Density functional theory study of adsorption pathways of TiCl$_4$ on Polyether Ether Ketone

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Abstract—In this study, a theoretical evaluation was conducted on the adsorption pathway of TiCl$_4$ on PEEK at room temperature (298 K) and pressure (101325 Pa). The thermodynamics of the complexation process on the ketone and ether functional groups were described using density functional theory. It was found that the adsorption of TiCl$_4$ at room temperature was not spontaneous, but it could be achieved by reducing the reacting temperature. The adsorption process only occurred through coordination to form a pentacoordinate TiCl$_4$-PEEK complex without dissociation. Moreover, dissociative chemisorption was not preferred. TiCl$_4$ only interacted with the carbonyl group when the carbonyl group was normal to the surface or slightly inclined, and not when it was parallel to the surface. There was no interaction between the TiCl$_4$ and the ether group.

Keywords—Polyether ether ketone (PEEK), TiCl$_4$, Density functional theory, adsorption

I. INTRODUCTION

Polyether ether ketone (PEEK) is a semi-crystalline thermoplastic inert polymer that has become a popular alternative to metals as an implant material in biomedicine. PEEK offers a significant advantage over metals by averting post-implantation complications such as stress shielding and ion toxicity associated with metal implants [1] while still offering robust mechanical properties as implants with high yield strength and elasticity of their amorphous form. Additionally, PEEK implants allow clear imaging using X-ray, computer tomography (CT), and magnetic resonance imaging (MRI) with clarity. Additionally, the polymer is easy to work with through moulding and additive manufacturing [2]–[6].

PEEK's inertness is its most significant limitation when used as a biomedical implant. It slows the healing process due to limited biocompatibility that limits protein adsorption and consequent tissue integration [5], [7]. Due to this limitation, surface functionalization post-forming is necessary. One technique employed in functionalization includes depositing metal compounds thin films on the PEEK surface. This method introduces different functional groups on the surface, including new phases. Aluminium oxide, hydroxyapatite, magnesium and titanium oxides [5], [8]–[10]films have been deposited on PEEK to improve bioactivity on the polymer surface using various methods such as vapour deposition and sol-gel method. The main challenge the grown films face is the film's adhesion to the surface [11]. The adhesion of films is highly dependent on the interaction of the polymer and the coating material [12].

PEEK is a polymer of repeating units of diphenyl ethers and diphenyl ketone linked at the ether groups [13]. Ketones and ethers are significantly reactive species due to the presence of lone pairs of electrons. They act as Lewis bases that donate electrons to electron-deficient Lewis acids [14]. A good Lewis acid in organic synthesis is titanium tetrachloride (TiCl$_4$). TiCl$_4$ contains a partially filled 3d orbital on the Ti atom, which can accept electrons to form a coordinate bond. Due to this property, TiCl$_4$ is used mainly in catalysis in acetylation reactions and the formation of cyclic units from either ethers or carbonyl organic molecules [14]–[16]. Complexation of TiCl$_4$ with organic compounds is also crucial in the growth of organic thin films [17]. Experimental and theoretical studies have been able to describe the complexation of TiCl$_4$ on both linear and cyclic ether and carbonyl organic molecules, including esters, and ketones [18], [19]. However, the complexation of TiCl$_4$ and carbonyls and ethers with diphenyl substituent groups has not been extensively studied.

This study, therefore, aims to report the nucleation of TiCl$_4$ on PEEK as a seeding layer for thin film growth through a theoretical evaluation of the reaction thermodynamics, i.e., the enthalpy, Gibbs free energy, and entropy changes during TiCl$_4$-PEEK interaction pathways, as well as the effect of PEEK's orientation on TiCl$_4$ adsorption.

