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Study of the Electronic Properties of (Cellulose Acetate/x-MoO_3)

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Abstract
Chromism-based optical filters is an interested field of research, due to their application as electrochromic materials. Typically, electrochromic transition metal oxides such as MoO_3 and are utilized in applications such as smart windows and electrochromic devices (ECD). Molecular modeling based on density functional theory (DFT) at B3LYP/ LanL2DZ was utilized to study the effect of addition of different concentration of MoO_3 on electronic properties of Cellulose Acetate CA. CA interacted with MoO_3 throughout the hydroxyl group (OH). Total dipole moment (TDM), HOMO-LUMO bandgap energy, and molecular electrostatic potential (MESP) are calculated for the studied structures. TDM found to be increased from 12.2694 for pure CA to 33.6527 for CA -3 MoO_3 also band gap energy decreases from0.6457 to 0.1439. MESP shows that the reactivity is increased with increasing the number of MoO_3 units attached to polymer. Obtained results confirmed that the proposed structure of CA-X-MoO_3 could be used as an electrochromic material.
Keywords: Cellulose acetate; MoO_3-NPs; DFT; HOMO-LUMO

1. Introduction:
Cellulose as well as its derivatives are polysaccharides present much properties in the last few years which make them interesting for use in many applications either in technology or in science [1-3]. Cellulose acetate (CA) made by treating cellulose. It offers some extra characteristics such as its resistance mechanically and thermally, dimensional and thermal stability and low cost [4]. support industries for plastics, fibers, photographic films as well as pharmaceuticals coating all are application for CA [5,6]. Incorporating inorganic materials into polymers have been experimented so as to enhance polymers properties [4]. Transition metal oxide Blending polymers have been used for improving polymer properties which enable polymer to enter many electronics, optics, electrical and photonics fields [7-11]. Lubricants, Catalysts, sensors, display devices, smart windows, battery electrodes are some applications of the enhanced material [12–16]. Molybdenum trioxide is a transition metal oxide have many characteristic gap energy of value 3.15 eV. It is more abundant other than all molybdenum compounds. Oxidation state of Molybdenum is +6 in Molybdenum trioxide compound [17]. MoO3 has a great field of applications such as using in fabricating gas sensors, smart windows, electrochromic, photochromic, imaging devices, heterogeneous catalysis, electro catalysis, field - effect transistors, electrodes of rechargeable batteries, and supported catalysts [18, 19]. MoO3 has also a broad range of usage as using as an adhesive as well as it used as an additive to industrial material such like steel and corrosion resistant alloys [20].

Chemical, physical and electronic properties of many systems especially those depend on nanomaterials can be studied through the using of molecular modeling with different levels and theories [21-22]. Either synthetic Polymers and/or natural could be studied using molecular modeling; some important parameters could be investigated, such like total dipole moment (TDM), HOMO-LUMO bandgap energy, and molecular electrostatic potential (MESP) [23-24]. Those physical characteristic reflecting the reactivity of structure under investigating [25-28].

The goal of this research is to study the interactions between the Cellulose Acetate (CA)/Molybdenum trioxide(MoO3). The polymer model interacted with MoO3 throughout the hydroxyl group (OH) located at the terminal. DFT at B3LYP/ LanL2DZ was carried out in order to investigate physical properties such as HOMO-LUMO band gap energy, TDM and MESP for the structures under studying.

Materials and Methods

The electronic properties of CA, together with its stability, are studied theoretically using quantum mechanics rules using DFT. DFT was implemented on Gaussian 09 which utilizes a basis set of Gaussian type orbital functions [29]. The Becke-three parameters-Lee-Yang-Parr hybrid functional (B3LYP) [29-31] with basis set LanL2DZ is employed in the calculations at Spectroscopy Department, National Research Centre. The effect of MoO3 presence on the physical properties of CA is presented in terms of TDM, bandgap energy (ΔE), and MESP.

