Density Functional Analysis of Chemical Impurities in Dielectric Polyethylene

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ABSTRACT

The effect of various chemical impurities in polyethylene on the electronic structure, trap depths, electron density, interchain interaction, etc. has been studied through the use of density functional theory. Quantum mechanical description of chemical impurity states is provided. The estimated depth of deep traps introduced directly by impurities and shallow traps introduced indirectly by impurity induced local disorder are in agreement with experimental estimates in the literature.

Index Terms — Polymers, polyethylene, high field phenomena, chemical impurities, computational quantum mechanics, DFT.

1 INTRODUCTION

POLYMERS are used widely as insulation in power apparatus such as capacitors and cables. As a result of the ever increasing design electric fields at which polymer dielectrics are employed, understanding of high field phenomena therein is increasingly important. The present understanding of the physical basis of high field conduction in common insulating polymers, such as polyethylene (PE), is incomplete [1, 2] in that an atomic level understanding of the role played by chemical impurities, disorder in the amorphous region, etc. is lacking. High field conduction is generally explained in terms of charge transfer between traps which results from the combination of thermal and electric field-induced charge transfer between traps [1, 3]. Chemical impurities are believed to introduce localized states in the PE band gap which can act as traps [2] and thereby affect low and high field conduction. Yet a clear identification of the physical basis of traps is lacking, in spite of extensive effort [1, 2, 4].

The present work is a step towards an atomic level understanding of the effect of chemical impurities on high field conduction in PE, which is an objective yet to be achieved. A computational quantum mechanical study of various chemical impurities in bulk PE has been undertaken using density functional theory (DFT) as implemented in the SIESTA code [5]. Our objective is to use DFT to identify the effect of common impurities at the atomic level on the physical and electronic structure of PE, provide a comparative quantum mechanical based description of chemical impurity-induced states, and discuss the relevance of such states to high field phenomena. Our DFT computations demonstrate that chemical impurities introduce states in the band gap which act as deep and shallow traps (or hopping sites) and provide estimates of the traps depths. Enhancement of interchain interaction in the vicinity of certain impurities is also established. In a previous paper, the authors examined the effect of carbonyl defects on the solid state physics of polyethylene [6]. The background information and methodology for the present contribution are very similar to that for [6] and will therefore be presented only briefly with emphasis on areas of difference.

2 COMPUTATIONAL METHODOLOGY

The ground state configuration of a system of electrons and nuclei which form a molecule or solid can be determined through a combination of DFT (for the electronic structure) and optimization of the nuclear positions based on energy minimization. In the present work, the quantum mechanical part of the electron-electron interaction is approximated using the local density approximation (LDA), and wavefunctions are expanded using a double zeta plus polarization (DZP) basis set. The DZP basis set employs more than twice the basis functions in a minimal basis set, and additional flexibility is available through inclusion of higher angular momentum basis functions which allow capture of atomic polarization. Within this basis set, the hydrogen, carbon, oxygen atoms are described by 5, 13 and 13 orbitals, respectively. The SIESTA basis functions are finite-range pseudo-atomic orbitals [5]. The DZP basis sets are sufficient to describe states above the vacuum level and to treat the CBM and states close thereto.

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Geometry optimization is based on requiring each component of the force on each atom (calculated according to the Hellman-Feynman theorem) to be less than 0.05 eV/Å. SIESTA determines the electronic eigenvalues (i.e., energy states) and wavefunctions (i.e., eigenstates) from which various properties of the system can be determined, including the electron density, density of states (DOS), and the projected density of states (PDOS). The DOS is the number of electronic states per unit energy and unit cell, as a function of energy. The PDOS is the contribution of any orbital, atom or group of atoms to the DOS of the system. While DFT involves numerous approximations, it remains the most successful implementation of computational quantum mechanics for systems involving hundreds of atoms, as it represents the best tradeoff between the computational time and accuracy [7,8]. The limitations of DFT are reasonably well understood as a result of its widespread use.

