

Density Functional Theory Studies on PVDF-based Composites and their Applications

Thesis Abstract

Five distinct polymorphs (α , β , γ , δ and ϵ) of polyvinylidene fluoride (PVDF) are formed depending on the crystallization conditions and processing techniques. Compared to the other polymorphs, β -PVDF possesses the highest technological importance owing to its higher dipole moment and spontaneous polarization per monomer unit, high Curie temperature (168°C), and a very high coercive electric field (120 MV/m at room temperature). PVDF is easy to fabricate, and to some extent more advantageous as compared to electroactive ceramics (e.g. BaTiO₃) because of low density (1000-2000 kg/m³), high flexibility, high response speed (μ sec to min), better resilience, and higher actuation strain. During melting or solvent casting, the stable and non-polar α -phase forms predominantly, which needs to be converted to the electroactive β -phase. Apart from the conventional mechanical stretching, electrical poling, and various high temperature-high pressure treatments, the addition of different types of second phase materials (fillers or additives) also helps in α to β transition. Nevertheless, computational studies on PVDF-based composites are still rare. This thesis intends to provide an in-depth quantum chemical clarification of the facile remarks on inter-fragment hydrogen bond interactions within PVDF/ionic liquid and PVDF/hydrated nitrate salt systems. Linear combination of atomic orbitals (LCAO)-based density functional theory (DFT) calculations are performed considering long-range dispersion correction for structural optimization and vibrational frequency analyses. PVDF/IL interactions are analysed for α - and β -PVDF tetramer chains, and ionic liquid 1-n-alkyl-3-methylimidazolium tetrafluoroborate ([C_nMIM][BF₄]). The effect of variation in the IL-cation chain length (n) on the physicochemical properties of PVDF/IL complex is explored for n = 2, 4, 6, 8, and 10. Explicit descriptions on PVDF/IL-cation and PVDF/IL-cation interactions are provided for PVDF/[BMIM][BF₄] in the gas phase and within three polar aprotic solvents, namely, tetrahydrofuran (THF), acetone, and n,n-dimethyl formamide (DMF). Hydrogen bond interactions within hydrated aluminum nitrate [PVDF/Al(NO₃)₃.9H₂O] added PVDF, PVDF-TrFE, and PVDF-HFP composite systems are analysed in the gas phase and within DMF. Subsequently, a quantum chemical perspective of the selective gas adsorption efficiency, from a mixture of CO₂, CO, CH₄, and H₂, of α - and β -polyvinylidene fluoride (PVDF)-supported imidazolium- and pyridinium-based six ionic liquid membranes. Membrane/gas interactions are described as weak hydrogen bond interactions between the gas and membrane. In the end, a combined DFT and molecular dynamics (MD) simulation study is performed to provide a comparative analysis on Li-ion interactions and diffusion properties within β -PVDF/ionic liquid/Lithium perchlorate (LiClO₄) and β -PVDF/propylene carbonate/LiClO₄ gel polymer electrolyte systems.

Keywords: LCAO-DFT; dispersion correction; PVDF; ionic liquid; hydrated salt; hydrogen bonding; membrane gas separation; gel polymer electrolyte.