3. Results and Discussion

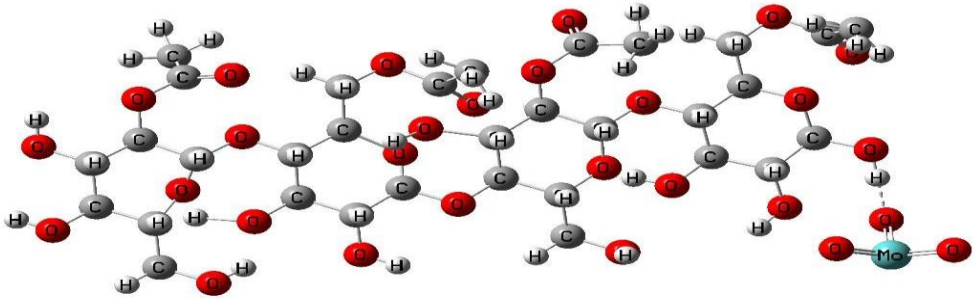
3.1. Building Model Molecules

Before the attachment of the studied metal oxide blend onto the CA surface, the polymer model is first explored. For the model molecule representing CA, three units of CA is proposed to interact with X-MoO3 where x equal 1, 2 and 3 units.

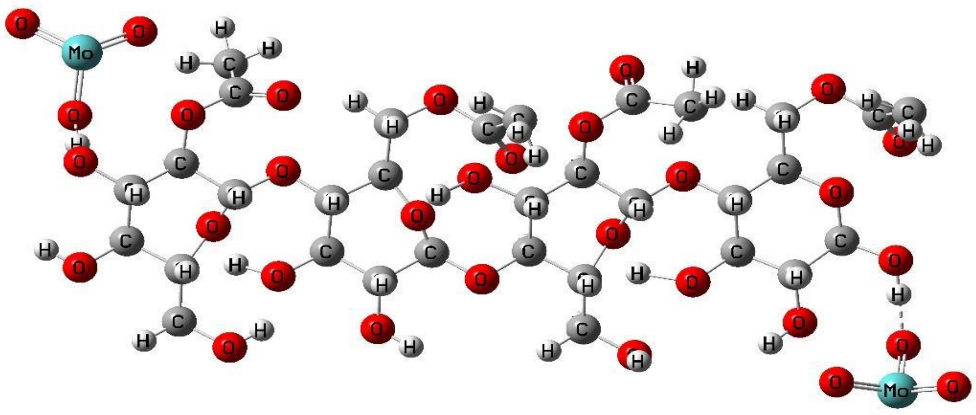
As cellulose acetate is a polymer which is rich with hydroxyl group, molybdenum trioxide metal oxide can interact with cellulose acetate through this active group [32]. Optical and electrical properties of cellulose acetate can be improved via interacting with molybdenum trioxide MoO3. Figure (1) presents the building model molecules representing SPEs based on cellulose acetate and cellulose acetate/X MoO3 where x equal 1, 2 and 3 units of MoO_3. Cellulose acetate with tetramer cellulose acetate blended with different concentration of MoO3 are optimized at B3LYP/ LanL2DZ.

(a)

(b)



(c)



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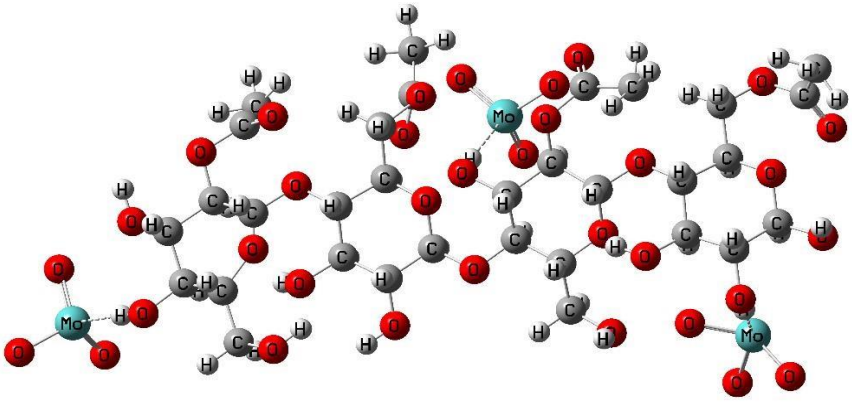


(e)

Figure (1). Model molecules representing a) tetramer cellulose acetate b) MoO3 molecule, c) tetramer cellulose acetate/1 MoO3, d) tetramer cellulose acetate/2 MoO3 and e) and tetramer cellulose acetate/3 MoO3.

