Synthesis, Characterization and Investigation of New Polymer Contain Heterocyclic Derivatives as Corrosion Inhibitor for Stainless steel in acidic medium

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ABSTRACT

A new series of Poly 2-[N-(5-vinyl-1H-1,2,3-triazol-3-methyl amino]benzo[d]thiazole(4) has been synthesized through reaction of 2-aminobenzimidazole with ethyl chloroacetate . The resulting ester was synthetically modified through hydrazine hydrate to acyl hydrazide which was condensed with acrylonitrile to afford the title 2-[N-(5-vinyl-1H-1,2,4-triazol-3-methyl) amino] benzo[d]thiazole(3). Finally, Using a controlled DC power supply, compound [3] electrochemical polymerization onto the S-steel (anode) electrode surface was carried out in a potentiostat. The polymer-coated and uncoated stainless steel corrosion safety test was studied in a solution of 0.2 M HCl, followed by Tafel and Potentiostatic procedures at temperature 293 K. Nano materials such as ZnO were applied to the monomer solution at different concentrations to enhance the resistance for corrosion the 316L stainless steel surface, so that tests showed that the performance values of corrosion protection for the polymer coating increase with the introduction of nano materials.[13C-NMR, 1H-NMR, and FTIR] were recorder to confirm the structure of polymers, measurement of some of its physical properties and atomic force microscope(AFM), scanning electron microscope(SEM).

Keyword: Electropolymerization, polymer, triazole, corrosion

1. INTRODUCTION

The heterocyclic compounds of five members; in particular, heterocycles of nitrogen ;Triazoles have been shown to have certain desirable characteristics, such as high acid / basic hydrolysis stability and metabolic degradation / resistance and reduction conditions[1]. The triazoles is currently regarded as an significant moiety in the design and synthesis of bioactive compounds associated with a broad variety of biological activities [2] For example, antifungal, antibacterial [3], antiinflammatory[4], anti-HIV[5] anti-tumor[6]. Additionally, there are analysis studies showing that 1,2,4-triazoles have a distinctive position in the field of medicinal and pharmaceutical chemistry[7] as well as in the agricultural and polymer applications[8,9].The development of a new generation of polymers has drawn a great deal of attention from researchers [10]. Many conductive polymers have been synthesized by electropolymerization methods[11], this approach allows for uniform coating on the surface of the electrode, whose
thickness can be easily changed by reaction conditions. Additionally, the approach to electropolymerisation is simple to apply and has the ability to better control the resulting polymer properties[12]. The use of polymers to protect metal from corrosion has been explored in several studies, these polymers are electrically conductive due to their widely π-conjugated backbone which allows the flow of layer metal current to suppress the corrosion reactions due to their reversible redox activity[13]. More recently, the emphasis has been on the manufacture of nanostructured polymers as these polymer nanostructures not only retain their unique properties but also have the characteristics of nanomaterials such as large surface area and quantum effect, the fascinating properties of these nanostructured polymer films have been used in a variety of applications[14]. And enhanced electrical, mechanical, magnetic, optical, and corrosion (properties far better than their individual components because of the electro-active and conductive nature of these polymers[15]. Nano-material polymers are the best candidates for minimizing the risk of corrosion on steel structures[16]. Via electropolymerization method, we synthesize new polymers in the main chain that include 1,2,4-triazole rings, then research the corrosion behavior of uncoated and coated (316) stainless steel with and without nanomaterials using Potentiostatic technique in 0.2 M HCl solution with different concentrations of Nano ZnO.

2. EXPERIMENTA

2.1. Materials and Measurements
All starting materials and solvents have been collected from(Fluka and Sigma-Aldrich). On aluminum coated TLC plates 60 F245 (E. Merck) the completion of the reaction and purity of all compounds is tested using ethyl acetate and hexane as the mobile phase and imagined under iodine vapour. (Softening points) were measured using a cofler-method thermal microscope. Thermovar to Reichert. SP. 10.25, 160 and the melting points were measured and uncorrected on GallenKamp capillary melting point apparatus. Measurements in the Shimadzu model (FTIR-8400S) were reported (FT-IR). Spectra (1HNMR and 13CNMR) were obtained with the Bruker ultra-shield spectrophotometer model at 400 MHz in DMSO solution with the TMS as internal standard. Zeiss / Sigma (SEM), Germany. AA3000/220V, Angstrom Advanced Inc. (AFM) U.S.A.

