Molecular properties of polyvinyl alcohol/ sodium alginate composite

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ABSTRACT

Molecular and bimolecular properties are important factors to judge the functionality of polymer/biopolymer composites. Accordingly, molecular modeling is conducted to study the electronic properties of Polyvinyl Alcohol (PVA); Sodium Alginate (SA) as well as their composites. Accordingly, Density functional theory (DFT) at B3LYB level using 6-31G (d, p) basis set is utilized to study the model structures. Total dipole moment (TDM), HOMO/LUMO energy gap, electrostatic potential (ESP) are calculated at B3LYB level for all studied structures. The results of TDM, HOMO/LUMO energy gap and ESP indicated that the TDM increased, HOMO/LUMO energy gap decreased and electro-negativity increased for the structures under study. Thermal parameters at PM6 are calculated including final heat of formation; free energy; entropy; enthalpy and heat capacity as a function of temperature. Thermal parameters show a variation with changing the site of interaction which indicated that the coordination of PVA/SA is an important factor for describing PVA/SA composite.

Keywords: PVA; SA; DFT; TDM and HOMO/LUMO band energy.

1. INTRODUCTION

Sodium alginate is a linear biopolymers belonging to polysaccharide family its chemical structure is (NaC6H10O6) and termed SA [1]. It is also described as derivative of alginic acid comprised of 1,4-β-d-mannuronic (M) and α-l-guluronic (G) acids, its molecular structure show many carboxyl groups [2-3]. SA has common features dedicates it for different applications. It is abundant, water-soluble, renewable, and nontoxic, accordingly it is also biodegradable and biocompatible. Although it is biological candidate for its important features, SA is also mechanically poor, which in turn allows bacteria to degrade it especially in waste water and extreme environmental conditions [4-7].

SA could be subjected to modification chemically or physically to improve its physicochemical properties and subsequently its biological activity. The modified SA is forming so called SA derivatives, which are dedicating for different types of application based on the type of modifications. [8-9]. Meanwhile, polyvinyl alcohol is made from the hydrolysis of polyvinyl acetate, it is termed as PVA, and it is water soluble [10]. In the last century it is worldwide applied in several industrial applications [11]. Rather than natural polymers, synthetic polymers such as PVA are non-renewable and non-biodegradable

2. MATERIALS AND METHODS

2.1. Calculation details.

Model molecules representing PVA, SA and PVA/SA composite are built up. Models are subjected to calculation using Gaussian 09 software [29] at Spectroscopy Department, National Research Centre, Egypt. Models are optimized with Density functional theory (DFT) at B3LYP level [30-32], with 6-31G (d, p) basis set. Physical quantities such as total dipole moment, HOMO/LUMO band gap energy and electrostatic potential (ESP) are computed at B3LYB level for a set of considered structures under study. Thermal parameters at PM6 are calculated including final heat of formation; free energy; entropy; enthalpy and heat capacity as a function of temperature. Thermal parameters show a variation with changing the site of interaction which indicated that the coordination of PVA/SA is an important factor for describing PVA/SA composite.

3. RESULTS

3.1. Building model molecules. Studying the electronic properties of PVA and SA was done through a number of stages. The first stage is the creation of the model molecules which represent PVA, Saand PVA interacted with SA. Three units of PVA (3 PVA or trimer PVA) and two of SA (2 SA or dimer SA) are considered in the present work. Figure 1 shows the supposed structures of PVA
and SA. The interaction between the functional groups of PVA and that of SA is supposed to be weak interaction. However, there are two possible ways of interaction. PVA in its trimer form contains three hydroxyl groups. Then SA can interact with PVA at the different positions of OH group. So that, the first way of interaction, is that each unit of dimer SA can interact with PVA separately at different positions. While, the second way is that, the model molecule representing dimer SA, as a bulk, is interacted with PVA throughout the hydroxyl groups of PVA which, are connected to carbon atom number 5, 10 and 21 respectively as presented in figure 2. All studied structures are subjected to single point energy calculations.

3.2. TDM and HOMO/LUMO band gap energy.

Based on the literature, the change in electronic properties of polymeric materials can be studied in terms of total dipole moment (TDM) and HOMO/LUMO band gap energy as they can predict the stability and reactivity of the molecular structures [34]. TDM as Debye and HOMO/LUMO band gap energy $\Delta E$ as eV are calculated at B3LYP/6-311g (d, p).

