^*$, which belongs to the excitation of carbonyl group of $C = O$ [19]. This shoulder disappears gradually with increasing anthocyanin volume percent. It refers to the role of anthocyanin in saturating the functional group of PVA/PVP blend as observed in FTIR analysis and the simulation. In general, this measurement gives an indication about the potential changes in the energy of molecular orbital and searches, the possible transitions which may happen for the electrons.

Through electron transition from band to band, valence band to the conduction band, the value and nature of the optical bandgap can be described by the equation [2], shows the relationship between the absorption coefficient ($\alpha$) and the incident photon energy ($h\nu$)[20]:

$$(\alpha h\nu)^n = A_n\left(h\nu - E_g\right) \ldots\ldots\ldots\ldots\ldots [2]$$

Where $A_n$ is the constant, $E_g$ is the material bandgap, the exponent $n$ depends on the type of transition. $n = \frac{1}{2}, \frac{3}{2}$ For allowed and forbidden direct transition respectively. However, plotting the variation on $(\alpha h\nu)^{1/2}$, versus photon energy $h\nu$ the band gap $E_g$ can be found in the PVA/PVP blend films as $\alpha = 0$, figure 4. The figure shows an inverse proportional between the energy gap and the volumetric percent of beet juice adding. This can be attributed to thecreation of additional energy levels in between the valence and conductive bands. Furthermore, increasing the number of electrons lower the bandgap [18].

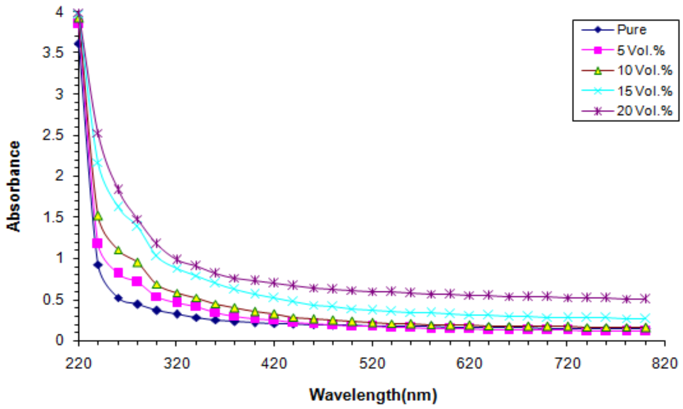


Figure 3: the absorbance versus wavelength for PVA/PVP blend of different adding of anthocyanin volumetric percentages.

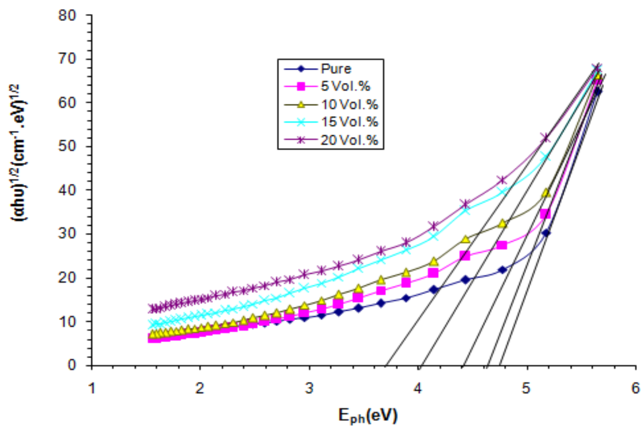


Figure 4: band gap decreasing for PVA/PVP blend with increasing the volumetric percentage of beet juice adding for the allowed direct transition.

Nonetheless, the induced polarization type of UV-Vis region is caused by electronic polarizability. In another word, the induced polarization works on deformation the electronic density of an atom. This effect depends on the type of atom and the frequency of the applied electric field (20,21).

## 4. Conclusion

By conducting an analysis of FTIR for the considered PVA/PVP blend of ratio (70:30). In addition to the samples of the same blend with adding a different volumetric percent of beet juice (5, 10, 15, and 20%). It is found a progressive physical interaction happens between the bio-additive and the matrix blend. The most notable result of this interaction is a strong binding and matching created by the anthocyanin and the blend. Likewise, there was a tendency to produce a blend of higher saturation proportional to the volumetric percentage of the beet juice. The results of the UV-Vis spectrum and its analyses show rising the absorbance of the PVA/PVP blend which is proportional to the volumetric percentage of the additive. The UV spectral region is the highest interaction due to the decreasing of the bandgap, which keeps it more consistent with the energy of the incident photon at the UV region. At a lower level of interaction, there is an attenuation for the longer wavelength of visible light which rises by increasing the adding of the beet juice. This effect occurs at higher values by increasing the ratio of beet juice due to more structural deformation, which causes lowering the bandgap. The simulation description of the blend and its components, as well as the calculation of their energy, gives the matching interpretation and support to the results of the practical part.Based on the above, the suggested bio-additive of beet juice offers support to the chemical structure of the PVA/PVP blend and rising its optical properties. Enhancing the radiation shielding of the blend to qualify it to get high quality in food protection.

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