Theoretical study of the impact of quantum chemistry parameters on the behaviour all effects of the coating of a new epoxy prepolymer

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Abstract
The aim of our work is to evaluate the performance behavior of the coating of macromolecule epoxy matrix, tri glycidyl ether ethylene of bisphenol A (TGEEBA) on the corrosion of the carbon steel E24 in a marine environment and examine its mechanism of the coating. Subsequently, we have studied the possible adsorption model on the surface of the carbon steel E24 corroded and can explain the understanding of the interactions between the coating macromolecule and the surface of the carbon steel E24. The coating effect on carbon steel E24 was studied by quantum chemical calculations. The adsorption of TGEEBA on the surface of the carbon steel E24 has been well described by the model Quantitative Structure Property Relationship (QSPR). The mechanism of the behavior of the coating was determined by a potential of zero-load measurement and some electronic parameters. The prediction of the behavior of the coating was carried out by the method of three Becke compounds of the parameter (UB3LYP) whose semi-empirical basis are PM6 and DFT for an eventual composite. These last were used on the basis of (6-311 G). All calculations were performed using Gaussian software bias (03).

Keywords: TGEEBA; macromolecule epoxy; coating; efficiency; QSPR; PM6; DFT.
1. Introduction
The development of a new polymeric material depends on its eventual use in a wide field of application [1-2]. The synthesis of the prepolymerms with the desired properties is a challenge which often involves a lot of time and resources [3-4]. The ability to predict the properties of the final product of new material is of great value, also an orientation that speeds up the process and the development cycle [5-6]. The stationary and transient electrochemical studies of the carbon steel E24 of the coating are one of the most widely used properties of organic prepolymerms and their composites. They determine the effectiveness of these prepolymerms for the treatment, the use of these materials and the conditions before anticipating and understanding other properties. There are many methods proposed to predict the coating behavior of prepolymer systems. These include empirical equations [7-8], molecular dynamics simulations [9-10], the semi-empirical methods [11] and mathematical tools, including the neuronal networks [12-13], the theory of fuzzy sets [14] and the graph of theoretical indices [15-16]. During this work, we examined the correlation of molecular properties of this prepolymer Epoxy (TGEEBA) synthesized in the laboratory [17], with the calculations of quantum chemistries.

2. Experimental

2.1. Macromolecular matrices
In this work, we have studied the coating behavior of the trifunctionalpolyepoxideprepolymer: triglycidyl ether ethylene of bisphenol A (TGEEBA) synthesized [17], which is presented in figure 1.

![Figure1: Semi-developed structure of triglycidyl ether ethylene of bisphenol A](image)

2.2. Software and calculation methodology
The quantum chemical calculations have been widely used to study the reaction mechanisms [18]. They are also approved to be a very interesting tool for studying the properties of molecules [19-20]. It had been shown that the physical properties can be linked the molecular structure and spatial electronics. In this study, we studied the relationship between the quantum chemistry parameters and the behavior of the epoxy prepolymer coating. The quantum chemical parameters have been calculated by the semi-empirical method of the neutral macromolecule matrix, charged negatively and positively, namely the parametric method (PM6 and DFT), based on the method of three parameters Becke compounds (UB3LYP). It self studied on the basis of (6-311G). All these calculations were performed by the Gaussian (03). The calculated quantum chemical parameters, namely the energy of the highest
occupied molecular orbital (E\textsubscript{HOMO}), the energy of the lowest unoccupied molecular orbital (E\textsubscript{LUMO}). These E\textsubscript{HOMO} and E\textsubscript{LUMO} molecular orbitals of the coating molecule are linked to the ionization energy (I) and to the electronic affinity (A), respectively I = -E\textsubscript{HOMO} and A = -E\textsubscript{LUMO}. The energy of gap (\Delta E = E\textsubscript{LUMO} - E\textsubscript{HOMO}), the softness (\sigma), the ionization potential (Pi), the electronegativity (X), the absolute hardness (\eta), the electrophilic character \omega and the function of the transferred electrons of the coating to the surface of the metal (\Delta N). These parameters are related according to Koopmans theorem [21].