2.2. Synthesis of Ethyl-2-(amino benzo[d]thiazol)acetate[17][1]
Dissolve 2-aminobenzimidazole (0.01 mole) in acetone (20 ml) with anhydrous potassium carbonate (0.01 mole). And added drop wise ethyl chloroacetate (0.01 mole). The mixture was refluxed for 12 hours after completion of the addition, and then allowed to cool down to room temperature. The acetone was evaporated, The precipitated was collected and recrystallized with absolute ethanol. Table( 1) gives the physical properties of the synthesized compound (1).

2.3. Synthesis of 2-(amino benzo[d]thiazol)aceto hydrazide[17][2].
hydrazine hydrate (0.02 mole) was added to a mixture of ethyl -2-(amino benzo[d]thiazol) acetate (1, 0.01 mole) and methanol (20 ml), than refluxed for 10 hours. The excess of
solvent was removed and the obtained solid was filtered then recrystallised from ethanol. Table (1) gives the physical properties of the synthesized compound (2).

**2.4. Synthesis of 2-[N-(5-vinyl-1H-1,2,4-triazol-3-methyl) amino] benzo[d]thiazole** (18)[3].

In the presence of THF as a solvent, a mixture of compound 2-(aminobenzo[d]thiazol)aceto hydrazide (2, 0.01 mole), acrylonitrile (0.01) mole and (0.02mol) of K₂CO₃ was reflux for 18 hours, cooling the product obtained, excess of solvent was removed. The solid separated was filtered and recrystallized with ethanol. Table (1) gives the physical properties of the prepared compounds (3).

3. Electrochemical polymerization

3.1 Electrochemical polymerization of 2-[N-(5-vinyl-1H-1,2,4-triazol-3-methyl) amino] benz[d]thiazole** (19) [3].

Using a controlled DC power supply, compound [3] electrochemical polymerization onto the S-steel (anode) electrode surface was carried out in a potentiostat. The electrodes were cleaned by acetone, deionized water and dried. Electropolymerization preparation solution involving dissolving (0.1 g) compound (3) in 100 ml of H₂O, then apply three drops of conc. H₂SO₄ (37 per cent), the polymerization was done at 1.1V and 293K. The polymer film was mounted on the electrode surface of the anode. In addition, nanomaterials involving Nano ZnO (0.02, 0.04) g were combined with monomer solution after dispersion and applied to the monomer solution to improve the corrosion protection performance of the film coating.

3.2 Electrochemical corrosion measurement

The corrosion cell, with all instruments(cell, electrodes and a working electrode holder) was performed using advanced potentiostat. The polarization curves were measured from the open circuit potential -200 to 200 mv and the corrosion current icorr respectively. Corrosion potentials Ecorr was tested for polarization curves at two concentrations using extrapolation of the cathodic and anodic Tafel axes. At temperature (293 K) the corrosion measurements for S.S were analyzed in solution of 0.2 M HCl.

### Table1: The physical properties of all compounds

<table>
<thead>
<tr>
<th>No. of comp.</th>
<th>Structure and names of polymer</th>
<th>Chemical formula</th>
<th>Color</th>
<th>Molecular weight</th>
<th>Melting Point °C</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethyl-2-(aminobenzo[d]thiazole) acetate</td>
<td>C₁₁H₁₂N₂O₂S</td>
<td>Pale yellow</td>
<td>236.29</td>
<td>133-135</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>Structure</td>
<td>Chemical Formula</td>
<td>Appearance</td>
<td>mp (°C)</td>
<td>Yield (%)</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-----------</td>
<td>------------------</td>
<td>------------</td>
<td>---------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Structure 2" /></td>
<td>C$<em>9$H$</em>{10}$N$_4$OS</td>
<td>white</td>
<td>222.27</td>
<td>222-224</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Structure 3" /></td>
<td>C$<em>{12}$H$</em>{11}$N$_2$S</td>
<td>Brown</td>
<td>257.31</td>
<td>106-108</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Structure 4" /></td>
<td>C$_{12}$H$_9$N$_2$S</td>
<td>Light yellow</td>
<td>255.29</td>
<td>190-200</td>
<td>69</td>
</tr>
</tbody>
</table>

4. Results and discussion

4.1. Synthesis:

Scheme 1 included all compounds synthesis. The experimental section contains data on characterisation of all compounds (1–4). All synthesized compounds received a favorable analysis of the suggest structures, which was confirmed using FTIR, 13CNMR and 1HNMR.

Scheme (3.29): The chemical steps for the synthesis of compounds (72-75).
4.2. FT-IR spectra

FTIR spectrum of compound [1] showed appearance of characteristic absorption bands at 1747 cm\(^{-1}\), which belong to \(\nu(C=O)\) ester together with band around 3278 cm\(^{-1}\) region for the (N―H) stretching characteristic. These two points are excellent proofs for the success of ester formation. Figure (1) and (Table 2) show the interesting stretching vibration bands for compound (1).