In this paper, chemical impurities are studied in a Core-Shell model of PE which provides a better representation of an amorphous environment than crystal bulk models commonly used in computational quantum mechanical studies of impurities in bulk material [9]. The rationale behind the Core-Shell model is to study chemical impurities in a PE chain which is sufficiently long to behave as infinite, while including the effect of neighboring chains in an amorphous like environment in which the chains have freedom to deform as a result of introduction of the impurity. The Core-Shell model consists of a Core chain, to which impurities are added, surrounded by six Shell chains in a supercell large enough to prevent interaction with chains in neighboring cells. Figure 1 shows the optimized Core-Shell system which includes three differing impurities. Introduction of the impurities results in deformation of chains in the vicinity of the impurities. Our computations suggest that the Core-Shell model, which is discussed in greater detail in [6], represents an acceptable approximation to amorphous PE which can be implemented with a reasonable number of atoms and periodic boundary conditions.

Systems of several thousand atoms may be required to treat the amorphous regions of polymers adequately. However treatment of such large systems is not presently practical using purely *ab initio* methods such as DFT. Mesoscale approaches have been employed in the past to investigate large-scale effects, e.g., morphology, texture, etc. [19]; however, such approaches are limited in the kinds of phenomena that can be studied. For example, local electronic effects caused by impurities, the primary subject of our investigation, cannot be studied directly using such methods.

The formation energy of an impurity "X" in bulk PE is defined as

$$\mathbf{E}^{\mathbf{f}}\left[\mathbf{X}\right] = \mathbf{E}\left[\mathbf{P}\mathbf{E}+\mathbf{X}\right] - \mathbf{E}\left[\mathbf{P}\mathbf{E}\right] - \sum_{i} n_{i}\mu_{i} \tag{1}$$

where E[PE+X] is the total energy of the bulk PE including the impurity X, E[PE] is the total energy of bulk PE without the impurity, n_i indicates the number of atoms of type *i* that were added (n_i positive) or removed (n_i negative) from bulk PE to create the impurity, and μ_i are the corresponding chemical potentials of these species [9]. The impurity formation energies for carbonyl, vinyl group, double bond, and conjugated double bond are 1.63 eV, -1.19 eV, -2.47 eV, and -4.41 eV respectively. The above formation energies depend on the choice of chemical potentials μ_{I} , of species added or removed from the bulk to form the impurity. The chemical potentials used in the present work are: μ_{O} as half the energy of the O₂ molecule, μ_{H} as the half the energy of H₂ molecule, and μ_{CH2} as half the energy of C₂H₄ molecule. The chemical reactions implied in forming the impurities are

X=Carbonyl:	$PE + \frac{1}{2} O_2$	\rightarrow	$(PE+X) + H_2$
X=Vinyl:	$PE + \frac{17}{2}C_2H_4$	\rightarrow	$(PE+X) + H_2$
X=Double bond:	PE	\rightarrow	$(PE+X) + H_2$
X=Conj. double bond:	PE	\rightarrow	$(PE+X) + 2 \bar{H}_2$



Figure 1. Core-Shell model minimum energy structure with a Core chain which includes three impurities, a carbonyl group, a carbon double bond and a vinyl side group. Bending of the Shell chains is evident, especially in the vicinity of impurities.

All impurities introduce local disorder in the PE structure, as the ethylene groups close to the impurities have shorter carbon-carbon bond lengths than those further away. The 6.8 eV band gap of the Core-Shell structure with the double bond impurity as shown in Figure 2 agrees with DFT estimates of PE band gap [12, 13]; however, DFT underestimates the band gap by about 2 eV relative to that determined experimentally. Such underestimation the band gap with respect to experiments, occasionally by as much as 50%, is a well-known deficiency of DFT. Nevertheless, relative electronic energies (e.g., work functions, band offsets, etc.) and relative changes in electronic structure are well represented by DFT [14].