II. METHODOLOGY

The adsorption of TiCl$_4$ on the ether and ketone functional groups of the PEEK molecule at room temperature and atmospheric pressure was carried out using the density

functional theory. The Becke's three-parameter functional together with the Lee Yang Parr gradient correlation (B3LYP) level of theory together with the 6-31G (d,p) basis set is used due to the proven accuracy and computational cost-effectiveness for both $TiCl_4$ and carbon-based organic compounds [20]–[24]. GaussView5 and Gaussian 09W software packages were used for molecule design and optimization for both reactants and products, as well as frequency calculations to obtain thermodynamic data and evaluate the stability of the molecules. Zero-order imaginary frequencies showed that the molecule is in a stable state. A relaxed coordinate scan was carried out to study the effect of the carbonyl-Ti bond angle on the $TiCl_4$-carbonyl interaction. The charges used in the calculations were 0 and 1, while the multiplicity was maintained at singlet. The thermodynamic data reported is relative to that of the reactant molecule(s). In this paper, chlorine atoms are represented using green balls; oxygen atoms are represented using red balls; carbon atoms are the dark grey balls; titanium atoms are the big light grey atoms; and smaller light grey balls represent the hydrogen atoms.

III. RESULTS AND DISCUSSION

A. Adsorption Mechanisms of TiCl₄ on Ketone Functional Group of PEEK

$TiCl_4$ anchors onto the ketone group by binding onto the lone pair of electrons on the oxygen atom in the carbonyl group. The $TiCl_4$ structure changes from a tetrahedral form with a Cl-Ti-Cl angle of 109.5^0 to a trigonal bipyramid structure with Cl-Ti-Cl interplanar angles nearing the ideal 90^0 while the equatorial bond angles are approximately close to the ideal 120^0. The observed Ti-O bond length is 2.08 Å, typical of the Ti-O bond of carbonyl $TICl_4$ complex as observed by Saied, Bachand and Wuest [18]. Introducing the extra pair of electrons on the Ti atom increases electron density within the Ti atom. This causes a repulsion between the new bonding orbital and the existing Ti-Cl bonding orbitals. The repulsive forces cause an increase of the Ti-Cl bond from 2.177 Å in the gaseous structure to a range of 2.23 Å and 2.25 Å in the adsorbed state, indicating a weakening of the Ti-Cl bonds. Wuest et al. [2] obtained a 168^0 C-O-Ti angle, but the carbonyl-titanium angle was 159.93^0 for this study. The difference in the Ti bend angle with respect to the surface may be due to the effect of steric repulsion from the aryl ring (C21) on chlorine (Cl39), shown in Fig. 1. A thermodynamic analysis of the adsorption process shows that the complex formation is exothermic at -43.798 kJ/mol while the entropy term decreases ($T\Delta S$=-47.684 kJ/mol). These observations closely tally with the enthalpy and entropy of complexation between $TiCl_4$ -ethyl acetate and $TiCl_4$- ethyl benzoate, respectively, as reported by Credendino et al. [14][14]. However, the process is non-spontaneous at room temperature and pressure, as Gibbs's Free energy (ΔG) increases by 3.885 kJ/mol. This state of exothermicity and non-spontaneity indicates that the reaction is significantly entropy-driven, and spontaneity can be achieved by reducing the entropy term. The reaction's equilibrium temperature (at $\Delta G = 0$) is predicted to be 273.85 K. The deposition process should, therefore, occur below 273.85 K for the product formation to be thermodynamically favoured. This operating temperature is feasible for gaseous atomic layer deposition given that the melting point of $TiCl_4$ is 249 K, 24 K lower than the required operating temperature. The lack of spontaneity for this
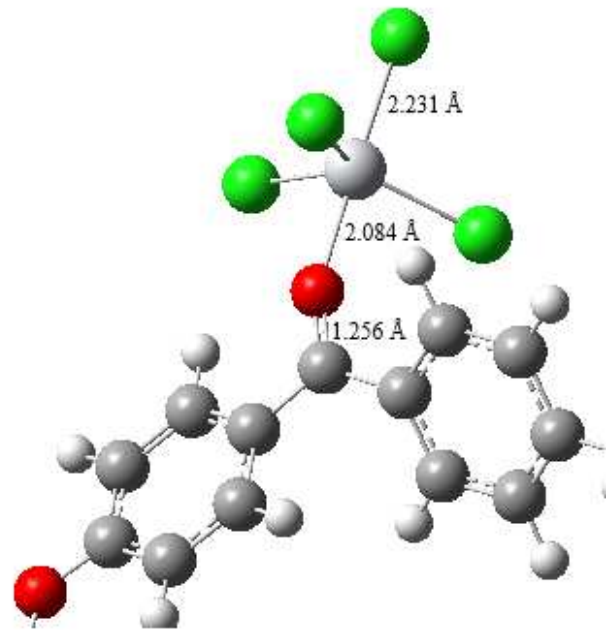

Fig. 1. TiCl₄-polyether ether ketone complex formed after coordination of TiCl₄ with the ketone

complexation might explain the negligible yield of the $TiCl_4$-benzophenone complex observed at 283 K by Schwartz [25].

