Theoretical study of structural and electronic properties of poly(vinyl chloride) nanotube inclusions

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ABSTRACT: The structural and electronic properties of inclusion or interconnection between NT and PVC were studied by quantum semieipirical approximation method using (PM3) self-consistent field molecular orbital method. The total structural energy, HOMO level energy, LUMO level energy, band gap (\( E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \)), and dipole moment of the compounds were calculated. Increasing the distance between NT and PVC led to decline the total energy difference which led to better interconnection between NT and PVC and vice versa when the distant is decreased. Therefore the more stable compound is \( f \). The best electronic energies were obtained at the structures 3c and 3b in the first distance respectively. The dipole moments for all structures have the following trend: \( b > d > c > e > f > a > g \).

Keywords: nanotube; PVC; PM3; HOMO; LUMO; dipole moment

Introduction

Poly(vinyl chloride) (PVC) is an important commercial thermoplastic, which is widely used as pipes, electric cables, building materials and other civilian products [1, 2]. PVC is used in many domestic and industrial applications in different forms such as composites, copolymers, and blends [3]. Low thermal stability, poor processability and brittleness are the main reasons behind the limitation of using PVC in some applications [4]. Polymer nanocomposites have unique properties over normal composites (short and long fibers) such as nanoparticle inclusion effect on the polymer brush configuration and free energies which depends strongly on inclusion shape, size, and inclusion location in

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PVC is an important for the occurrence of structural defects [6]. PVC has many important applications such as employed in the field of sensors based on their membranes [7], and can be used as a matrix material for low-temperature photochemical studies [8]. Another study indicated that the conversion is depending on defect structures in radical suspension polymerization of vinyl chloride, which proved that the polymer-rich phase becomes extremely dense, making the diffusion coefficient of the monomer much lower than that in the monomer-rich phase, which led to substantial reduction in the propagation rate, thereby allowing the chain-transfer processes to compete more effectively [9]. The physical properties and the morphology of PVC resins are depending on their microstructures, which are function of the distributions and concentrations of internal double bonds, branches, and the relative configurations of the stereogenic centers [10]. The Effect of different feeding methods of the monomers and initiators on the morphology properties of core-shell particles such as the deformation of PVC/MBS2 blend led to absorb massive impact energy, and MBS2 led to enhance the toughness properties of PVC matrix efficiently [11]. The molecular weight and its relationship to the internal double bonds in PVC at various monomer conversions have been studied. The concentration of these defects structure per chain was largely constant as a function of molecular weight [12].

During the recent period, there are number of studies on PVC polymer like nanoclay-fillers [13, 14], dispersing of nano-sized silica (SiO2) in PVC-blend-based polymer electrolytes which may be a potential candidate for all solid lithium rechargeable batteries [15], to improve the thermal and mechanical properties of PVC. Specific interfacial interactions between the π-electronic system of carbon nanotube CNT and the polymer functional groups (CNT based polyacrylonitrile (PAN) composites), which shown to be effective when stable uniform dispersions of carbon nanotubes were obtained with the aid of surfactants having multiple unsaturated carbon bonds, as a result of the unique set of properties of (CNT) [16]. Glass transition temperature and melting temperature are an increase for the composites of multiwalled carbon nanotube (MWCNT)/PVC with respect to pure PVC, and the modulus of the MWCNT/PVC composites increased while there was a reduction in their tensile strength, pointing out a decrease in polymer toughness [17]. In the same context, for the segregated system PVC/MWNT, it was found that the conductivity and magnetic properties of the system are depending on concentration of the nanotubes in wide temperature and frequency ranges [18]. The use of MWNT-PVC composite coated wire electrode allows the electrochemical detection by potentiometric method [19]. Increasing in glass transition temperature (Tg) of PVC was observed with increasing in the contain of MWCNT [20].
The characterization of defects in (PVC) was investigated theoretical–experimental by combining quantum chemical calculations (DFT) and NMR chemical shifts measurements [10]. However, nanoinclusions can be chosen as insulators to lower the thermal conductivity and scatter carriers which reduce the electrical conductivity [21]. One of the important theoretical researches on the nano inclusions is molecular dynamics (MD) simulations of effects of different kinds of nano inclusions (bucky-ball, graphene, single-walled-carbon-nanotube (SWNT), X-shaped SWNT junction and Y-shaped SWNT junction) into polyethylene (PE) matrices on structural and physical properties of PE matrices [22].

The main objective of this study is to investigate the physical properties of different types of nanotube conformations with PVC using computational quantum methods, by semiempricil PM3 (Parameterized Austin Model 3).

**Material and Methods**

*Computational procedure*

Semiempirical methods can be defined by the set of approximations used and by the values of the parameters [23]. Calculations on the electronic and structural properties of our model were carried out using (PM3) self-consistent field molecular orbital method [24-26]. All calculations were performed using the Gaussian 09 package [27]. The electronic properties such as highest occupied molecular orbital ($E_{HOMO}$) energy, lowest unoccupied molecular orbital ($E_{LUMO}$) energy, and the energy gap ($E_{g} = E_{LUMO} - E_{HOMO}$), the dipole moment ($\mu$) were calculated.