All chemical impurities studied introduce an occupied state above the VBM and an unoccupied state below the CBM in the band gap of PE, similar to those shown in Figure 2 but with energies which depend on the impurity. The cause of the impurity state was determined through comparison with the DOS of defect-free PE and the PDOS, which determines how much each atom and orbital in the structure contributes to each state. The defect-free PE was a Core-Shell structure without impurities, in which the minimum energy chain orientation and bond lengths are almost unperturbed compared to crystalline bulk PE. With the addition of impurities, the band gap of the Core-Shell structure remained very close to that of crystalline PE [6]. A detailed description of the impurity states is provided in Table 1, including the energy difference between the state and the nearest band edge and the type of orbitals which form the state, based on the PDOS analysis and wavefunctions plots. The square of the unoccupied impurity state wavefunctions, which indicates the spatial probability distribution of electrons in that state, is shown for each impurity in Figure 3.



Figure 2. DOS from a Core-Shell structure showing the impurity states caused by a carbon double bond impurity. The vacuum level is taken as the reference energy.

Impurity	Occupied state, Energy above VBM (eV)	Unoccupied state, Energy below CBM (eV)		
Carbonyl group	π_{2p} , 0.95	$\pi^{*}_{2p}, 1.96$		
Vinyl group	π_{2p} , 1.0	$\pi^{*}{}_{2p}, 0.97$		
Carbon-carbon double bond	π_{2p} , 1.06	$\pi^{*}{}_{2p}, 1.06$		
Carbon-carbon conjugated double bond	π _{2p} , 1.53	$\pi^{*}{}_{2p}, 1.85$		

Table 1. Impurity States

In addition to the impurity states discussed above, which are deep in the band gap, the carbonyl, vinyl group, and conjugated double bond impurities introduce unoccupied states slightly below the CBM. The carbonyl and vinyl group impurities are responsible for the introduction of such states indirectly, as the PDOS analysis and wavefunction plots show that the orbitals of the carbon atoms adjacent to those impurities are the main source of the shallow impurity states as a result of the perturbation in bond lengths of those carbon atoms. However, the shallow impurity state introduced by the conjugated double bond, shown in Figure 4, is caused mainly by the orbitals of the impurity atoms. In all cases, the shallow impurity states are within 0.45 eV below the CB edge with the state caused by the conjugated double bond deepest within that range. Although we have used a local orbital basis set, we believe that the CBM and the shallow impurity states are treated adequately (although they may suffer from the inherent deficiencies of the LDA within DFT). The basis set used (DZP) includes a generous number of unoccupied states which tend to be "diffuse" or "delocalized", i.e., they extend into the region away from the corresponding atoms. Thus linear combinations of these functions have significant "presence" in the region between chains (e.g., between the Core and Shell chains) so that states localized in such regions can be captured adequately by our treatment.

Interchain interaction: The PDOS, wavefunctions, and electron density reveal enhanced interchain interaction in the vicinity of impurities, in particular around the carbonyl [6] and vinyl groups. While the impurity states in the band gap are caused mainly by impurity orbitals, PDOS analysis shows minor contributions from orbitals associated with the atoms of neighboring chains. The unoccupied state normalized wavefunctions have low amplitude peaks around neighboring chains in spite of being localized mainly around the impurity atoms, as shown in Figure 3. The low amplitude peak near a neighboring chain is greatest in the case of the vinyl impurity, followed by the carbonyl group [6] and the double bond. The conjugated double bond shows no peak associated with a neighboring chain on the probability scale employed in Figure 3. Electron density plots also reveal an increase of interchain interaction caused by certain impurities [15]. As shown in Figure 5, the charge density contour lines extend across the chains only in the vicinity of the carbonyl and vinyl group.



Figure 3. Square of the wavefunctions of the unoccupied carbonyl impurity state (top left), side vinyl impurity state (top right), conjugated double bond impurity state (lower left), double bond impurity state (lower right) in the Core-Shell structure plotted in the XY plane. The plot scale and location were selected to demonstrate the low amplitude peak of the wavefunction at a neighboring shell chain if such a peak existed.