As depicted in table 1 that trimer PVA (3PVA) and dimer SA (2 SA) possess a TDM of 4.2172 and 9.2543 Debye respectively. However, the calculated HOMO/LUMO band gap energies of 3PVA and 2 SA are 7.4478 and 2.5293 eV respectively. As a result of adding 2SA to the proposed structure of PVA, it was observed that both TDM and HOMO/LUMO band gap energies of trimer PVA and dimer SA suffers strong changes in their values. Where, for the first way of interaction, the TDM was increased to 20.6941 and 24.6199 Debye for Term ISA - 3PVA- Term ISA and Term ISA - 3PVA- Mid ISA respectively. However, HOMO/LUMO band gap energy was decreased to 0.9559 and 0.5706 eV for the same sequence. The distribution of HOMO/LUMO band gap energies were presented in figure 3 for 3PVA, 2SA, Term ISA -3PVA- Term ISA and Term ISA-3PVA- Mid ISA.

3.2.1. TDM and HOMO/LUMO band gap energy for different structures

3.2.2. HOMO/LUMO band gap energy for different structures

3.2.3. Calculated ESP for different structures

Figure 3. HOMO/LUMO band gap energy calculated at B3LYP/(6-311) G (d, p) for: a) 3PVA; b) 2SA; c) 3PVA - Term ISA - Term ISA and d) 3PVA - Term ISA - Mid 1Na.

Figure 4. HOMO/LUMO band gap energy calculated at B3LYP/(6-311) G (d, p) for: a) 3PVA - (C5) 2SA; b) 3PVA - (C10) 2SA and c) 3PVA - (C21) 2SA.

Figure 5. Calculated ESP at B3LYP/(6-311) G (d, p) as contour action for: a) 3PVA; b) 2SA; c) 3PVA - Term ISA - Term ISA and d) 3PVA - Term ISA - Mid 1Na.
Figure 6. Calculated ESP at B3LYP/ (6-311) G (d, p) as contour action for: a) 3PVA- (C5) 2SA; b) 3PVA- (C10) 2SA and c) 3PVA- (C21) 2SA.

On the other hand, for the second possibility of interaction as presented in table 2, TDM increased slightly to 8.0586, 12.2080 and 7.2146 Debye for 3PVA- (C5) 2SA, 3PVA- (C10) 2SA and 3PVA- (C21) 2SA respectively. Meanwhile, HOMO/LUMO band gap energy was changed to 2.9772, 0.2908 and 2.1511 eV (see table 2) for 3PVA- (C5) 2SA, 3PVA- (C10) 2SA and 3PVA- (C21) 2SA respectively. Figure 4 shows the calculated band gap energy for 3PVA- (C5) 2SA, 3PVA- (C10) 2SA and 3PVA- (C21) 2SA respectively.

3.3. Electrostatic potential (ESP).

Electrostatic potentials (ESPs) are calculated also for all structures at B3LYP/ (6-311) G (d, p) level. The reactivity of polymeric materials can be estimated by studying their ESP. Figures 5 and 6 present the calculated ESPs for all model molecules as contour action. It is stated that, the reactivity of molecular structures can be studied by following a color map ranging from high to low values as follow: red > orange > yellow > green > blue. This sequence of colors refers to the distribution of charges within the structures. The red color, which is distributed around the molecules, refers to that electro-negativity is high and also the reactivity of those molecules increased. However, the neutral charges and positive ones can be noticed with yellow and blue colors respectively [35-37]. So, as shown in the figures, that the PVA reactivity was increased by interaction with SA.

The changes of the values of TDM and that of HOMO/LUMO band gaps, together with ESP results, refers to the strong interaction that takes place between the proposed structures of PVA and SA. This can be attributed to the presence of hydroxyl groups in PVA and SA structures.

Figure 7. Heat of formation as a function of temperature for a) 3 PVA, b) 2 SA c) term SA- 3PVA- mid SA d) term SA- 3 PVA- term SA e) 3 PVA - 2 SA - C5 f) 3 PVA - 2 SA - C10 and g) 3 PVA -2 SA -C21 calculated at PM6 level of theory.

3.4. Calculated thermal parameters.

Thermal parameters of polymeric materials and their composites are very important in order to know their possible applications and functionality. In this work there are different ways of composite interaction sites so that some parameters will be calculated.

Figure 8. Free energy as a function of temperature for a) 3 PVA, b) 2 SA c) term SA- 3PVA- mid SA d) term SA- 3 PVA- term SA e) 3 PVA - 2 SA - C5 f) 3 PVA - 2 SA - C10 and g) 3 PVA -2 SA -C21 calculated at PM6 level of theory.