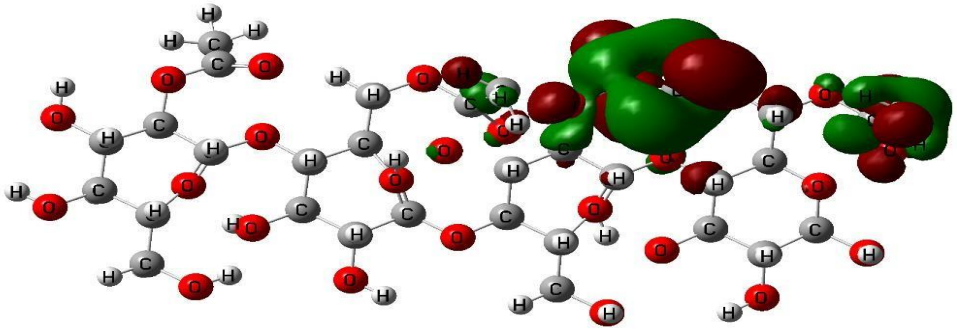
3.2. Electronic properties.

Both TDM and band gap energy ΔE are calculated in order to study the changes that occurred in the electronic properties of CA model molecule and any other materials as a result of the chemical modifications in its structures. For model molecules, TDM as Debye and HOMO/LUMO band gap energy ΔE as eV are computed at B3LYP/LanL2DZ. As shown in Table (1) that cellulose acetate TDM is changed, due to the addition of MoO3, from 12.2694 Debye pure cellulose acetate to 18,7255, 26.0018 and 33.6527 Debye for the interactions of (1, 2, 3 units) of MoO_3. Meanwhile, as depicted in Table (1), the band gap energy of cellulose acetate was changed as a result of blending of MoO3. Where, it is changed from 0.6457 eV for pure cellulose acetate to 0.2329, 0.2029 and 0.1439 eV for the interactions of (1, 2, 3 units) of MoO3.

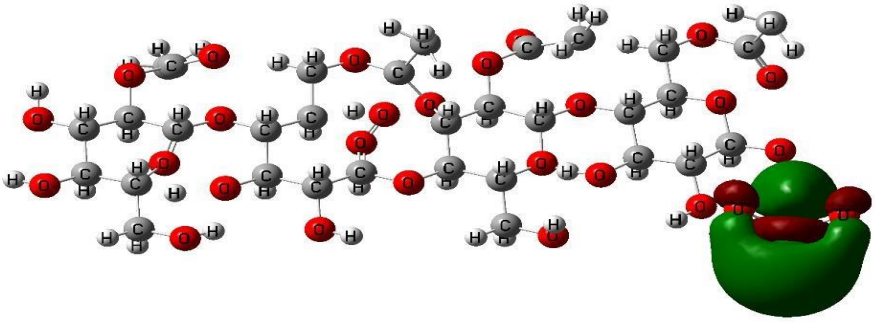
Figure (2) shows the changes occurred in the distribution of both HOMO and LUMO due to blending cellulose acetate with MoO3 different concentration.

Table (4-6). Computed total dipole moment (TDM) as Debye; HOMO-LUMO band gap energies(ΔE) as eV for: tetramer cellulose acetate/X MoO3 where X refers to the number of MoO3 molecule units and equals 1, 2 and 3.