The interchain interaction identified in the present work, in particular for vinyl and carbonyl impurities, should enhance interchain charge transfer and thereby affect high field conduction. To probe the role of unoccupied impurity states in interchain charge transfer, the planar average of the square of the wavefunctions was studied. The vinyl group state is the most extended toward neighboring chains, followed by the carbonyl state and the double bond. Although the deep conjugated double bond state approximately 1.06 eV below the CBM is less extended toward neighboring chains, the shallow impurity state shown in Figure 4 extends towards neighboring chains. We have identified qualitatively similar, yet quantitatively more significant aspects of interchain interaction for I₂ molecules in PE, which is known to increase conduction significantly, probably by enhancing interchain charge transfer [10]. More detailed study of the role of chemical impurities in enhancing interchain charge transfer will be pursued in the future.



Figure 4. DOS of Core-Shell structure which shows impurity states from the conjugated double bond including a shallow impurity state below the CBM. The vacuum level is taken as reference energy. Comparison with Figure 2 shows that the band gap, VBM and CBM energies of the optimized Core-Shell structure is independent of the impurity introduced in the Core chain the effect of which is to generate deep and/or shallow impurity states in the band gap.

3 IMPURITY STATES AND HIGH FIELD PHENOMENA

The deep and shallow states introduced below the CBM by chemical impurities reduce the barrier between VB and CB electrons in the vicinity of the impurities. However, the 20-30% reduction of the barrier (referred to the experimental band gap of 8.8 eV) is unlikely to increase significantly the number of carriers activated from the VB to the CB and is therefore not expected to have a significant impact on high field conduction. However the deep and shallow unoccupied impurity states below CBM identified in the present work could play a major role in space charge formation and high field conduction by providing trapping and hopping sites for electrons. Since trends in the energy of impurity states in the band gap near the CBM or VBM relative to the respective band edge are rendered with reasonable accuracy [14], the energy difference between the impurity states and CBM provide a reasonable estimate of trap depths for electrons. Similarly, the occupied impurity states above the VBM provide an estimate for hole traps. Traps for electrons, the main carrier at high fields, have been reported in the range of 0.3 to 2.0 eV [1, 2, 4, 16]. Traps caused by chemical impurities are believed to be deeper than those caused by physical disorder. The trap depths identified during the present work of $\sim 2 \text{ eV}$ (conjugated double bond and carbonyl) and $\sim 1 \text{ eV}$ (vinyl group and double bond) are within estimates in literature for deep traps caused by chemical impurities [1, 2, 4, 16]. The shallow traps (hopping sites) within 0.45 eV of the CBM are also within estimates in literature of shallow traps believed to be caused by physical disorder [2]. The shallow states associated with chemical impurities suggests that the dielectric properties of PE may be dominated by such impurities as they can account for the observed solid state features of the material, although we do not know the degree to which disorder in the amorphous region may contribute similar states even without chemical impurities.



Figure 5. Electron densities in the vicinity of various impurities. Top left carbonyl, top right vinyl group, lower right no impurity, lower left double bond. Electron density scale chosen to demonstrate the relative effect of different impurities. The plots are in the XY plane where the Z direction is along the chain backbone and into the paper.

Computations of the Core-Shell model with more than one impurity in the Core chain demonstrate that as long as the impurities are separated by more than five carbon atoms along the polymer backbone, the states which they introduce into the band gap are independent of other impurities. The DOS for PE, with the shallow and deep trap states as identified above, may account for aspects of high field conduction properties of PE. In addition, the overlap between impurity state wavefunctions and those of adjacent polymer backbones promotes tunneling between such states which is also relevant to high field conduction [1, 3].

4 FUTURE WORK

Future work will include investigating the effects of other chemical impurities commonly found in PE, in particular those which reside in between chains, and studying of the role of chemical impurities on enhancing interchain charge transfer and the effect thereof on conduction. In the long term, we hope to incorporate the results of DFT computations into quantitative models for conduction in polymers, along the lines of prior investigations of charge transport in PE based on *ab initio* computations [17-18].

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