Compound[2]: By contrasting FTIR spectra of products, figures (1) with those in figure (2), it is easy to see the disappearance of \((C=O)\) ester stretching band at \((1737)\) cm\(^{-1}\) as well as vibration bands that corresponds to \((C=O \text{ amide})\) at \((1670)\) cm\(^{-1}\) which are appeared, table (2) show the IR spectrum for compound (1).

Compound[3]: In figures (3) can see the disappearance of \((-\text{NH}_2)\) stretching band at \((3486,3384)\) cm\(^{-1}\) as well as vibration bands that corresponds to \((C=C \text{ olefin})\) at \((1630)\) cm\(^{-1}\) which are appeared, table (2) show the IR spectrum for compound (3).

Compound[4]: FTIR spectrum of compound [4] and figures (4) showed disappearance of \((C=C)\) stretching band at \((1630)\) cm\(^{-1}\), in table (2) can see the IR spectrum for compound (4).

Table 2: Characteristic IR absorption bands of compounds (1-4)

<table>
<thead>
<tr>
<th>poly. No.</th>
<th>Characteristic IR Absorption Bands (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\nu) C-H aromatic</td>
</tr>
<tr>
<td>72</td>
<td>3062</td>
</tr>
<tr>
<td>73</td>
<td>3053</td>
</tr>
<tr>
<td>74</td>
<td>3063</td>
</tr>
<tr>
<td>75</td>
<td>3033</td>
</tr>
</tbody>
</table>
4.3. NMR Spectra:
The spectrum of compound\textsuperscript{(21)} \textsuperscript{1}HNMR and \textsuperscript{13}CNMR (3) are mentioned in Table 3.

**Table (3) \textsuperscript{1}HNMR and \textsuperscript{13}CNMR data (3) for compound in ppm.**

<table>
<thead>
<tr>
<th>poly. No.</th>
<th>polymer structure</th>
<th>\textsuperscript{1}HNMR data in ppm</th>
<th>Fig. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>(\text{HNMR data in ppm})</td>
<td>(\delta 3.53 (s, -2H, CH_2), \delta 4.04 (s, -1H, NH), 7.35-7.83 (m, 4H, ArH), \delta 8.48 (1H, NH triazole ring), 6.33 (dd, 1H, H-1), 5.04 (dd, 1H, H-2), 4.46 (dd, 1H, H-3))</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>poly. No.</th>
<th>polymer structure</th>
<th>\textsuperscript{13}C-NMR data in ppm</th>
<th>Fig. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>(\text{HNMR data in ppm})</td>
<td>(C_1, C_2, C_6, C_7, C_8, C_9, C_{10}, C_{11}=116.66-137.16; C_3 = 147.70; C_4 = 35.05; C_5 = 161.40)</td>
<td>6</td>
</tr>
</tbody>
</table>
4.4. Mechanism of polymerization

A cationic \(^{(22,23)}\) or a radical mechanism\(^{(24-26)}\) may be proposed on the basis of the published literature to describe electro polymerization reactions and, in particular, the grafting and development of the (polymer 4) films.

Cationic mechanism (Scheme 1) is considered: Applying anodic potential to a compound solution (3) implies passing one electron from the monomer to the working electrode (A1). This transfer contributes to the formation of an adsorbed radical cation on the surface of the electrode which is represented in A2, if the lifetime of A2 is sufficiently long compared with the mean time that an compound(3) molecule diffuses toward the electrode, then the compound(3) molecules can be attached to the charged ends of the adsorbed oxidized compound(3)(A4) through a cationic mechanism. This propagation mechanism contributes to the creation of a grafted polymer.

Again with the (scheme 1): consider a radical mechanism. The radical counterpart of A is B. First, the chemisorbed radical illustrated in B can not be the product of an electrochemical operation. If we conclude that the grafting phase is detached from the electrochemical process, we are nevertheless confronted with the fact that under the current electrochemical, conditions the radical mechanism is not especially desirable. Indeed, a hemolytic scission of the double bond (Scheme 1B) continues via the radical process. Homolytic breakup of the C = C bond, however, is highly unlikely considering the bond's initial polarization which is further enhanced under the field provided by the electric double layer. In addition, this electric field causes a molecule reorientation\(^{(27)}\). This all together makes the radical mechanism very unlikely under anodic electrochemical conditions to account for the grafting and the development of PBM films.
4.5. Atomic force microscope (AFM)

Using the AFM process, the surface topography of polymer-coated stainless steel in the absence and presence of Nano materials [ZnO, (0.002, 0.04) g] was analyzed, showing AFM 3D images of all coated films (Figure 7). The most widely used parameters for characterizing surface roughness in the A analysis are the average diameter, the average roughness (R) and the square of the root mean. These parameters are shown in the table, the results indicate a decrease in surface roughness with an average decrease diameter for three films, the lower rugged surfaces act as a strong barrier to corrosion safety (28).