The ionization potential (Pi) of coating behavior is calculated using the following equation.

\[ P_i = \frac{E\textsubscript{HOMO} + E\textsubscript{LUMO}}{2} \]  

The electronegativity (\chi) and the absolute chemical hardness (\eta) can be evaluated using the following equations [22]:

\[ \chi = -P_i \]  
\[ \eta = \frac{\Delta E}{2} = \frac{E\textsubscript{LUMO} - E\textsubscript{HOMO}}{2} \]

The chemical sweetness (\sigma), which describes the ability of an atom or a group of atoms to accept electrons, is calculated according to the following equation [23]:

\[ \sigma = 1 - \frac{2}{\eta} \frac{E\textsubscript{HOMO} + E\textsubscript{LUMO}}{2} \]

Otherwise, the electrophilic character \omega is a reactivity descriptor allowing a quantitative classification of the electrophilic nature of a compound on a relative scale. We have proposed \omega as a measure of the lowering of the maximum energy due to electron flow between the donor and the acceptor, \omega is defined by the following relation [24]:

\[ \omega = \frac{\chi^2}{2\eta} \]

The number of transferring electrons (\Delta N) was calculated according to the chemical quantum method by the following equation [25]:

\[ \Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \]

The constituents present in the steel E24 are grouped in table 1:

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Carbon</th>
<th>Manganese</th>
<th>Phosphorus</th>
<th>Sulfur</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (%)</td>
<td>0.19</td>
<td>0.75</td>
<td>0.045</td>
<td>0.045</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The manganese is the majority compound in steel E24, whose electronegativity of manganese was used to calculate the number of transferring electrons (\Delta N). Where \chi_{Fe} and \chi_{inh} represent absolute electronegativity of carbon and the molecule of the coating, \eta_{Fe} and \eta_{inh} designate respectively to the absolute hardness of manganese and the molecule of the coating. In this study, we used the theoretical values of \chi_{Fe}= 7 and \eta_{Fe}= 0 for the calculation of the number of electrons transferred.

The local reactivity was performed at the level of the Fukui indices. This study indicates the region of reactivity an atom or the set of atoms, which are responsible for the nucleophilic and electrophilic attack of each of these atoms in the molecule tested.

3. Results and discussion

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The experimental results concerning the behavior of the steel E24 coating in a marine environment obtained using potentiodynamic mode/stationary method and Nyquist mode/transient method simultaneously showed that the protection efficiency of the metal by the different formulations E1 and E2 derived from the macromolecular structure of new epoxy resin synthesized triglycidyl ether ethylene of bisphenol A (TGEEBA) are very good. In order to confirm the adhesion sites of the epoxide polymer which are responsible for the experimental acquisition results, thus reflecting the good adherence of our epoxide trifunctional macromolecular matrix [17], composed of six aromatic nuclei on one hand and an ethylenic radical on the other hand, we carried out the calculation study of quantum chemistry using Gaussian software (03). To perform the calculation of the quantum chemistry parameters of the epoxide resin, several descriptors have been studied on the electronic steric basis and the thermodynamic effect. The calculation of the different descriptors was performed by two different methods, the first semi-empirical (PM6) and the second based on the electron density (DFT) using Gaussian software (03). The main results of this study are summarized in table 2.

<table>
<thead>
<tr>
<th>Method</th>
<th>DFT</th>
<th>PM6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loads</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_HOMO (eV)</td>
<td>-0.16899</td>
<td>-0.35116</td>
</tr>
<tr>
<td>E_LUMO (eV)</td>
<td>-0.09327</td>
<td>-0.16525</td>
</tr>
<tr>
<td>ΔE (eV)</td>
<td>0.07572</td>
<td>0.18591</td>
</tr>
<tr>
<td>μ (Debye)</td>
<td>7.7777</td>
<td>9.5543</td>
</tr>
<tr>
<td>I(eV)</td>
<td>0.16899</td>
<td>0.35116</td>
</tr>
<tr>
<td>A (eV)</td>
<td>0.09327</td>
<td>0.16525</td>
</tr>
<tr>
<td>Pi(eV)</td>
<td>-0.13113</td>
<td>-0.16525</td>
</tr>
<tr>
<td>χ (eV)</td>
<td>0.13113</td>
<td>0.25820</td>
</tr>
<tr>
<td>η (eV)</td>
<td>0.03786</td>
<td>0.09295</td>
</tr>
<tr>
<td>σ 1/(eV)</td>
<td>26.4131</td>
<td>10.3655</td>
</tr>
<tr>
<td>ω (eV)</td>
<td>0.227</td>
<td>0.358</td>
</tr>
<tr>
<td>ΔN</td>
<td>0.117</td>
<td>0.1231</td>
</tr>
<tr>
<td>E Total KJ (10^-29)</td>
<td>-471.132</td>
<td>0.142</td>
</tr>
<tr>
<td>Sum</td>
<td>-436.746</td>
<td>55.946</td>
</tr>
<tr>
<td>Mean</td>
<td>-39.704</td>
<td>5.086</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>143.312</td>
<td>4.231</td>
</tr>
<tr>
<td>Range</td>
<td>497.545</td>
<td>45.305</td>
</tr>
</tbody>
</table>
To better understand the adsorption mechanism of behavior coating studied on the surface of steel E24, the use of optimization analysis to estimate the active coating adsorption centers, quantum chemical calculations were performed, specifically by the method PM6 and DFT. The optimized geometric structures and the electron density distributions $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ for this coating are presented in figures 2, 3, 4, 5, 6 and 7. The quantum chemical parameters were calculated and analyzed in order to explain the reactivity of the electropositive sites and the electronegative molecule of the TGEEBA is grouped in table 2.