**Results and Discussion**

*Structure determination*

Our model consists of five optimized units of Carbon Nanotube (NT) with length (11.065 Å) and radius (8.135 Å) as in Figure 1 and five optimized units (monomer) of the PVC as in Figure 2. The electronic and structural properties were calculated without any geometry constraints for full geometry optimizations. First structure was a chain of PVC in the middle of NT by distances (1.918, 2.416, 2.915, 3.414, and 3.913 Å) between PVC chain and NT as shown in Figure 3a with an increase of 0.5 Å after each distance. The second structure was a PVC chain parallel to NT with distances (1.419, 1.919, 2.419, 2.919 and 3.419 Å respectively) between PVC chain and NT as can be seen in Figure 3b with an increase of 0.5 Å after each distance. With regard to structures 3c, 3d and 3e, the process and the distance between NT and PVC chain are the same in the second structure, except increasing three, four, and five chains of PVC related to the NT as shown in Figures 3c, 3d and 3e respectively.
Structures, \(3f\) and \(3g\), the chain of PVC are parallel to the ends of NT with distances (2.580, 3.080, 3.533, 3.998, and 4.470\(\AA\)) between the PVC chain and NT as demonstrated in Figure 3f and 3g respectively.

![Figure 1: Nanotube structure (NT)](image1)

![Figure 2: PVC structure](image2)

**Structural Energy**

The results of the total structural energy as a function of distance for all studied structures are shown in the Figure 4. The structural energy in the form of energy difference between the total energy of the system (NT-PVC), total energy of (NT) and total energy of (PVC) was calculated using Equation 1.

\[
\Delta E_{\text{Total}} = (E_{\text{NT-PVC}}) - (E_{\text{NT}}) - (E_{\text{PVC}}) \quad (1)
\]

According to the calculations, the highest energy differences 4.280, and 4.057 a.u were obtained of \(3d\) and \(3e\) structures respectively in the distance 1.419\(\AA\). The energy difference for \(3c, 3b, 3a, 3g,\) and \(3f\) structures decrease in turn to reach the lowest value of 0.0537 a.u was found in the structure \(3f\) at distance 4.470\(\AA\). Generally, energy difference decreases connected with increasing in the distance NT-PVC and contradictory result was found with decreases the distance. As a conclusion, the large energy difference led to more stable structure. However, small energy differences produce more facility of NT-PVC formation.
Figure 3. (a) PVC in the middle of nanotube NT with different distances (D), (b) 1 PVC chain parallel to NT, (c) 2 PVC chain parallel to NT, (d) 3 PVC chain parallel to NT, (e) 4 PVC chain parallel to NT, (f) PVC is parallel to the ends of NT, (g) two chain of PVC are parallel to the ends of NT.
Figure 4. Total energy as a function of distance of NT-PVC inclusions

Electronic Properties

The results of electronic energies of compounds are shown in the Figure 5. The values of occupied molecular orbital (E\textsubscript{HOMO}) and unoccupied molecular orbital (E\textsubscript{LUMO}) were discussed with regardless to their sing. The result indicated that the highest E\textsubscript{HOMO} energy has the highest value of -7.850 eV at 3g-4 (fourth distance) and the lowest value of -6.437 eV at 3d-1 (first distance), while the lowest E\textsubscript{LUMO} energy has the highest value of -3.752 eV at 4g-4 (fourth distance) and the lowest value of -1.387 eV at 3e-1 (first distance). The energy gap (E\textsubscript{g} = E\textsubscript{LUMO} − E\textsubscript{HOMO}) has the highest value of 5.325 eV at 3e-1 (first distance) and the highest value of 2.873 eV at 3d-1 (first distance). This means that the best electronic energies were obtained at the compound E\textsubscript{1} and 3d-1 (first distance). The comparison between these energies with the energies of NT [(E\textsubscript{HOMO} = -7.630 eV), (E\textsubscript{LUMO} = -3.527 eV) and (E\textsubscript{g} = 4.102 eV)] and the energies of PVC [(E\textsubscript{HOMO} = -7.9163 eV), (E\textsubscript{LUMO} = 1.324 eV) and (E\textsubscript{g} = 9.241 eV)] both separately is leading to find out that NT energies have the greatest influence in the system. Finally was found out that the high energy of LUMO suggests a high stability.

Dipole Moment

The most important parameters affecting the electric charge transport properties of polymers are the Dipole Moments (μ). The electrical conductivity of a polymer chain is altered when its orientation and consequently its symmetry and non-isotropic interactions are changed [28]. It can also be seen in Figure 6 that the dipole moments for all compounds have the following order: b > d > c > e > f > a>g. The dipole moment for structures b and d is greater than other structures. The polarization and
distance are affecting the value of dipole moment. The biggest value of dipole moment of 24.298 Deby was detected with \textbf{b} structure specifically in the first distance \textbf{3b-1} while the lowest dipole moment of 0.287 Deby was detected with \textbf{C} compound in the first distance \textbf{c-5}. This effect can be ascribed to quite strong polarization of the structure between the electron donating – electron accepting of NT – PVC. These characteristics increase the efficiency of electrochemical polymerization processes of these compounds [28].

**Figure 5.** Electronic energies as a function of distance of NT-PVC inclusions

**Figure 6.** Dipole Moment as a function of distance of NT-PVC inclusions

**Conclusion**

The inclusion process between NT and PVC and the possible obtaining of new stable structures were studied using quantum mechanical PM3 method. The distances
between NT-PVC interconnections were found to have a direct effect on the system total energy. Comparison with the energies of NT and PVC the best electronic energies were obtained at the compound e-1 and d-1. The strong polarization between the electron donating – electron accepting of NT – PVC led to the biggest value of dipole moment for compound b in the first distance b-1. In addition, any further characteristics of the structures and the stability of these complexes can be performed by taking into consideration the polarization effect in process calculation.

References and Notes

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