![Scheme 2: suggest Cationic (A) and Radical (B) Mechanisms for the Growth of polymer (4) Films.](image-url)
4.6. Scanning electron microscope (SEM).

The SEM\(^{(29)}\) images shown in (Figure 8) a degree of agglomeration, more cracks appeared for S.S coated with polymer 4 led's to protection to metal reached to 87.27%, but in other side showed homogeneous layer for coating with nanocomposite with a protection efficiency 94.29%
Figure (6): SEM image of (A) Stainless steel (polymer4) coated without nano material (B) Stainless steel polymer4 coated with ZnO (0.04)

4.7. Potentiostatic polarization measurement

The effect of polymeric coating film has been studied on S-steel's anodic and cathodic polarization curves in (0.2 M HCl) solution at temperature (293)K. The effect of introducing compound nanomaterials (ZnO nano) is shown in Figure(9). The current density of corrosion (Icorr) was determined by extrapolating the anodic and cathodic Tafel lines.

Table(5) shows the effect of polymer coating, with and without nanomaterial on S.S electrode corrosion parameters in a solution of 90.2 M HCl). These parameters are: cathodic Tafel slope (bc), anodic Tafel slope (ba), corrosion current (Icorr), corrosion potential (Ecorr), IE, weight loss and lack of penetration. The following equation (30) indicate the protection efficiency (PE %)

\[ PE\% = \frac{(I_{corr})\text{ uncoated} - (I_{corr})\text{ coated}}{(I_{corr})\text{ uncoated}} \]

The corrosion potential changed to more favorable values, and when the nanomaterial compound added to the monomer solution indicating, the inhibiting effect of these compounds, Icorr decreased. The corrosion potential changed to the noble side when, the polymer film designed with nanomaterial coated on the S-steel. This suggests a film formed on the metal surface of anodic sites (31).

Figure (9) Polarization plots of 316(S-steel ) coated with polymer and nanomaterial in 0.2M HCl at 293K.

Table (5): Corrosion data of 316(Stainless -steel in 0.2M HCl ) with and without coating

<table>
<thead>
<tr>
<th></th>
<th>T/K</th>
<th>Ecorr (mV)</th>
<th>Icorr (μA/cm²)</th>
<th>-bc (mV/sec)</th>
<th>Ba (mV/sec)</th>
<th>WL (g/m².d)</th>
<th>PL (mm/y)</th>
<th>PE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated S.S</td>
<td>293</td>
<td>63.8</td>
<td>34.33</td>
<td>210</td>
<td>234.5</td>
<td>2.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coated S.S with polymer (4)</td>
<td>293</td>
<td>158.4</td>
<td>4.37</td>
<td>119.7</td>
<td>130.5</td>
<td>3.5*10⁻¹</td>
<td>4.75*10⁻¹</td>
<td>87.27</td>
</tr>
<tr>
<td>Coated S.S with polymer (4) modified with 0.02g ZnOn</td>
<td>293</td>
<td>87.7</td>
<td>3.44</td>
<td>96.6</td>
<td>130.9</td>
<td>2.77*10^-1</td>
<td>3.74*10^-2</td>
<td>90</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>-----</td>
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</tr>
<tr>
<td>Coated S.S with polymer (4) modified with 0.04gZnOn</td>
<td>293</td>
<td>23.8</td>
<td>1.96</td>
<td>73.9</td>
<td>109.3</td>
<td>1.58*10^-1</td>
<td>2.14*10^-2</td>
<td>94.29</td>
</tr>
</tbody>
</table>

5. Conclusion

Using of electropolymerized to synthesis of new polymer having heterocycles ring, was found to providing inhibit the corrosion rate in 0.2 M HCl solution. Polymer protection performance increases considerably with the introduction of diffrante concentration of (ZnO nano) materials to the monomer solution, the corrosion potential principles of the coated film on stainless steel moved to the noble path. The corrosion current density (icorr) and corrosion potential (Ecorr) decreased as the concentration of (ZnO nano) increased. The AFM analysis for (polymer 4) with and without nano materials (ZnO) shows that the roughness of the surface decreases as the average diameter decreases and that the smooth, and uniform surfaces serve as a strong barrier to the safety of coatings.

6. References

1. ŞERBAN, G. 2016. 1, 2, 4-Triazoles as Intermediates for the Synthesis of Hybrid Molecules. FARMACIA, 64(4), 549-552.