Figure 9. Entropy as a function of temperature for a) 3 PVA, b) 2 SA c) term SA- 3PVA- mid SA d) term SA- 3 PVA- term SA e) 3 PVA - 2 SA - C5 f) 3 PVA - 2 SA - C10 and g) 3 PVA -2 SA -C21 calculated at PM6 level of theory.
PM6 semi-empirical quantum mechanical method is utilized to calculate thermal parameters namely final heat of formation; free energy; entropy; enthalpy and heat capacity. These thermal terms could be defined simply as in the following [27-28]. The heat of formation is the amount of heat released or absorbed during the formation of certain pure substance from its constituents elements at constant pressure. Free energy could be defined as the energy-like property it is meaning that its magnitude depends on the amount of a substance in a given thermodynamic state.

Entropy is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Because work is obtained from ordered molecular motion, the amount of entropy is also a measure of the molecular disorder, or randomness, of a system. When certain substance changes at constant pressure, Entalphy tells how much heat and work were added or removed from this substance. Finally, the heat capacity is defined as the amount of heat required to change temperature of the substance by one degree. The studied thermal parameters as function of temperature in the range of 200 to 500 K are described as indicated in figures 7 to 11.

Figure 7 presents the PM6 calculated heat of formation as a function of temperature for all the studied structures and that 3PVA possesses the highest values of free energy. Also, like the heat of formation, the free energy following the same sequence as 3 PVA> 2 SA> 3 PVA- 2 SA- (C5 = C10 = C21)> (term SA- 3 PVA- term SA = term SA- 3PVA- mid SA) in its values.

Figure 10. Enthalpy as a function of temperature for a) 3 PVA, b) 2 SA c) term SA- 3PVA- mid SA d) term SA- 3 PVA- term SA e) 3 PVA - 2 SA - C5 f) 3 PVA - 2 SA - C10 and g) 3 PVA -2 SA - C21 calculated at PM6 level of theory.

Figure 11. Heat capacity as a function of temperature for a) 3 PVA, b) 2 SA c) term SA- 3PVA- mid SA d) term SA- 3 PVA- term SA e) 3 PVA - 2 SA - C5 f) 3 PVA - 2 SA - C10 and g) 3 PVA -2 SA - C21 calculated at PM6 level of theory.

Moreover, the entropy as Cal/K/Mole was also calculated for the proposed structures of trimmer PVA, dimer SA, term 1SA-3PVA- term 1SA, term 1SA- 3PVA- mid 1SA, 3PVA- (C5) 2 SA, 3PVA- (C10) 2SA and 3PVA- (C21) 2SA.

Table 1. B3LYP/6-311G (d,p) computed total dipole moment (TDM) as Debye; HOMO-LUMO band gap energies (ΔE) as eV for 3 PVA; 2 SA; 3PVA- Term 1SA -Term 1SA and 3PVA- Term 1SA -Mid 1Na.

<table>
<thead>
<tr>
<th>Structure</th>
<th>TDM</th>
<th>ΔE</th>
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<tbody>
<tr>
<td>3PVA</td>
<td>4.2172</td>
<td>7.4478</td>
</tr>
<tr>
<td>2 SA</td>
<td>9.2543</td>
<td>7.5293</td>
</tr>
<tr>
<td>Term 1SA - 3PVA - Term 1SA</td>
<td>20.6941</td>
<td>0.9559</td>
</tr>
<tr>
<td>Term 1SA - 3PVA - Mid. 1SA</td>
<td>24.6199</td>
<td>0.5706</td>
</tr>
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Table 2. B3LYP/6-311G (d,p) computed total dipole moment (TDM) as Debye; HOMO-LUMO band gap energies (ΔE) as eV for 3PVA- (C5) 2SA; 3PVA- (C10) 2SA and 3PVA- (C21) 2SA.

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results of heat of formation, free energy and entropy agree with the results of calculated TDM, HOMO/LUMO band gap and ESP. Additionally, figure 10 and figure 11 represents the variation of both enthalsy as (Cal/Mole) and the heat capacity as (Cal/Mole/K) with temperature for all the studied structures. The same behavior of entropy was observed in figures 10 and 11 for enthalsy and heat capacity. Where the highest values of both quantities belong to the model molecule representing Term 1SA - 3PVA- Mid. 1SA and Term 1SA - 3PVA- Term 1SA.

The overall thermal parameters show a variation in its studied values as the site of interaction is changing so that the coordination of PVA/SA is an important factor for describing PVA/SA composite

4. CONCLUSIONS

Studying the electronic properties of PVA and SA based on DFT principals was carried out. The total dipole moment, HOMO/LUMO band gap energy and electrostatic potential were studied. As a result of the interaction of PVA with SA, it was found that generally, TDM of PVA and that of SA was increased. Where, for the first probability of interaction, TDM was increased to 24.6199 Debye. Meanwhile, the band gap energy was decreased to 0.5706eV as a result of interaction. However, for the second probability of interaction, the highest TDM was 12.2080 Debye.

5. REFERENCES


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