After deposition, the dissociation of $TiCl_4$ to $TiCl_3$-PEEK complex was assessed. The geometrical aspects of this complex, including the Ti-O bond and the adsorbed titanium complex, are shown in Fig. 2. It can be seen that the Ti-O bond length measures 1.81 Å, which is 0.2 Å shorter than in the adsorbed $TiCl_4$ state. Shortening of the bond length indicates a stronger Ti-O bond that is closer to the experimental recorded 1.85 Å Ti-O bond in brookite TiO_2 structures [26]. The adsorbed Ti complex was restructured to a tetrahedron with ligand angles around the Ti centre close to the 109.5^0 angles. The complexation also leads to the delocalization of
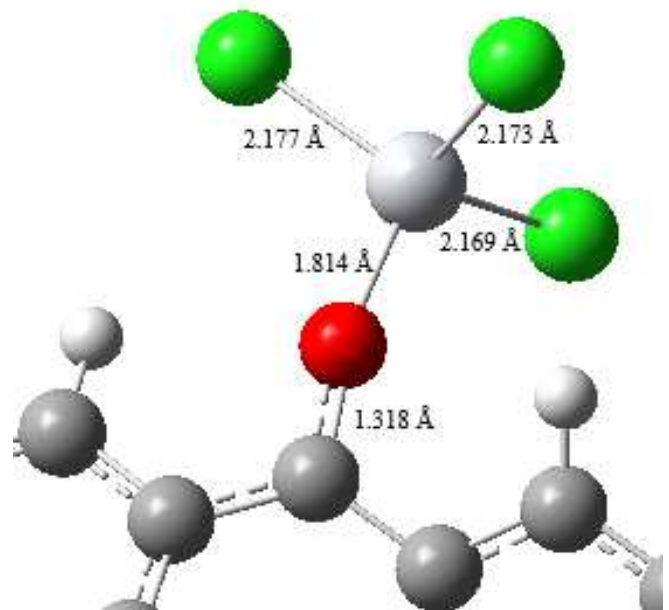

Fig. 2. TiCl₃-polyether ether ketone complex formed by dissociation of TiCl₄ and releasing chlorine atom

the double bond between the carbonyl group and adjacent carbon atoms in the aryl group. Reaction thermodynamics shows that this process is highly endothermic at +2301 kJ/mol while the free energy for the process is +2266 kJ/mol, and the change in entropy is +0.80 kJ/mol. The high endothermicity might be due to the high energy required to break the Ti-Cl bond, the C-O bond relative to the energy released forming the new Ti-O bond.

Another structure formed from the dissociation of the $TiCl_4$ to $TiCl_3$ on the surface leads to the complexation of the chlorine atom with the polymer at the carbonyl carbon atom, which leads to breaking the C-O double bond to form a single bond of 1.413 Å and a 1.869 Å C-Cl bond. Formation of this complex shown in Fig. 3 from the $TiCl_4$ complex in Fig. 2 is an endothermic process that requires +67.91 kJ/mol enthalpy, and the change in free Gibbs energy associated with the process is +64.77 kJ/mol at standard temperature and pressure. Thus, under these conditions, the adsorbed $TiCl_4$ cannot undergo dissociation to form $TiCl_3$ on the PEEK surface using this path which creates an oxychloro group in place of the ketone.

The direct dissociation of $TiCl_4$ into the $TiCl_3$ and the chlorinated PEEK surface is also endothermic (+24.97 kJ/mol), but the free energy is slightly higher by 3.99 kJ/mol (ΔG=+68.77 kJ/mol). The entropy, however, decreases by 0.147 kJ/mol. This thermodynamic relationship between the reactant and product shows that dissociative chemisorption of $TiCl_4$ on PEEK to form the complex in Fig. 3 is highly unlikely.