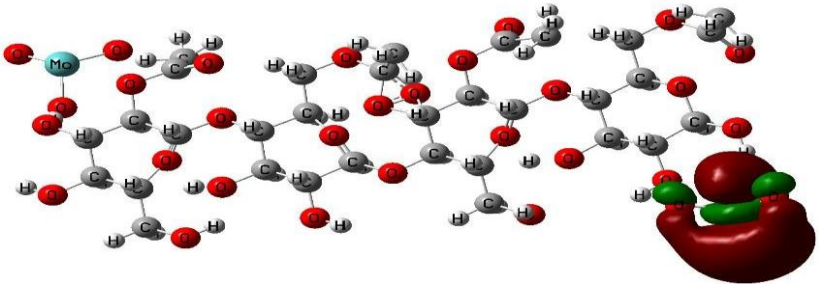
Structure	TDM	ΔE
4CA	12.2694	0.6457
4CA/1MoO3	18.7255	0.2329
4CA/2MoO3	26.0018	0.2029
4CA/3MoO3	33.6527	0.1439



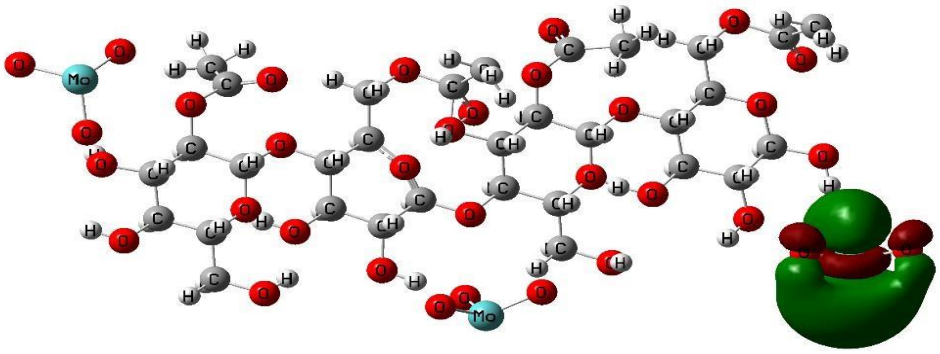
(a)



(b)



(c)



(d)

Figure (4-33). HOMO/LUMO band gap energy calculated at B3LYP/LanL2DZ for: a) tetramer cellulose acetate, b) tetramer cellulose acetate/1 MoO3, c) tetramer cellulose acetate/2 MoO3 and d) and tetramer cellulose acetate/3 MoO3.

It is observed that the value of TDM is increased upon linkage one MoO3 units to cellulose acetate and increased by increasing the concentration of MoO3. The band gap energy is also observed to decrease upon linkage one MoO3 units to cellulose acetate and decreases by increasing by increasing the concentration of MoO3. The obtained results indicate that the reactivity of cellulose acetate is increased by increasing MoO3 content to cellulose acetate.

3.3. Molecular electrostatic potential (MESP):

Additionally, electrostatic potentials (ESPs) are determined also for all models under study at B3LYP/LanL2DZ level. ESP study also can be used in predicting the behavior of polymeric materials (specially the reactivity and stability) due to blending of other materials, salts or acids. Figures (4-34) represents the calculated ESPs, for all model molecules, designed as contour action. It is stated that the reactivity can be studied through following a color map ranging from high to low values as presented: red > orange > yellow > green > blue. This sequence of colors demonstrates the distribution of charges within the studied model molecules. The regions in the molecules which exhibits high electro-negativity are mapped using red color which refers to the high reactivity of that molecule. However, the neutral charges and positive ones can be noticed with yellow and blue colors. So, as shown in the Figures that the cellulose acetate reactivity is observed to increase with increasing the concentration of MoO_3.

The changes of the values of TDM and that of HOMO/LUMO band gaps, together with ESP results, refer to a strong complexation between cellulose acetate and MoO_3. This can be due to the existence of hydroxyl groups in cellulose acetate structure which enables MoO_3 interaction with cellulose acetate. The theoretical obtained results are compatible with the experimental results.

4. Conclusion

Molecular modeling as a computational tool could be useful tool to understand the mechanism of interaction of the studied polymer blend as an important step toward investigation of electronic properties of polymers. Such electronic properties are the key role for investigation of new materials for different applications. It is observed that the value of TDM is increased by increasing the concentration of MoO_3. The band gap energy is also observed to decrease by increasing by increasing the concentration of MoO3. The obtained results indicate that the reactivity of cellulose acetate is increased by increasing MoO3 content to cellulose acetate. It is observed that the changes of the values of TDM and that of HOMO/LUMO band gaps, together with ESP results, refer to a strong complexation between cellulose acetate and MoO3.

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