The $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the orbital of the epoxy prepolymer with neutral ethylenic acid, positively charged and negatively charged with two methods studied are respectively shown in the figures below. This clearly shows that the electronic effect reacts with the behavior of the coating on the epoxy-diamine system studied.

<table>
<thead>
<tr>
<th></th>
<th>0.075</th>
<th>0.069</th>
<th>0.022</th>
<th>0.113</th>
<th>0.106</th>
<th>0.087</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sum of squares</td>
<td>222</td>
<td>224</td>
<td>297</td>
<td>215.219</td>
<td>213.07</td>
<td>220.559</td>
</tr>
</tbody>
</table>

**Figure 2:** $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the neutral TBEEBA according to the DFT method

**Figure 3:** $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the TBEEBA charged negatively according to the DFT method
Figure 4: $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the TBEEBA charged positively according to the DFT method.

Figure 5: $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the neutral TBEEBA according to the MP6 method.

Figure 6: $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the TBEEBA charged negatively according to the MP6 method.

Figure 7: $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the TBEEBA charged positively according to the MP6 method.
E$_{\text{HOMO}}$ generally describes the ability of a compound to donate electrons. A large value of energy of HOMO orbital facilitates the tendency of molecules to yield electrons to acceptable species of electrons with unoccupied molecular orbital whose energy level is low. However, the E$_{\text{LUMO}}$ is related to the ability of a molecule to accept electrons, a low value of the LUMO energy indicates that the molecule certainly accepts electrons. So, the adsorption of energy between the behavior coating and the metal surface of the steel E24 increases when the gap energy ($\Delta E=E_{\text{LUMO}}-E_{\text{HOMO}}$) decreases [26-27]. The high ionization energy indicates high stability [28-29], the $\Delta N < 3.6$ indicates the tendency of a molecule to donate electrons to the metal surface [30-31]. From the analysis in table 2, we observed that the values of energy gap are lower between the molecular orbital boundaries of the donor and the acceptor. This result indicates that the quality of the film formation is well formed. Concerning the orbital’s electron molecular donor. We have observed in figures 2, 3, 4, 5, 6 and 7 that the electron density (HOMO) is located respectively on the surface of aromatic and the epoxy group for the DFT method (neutral, negatively charged and positively charged) and on the surface of the aromatic cycle for the DFT method (neutral, negatively charged and positively charged). On the other hand, the electronic densities (LUMO) are respectively located on the surface of epoxy for the DFT method (neutral) cycle, on the surface of the aromatic ring for the method DFT (negatively charged), on the aromatic ring surface and the ethylenic nucleus For both PM6 and DFT methods (positively charged). The results obtained indicate that the efficiency of the adsorption of behavior coating increases the ionization potential (Pi), because this property is directly related to E$_{\text{HOMO}}$. In other words, the adsorption of the behavior coating or the adhesion of the epoxy macromolecule resin to the metal support takes place on the level of the aromatic rings, epoxide rings and the ethylenic radical with respect to the micro-gaps on the surface of the epoxy resin substrate.

4. Conclusion

In our work, after having synthesized the macromolecular matrix triglycidyl ethylene ether of bisphenol A, which was used as a coating on carbon steel in standard E24 and composite forms. We studied the impact of electronic effect on the performance properties of the coating triglycidyl ether of ethylene bisphenol A. We studied the impact of the electronic effect on the behavior coating properties of the triglycidyl ether ethylene of bisphenol A. This calculation allowed establishing the QSPR model to calculate the values of some quantum chemistry parameters (descriptor). These were found by the method of three compounds of parameter Becke (UB3LYP) has been used on the basis of (6-311 G) of semi-empirical methods of the macromolecule matrix neutral, negatively charged and positively charged to namely, the parametric method (PM6 and DFT). The distribution of electrons influences on the density of behavioral coating properties of the epoxy resin studied between the electron phenomenon and the effect of the behavior of the coating is completely correlated. All these calculations were performed by the Gaussian (03). Finally, the prediction of the behavior coating was carried out by the semi-empirical methods PM6 and DFT, carried out using the Gaussian software (03), confirming the adhesion sites of the epoxy macromolecular matrix.

References


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