Results from the adsorption paths studied above show that the titanium metal source will retain its pentacoordinate structure after adsorption onto PEEK without further dissociation. However, the process must be carried out at temperatures below 273.85 K for the nucleation of $TiCl_4$ on the PEEK to occur. It also shows that $TiCl_4$ cannot undergo dissociative chemisorption on impact with the oxygen on the ketone group, as reported for other inorganic surfaces such as silicon and titanium [27], [28].
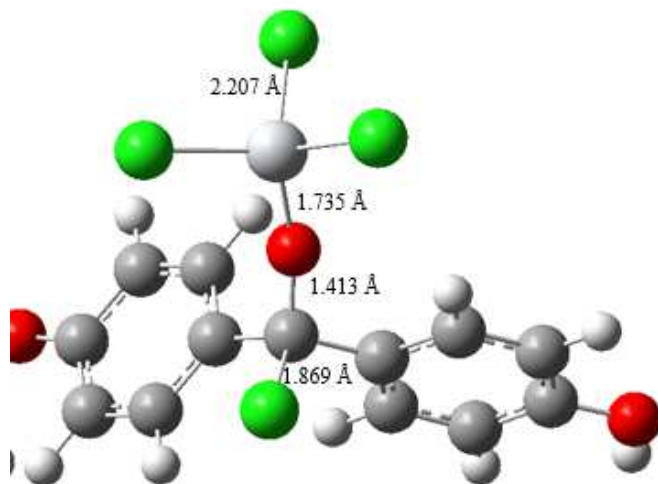
B. C-O-Ti Bond Angle and TiCl₄ Adsorption

$TiCl_4$'s optimum adsorption angle on the ketone group (C-O-Ti) is 159.93^0. A potential energy scan across the C-O-Ti from 180^0 to 90^0 reveals, as in Fig. 4, that $TiCl_4$ can adsorb on the PEEK polymer at smaller angles up to 110.98^0 before any interaction with the surface is hindered. As shown in Fig. 5, the Ti-O bond length increases with a maximum calculated distance of 2.321 Å between the oxygen and titanium atoms as the bond angle decreases. Below the 110.98^0 angle, the $TiCl_4$ is repelled from the surface due to steric repulsion by the aryl ring electrons. Despite the decrease in bond length from 2.084Å at the optimized structure to 2.044Å at 180^0 C-O-Ti angle, the molecular energy diverges from the minimum energy, showing that instability is introduced to the complex due to repelling electrons from the chlorine and arene rings being brought closer together.

The Ti metal source, $TiCl_4$ takes up a trigonal bipyramidal structure in all the adsorbed states, which is observed up to 110.98^0, below which it changes to a tetrahedron, the stable structure in the gaseous state. Additionally, between 138.95^0 and 110.98^0, the Ti is only physiosorbed onto the surface through electrostatic interaction between the Ti centre and the O on the carbonyl group. Thus, interactions are temporary and reversible. Any film formed on such initial Ti-polymer
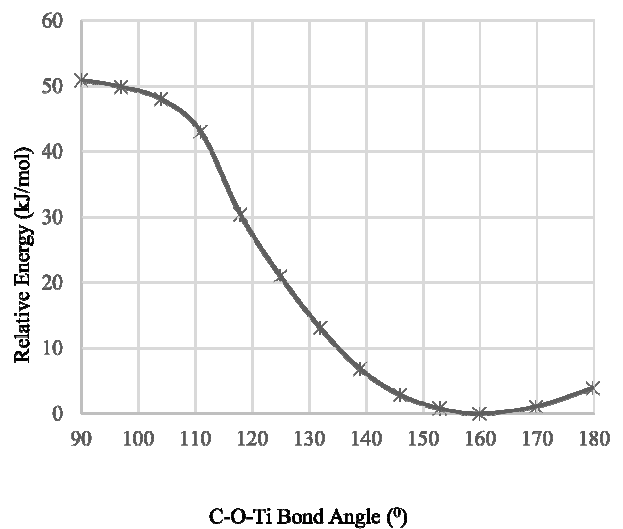

Fig. 4. Relative change in interaction energy between $TiCl_4$ and O on carbonyl group at different C-O-Ti bond angles.
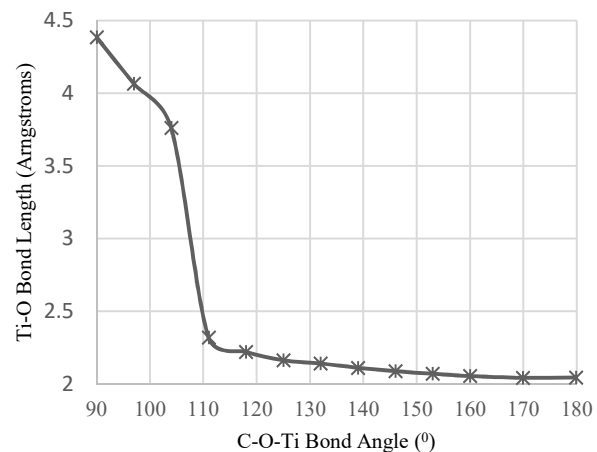

Fig. 3. $TiCl_3$-oxychloride-polymer complex formed after dissociation of $TiCl_4$

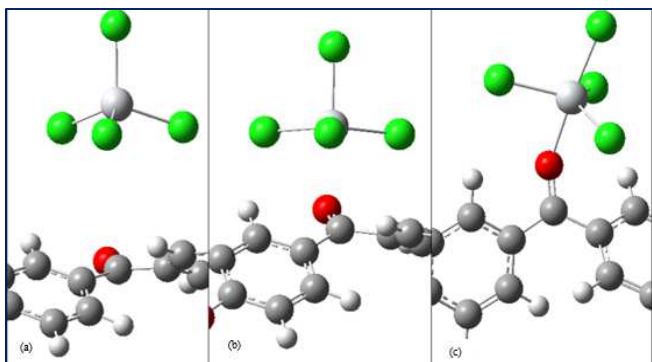Fig. 5. Variation of the Ti-O bond length at different C-O-Ti bond angles.

Fig.6. $TiCl_4$ Orientations at different C-O-Ti bond angles. (a) $TiCl_4$ orientation between 90^0 and 103^0. (b) $TiCl_4$ orientation on the carbonyl group between 110^0 and 138^0 C-O-Ti bond angles, and (c) represents the $TiCl_4$ orientation between 145^0 and 180^0 C-O-Ti bond angles.

interaction will only weakly adhere to the polymer. Fig.6 illustrates the different $TiCl_4$ orientations on PEEK at different C-O-Ti bond angles.

C. Adsorption of TiCl₄ on Ether Functional Group of PEEK

$TiCl_4$ does not absorb oxygen in the ether group. Despite lone electron pairs on the oxygen atom that can form a coordinate bond, the aryl rings on either side of the ether shield these lone electrons from interacting with the titanium tetrachloride. The electron cloud around the aryl rings repels the chlorine ligands as $TiCl_4$ approaches the ether group. This is a case of steric repulsion. Therefore, it is recommended that a polymer with a higher ketone concentration is used for a higher nucleation rate. Polyether ketone (PEK) and poly ether ketone ketone (PEKK), which have higher ether-ketone ratios, can be used. These two alternatives also possess similar mechanical and chemical properties to PEEK.

IV. CONCLUSION

The nucleation pathway of $TiCl_4$ on polyether ether ketone polymer was investigated in this study. The results show that $TiCl_4$ can only adsorb on the carbonyl group through coordination on the lone pair of electrons on the ketone, but the same is not possible with the ether group. Additionally, it has been established that $TiCl_4$ interacts with the surface when the carbonyl group is normal to the surface rather than when it is oriented parallel to the surface. This study has also proposed that $TiCl_4$ and the ketone should be reacted at temperatures below 273.85 K for coordination to occur.

V. LIMITATIONS OF THIS STUDY

The reaction paths were studied with a simplified model that assumes that both reactants are in a gaseous state. However, in real-life situations, $TiCl_4$-PEEK adsorption is a heterogeneous solid-gas or solid-liquid interaction. Thus, the simplified model may correctly depict the reaction's heterogeneity. Additionally, the assumption that the PEEK monomer and $TiCl_4$ interact with each other without interference from solvents and carrier gases may be inaccurate since solvents and carrier gases influence the reaction thermodynamics [14]. Finally, the calculation was carried out at a constant pressure of 101325 Pa. Hence, the data obtained may not be accurate for varying pressure if the reaction thermodynamics are pressure-dependent.

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