Polyamide Nanofibers Coating by Electrospinning Technique for Anti Corrosion Behavior

Abstract—Poly amide (PA-6) nanofiber coatings on aluminum surface using electrospinning technique under two different voltage (24 kV & 34 Kv) were prepared. The coating morphology, roughness and 3D structural properties tested by using Atomic force microscopes (AFM), surface characterized by (SEM) microscopy, and high resolution optical microscopy (HROM). Contact angle for hydrophobic behavior was tested by shape drop analyzer, and FTIR analysis for changing in crystalline structure was performed. The AFM images showed that the PA coating on the aluminum surface have a tight and twisted nanofiber structure with some beads through its morphology. SEM images shows the morphology beads of surface nanofibers. The electrochemical corrosion of aluminum without and with PA coating studied by subjected it to aerobic solutions of 3.5 wt.% sodium chloride (NaCl). It has been found that the PA coatings decrease the corrosion currents and corrosion rate as well as increase the corrosion resistance for aluminum in the NaCl solution.

Keywords—anti-corrosion, nanofibers coating, metal protection, electrospinning

1. Introduction

Electrospinning is a technique to nanofibers prepared with average diameter between (1 nm to some hundreds nm) by using electrostatic forces. These nanofibers have extra excellent properties such as thinner diameter and a larger surface area than those obtained with other spinning processes. [1]. The nanofibers which produce by this method is successfully used in engineering, medicine field, tissue engineering, also it used in industrial application such as coating surface for different applications [2]. Recently, electrospinning is the best technique for prepare coating nanofibers compare with other techniques which used to prepare polymer nanofibers; such as : synthesis of the template, drawing, phase separation, and self-assembly [3-7]. Electrospun nanofibers coating used to improve the corrosion resistances of the coated materials and can be used in a various industries such as coating of pipes and tanks. In addition that nanofibers textile used in filter media involve (gas, liquid, and molecule) filtrations. [8] Corrosion usually occurs at a rate determined by balance between dissimilat electrochemical reactions. The first is the anodic reaction, which a metal is corroded. The other is the cathode reaction, where a solution species (often H⁺ or O₂) is decreased, stripping electrons from the metal. When these two reactions are in balance, the flow of electrons from each reaction is stable, and no obvious electron flow. The two reactions can occurred on one metal or on two various connected metals. We can calculate the corrosion rate from the following equation, also table (1) show the corrosion rate constant

\[
C_{Corrosion} = \frac{I_{corr} \cdot K \cdot E_W}{D \cdot a}
\]

where, \( I_{corr} \) = the current of corrosion (Amps)
\( K \) = a constant according to units of corrosion rate ( = 3272)
\( EW \) = the equivalent weight (= 9)
\( D \) = density (2.7 g / cm³)
\( a \) = area of sample (cm²) = (2 * 2.5 cm²)

Table 1: Corrosion Rate Constants.

<table>
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<tr>
<th>Units of Corrosion Rate</th>
<th>Units</th>
<th>K</th>
<th>Units</th>
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<tr>
<td>milli-inches/year</td>
<td>1.288x10³</td>
<td>mm/year</td>
<td></td>
</tr>
<tr>
<td>(mpy)</td>
<td></td>
<td>3272</td>
<td>mm/(amp-cm-year)</td>
</tr>
<tr>
<td>mm/year</td>
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Our present paper aim to prepare a nanofiber coating of polyamide - 6(PA - 6) on the aluminum surface using the electrospinning technique. This is
for the studying of the effect of PA on the corrosion resistance of aluminum in freely ventilation solutions of 3.5 wt. % (sodium chloride). Tafil's electrochemical corrosion method used for studying the corrosion behavior of samples (with and without coating) under different preparation conditions.

2. Experimental Part

I. Electrospinning of nanofibers coatings

(0.15 Con. %) wt% of (PA + formic acid) solution was prepared for electrospinning pump. This solution stirring with heating (50 -60 °C) for (24 hr). Two samples prepared by electrospinning technique under two different voltage (24, 34 ) kV, and other constant conditions " 15cm electrospinning distance, and 0.3 ml/h solution flow rate. The electrospun nanofibers collected on Aluminum foil surfaces

II. Nanofibers morphological analysis

Surface morphology of electrospun nanofibers coating layers on aluminum surfaces were investigated using optical microscopic with high analysis resolution and atomic force microscopy (AFM). Thickness of coating nanofibers measured by digital micrometer.

III. Corrosion test

A 3.5 wt.% of an aqueous solution of sodium chloride salt used for perform the Tafel's test. The PA aluminum coated and non-coated samples for corrosion measurements were prepared by fixing these samples on glass slide with (2.5 * 3 cm²) area then it connected with insulated copper wire to sample by aluminum conducting tape. The cyclic potentiodynamic polarization (CPP) curves were obtained by sweeping the potential from -1800 mV in the positive direction up to -700 mV vs. corrosion current measured by this test then corrosion rate is calculated from eq. (1).

3. Results and Explanation

I. Surface morphology verification

Figs (1 a,b) show the surface morphology for (a) PA coated aluminum under (24 kV) and (b) PA coated aluminum under (34 kV). All these images were taken using high resolution optical microscopy. Notice from Fig. (1.a) that the PA needle structure layers are tight and homogeneously distributed on the surface. Also with (34 kV) condition for preparation the nanofibers coating leads to more homogenously coating than (24 kV).

Fig (2 a) show the AFM image for PA coating under (24 kV) and fig (2 b) show the AFM image for PA coating under (34 kV) at three dimensions analysis, notice that the nanofibers which preparation under (24 kV) is about (3 µm) and it is more thick than (34 kV) which about (2.5 µm) but it is less compact than (34 kV). this is because increasing of high voltage in electrospinning technique leads to small nanofibers diameter with beads which leads to more compact coating and more roughness. Fig (3) show the SEM images of electrospun coating under (34 kV).

Figure 1: optical images of surface coated by PA nanofibers (a) under (24 kV) (b) under (34 kV)

Figure 2: AFM images of surface coated by PA nanofibers (a) under (24 kV) (b) under (34 kV)
II. contact angle analysis

Fig (4 a) show the contact angle of Al surface is (61°), while it increase to (66°) after coating by PA Nanofibers under (24 kV), as in fig (4 b), and it increases to (129°) after coating by PA nanofibers under (34 kV) as in fig (4 c), this is because the hydrophobic behavior of PA nanofibers specialty under high voltage preparation condition which leads to compact coating with small nanofibers diameter. The hydrophobic effect represents the penchant of water to eliminate non-polar molecules. The effect result from the perturbation of highly effective hydrogen bonds between molecules of liquid water.

III. FTIR Analysis

Fig (5 a) show the FTIR analysis of pure PA , and fig (5 b) show the FTIR analysis of PA nanofibers. Notice that there are a new bonds create after transformation the PA from macrostructure to nanostructure . Also notice from these figs the PA electrospinning nanofibers have more crystallinity than PA macrostructure , increasing of amorphous structure leads to increase the crystalline peak broadness and intensity. Also the nanofibers with high degree of crystallinity consequently the sample of nanofibers coating show the weakest peak. [9], this is proved by Zimba et al. [10] who observed these peaks more clearly in amorphous PA structure than nanocrystalline structures.

IV. corrosion test

Table (2) show the results of corrosion current and corrosion rates for all samples :

Figs ( 6 a,b,c) show the Tafel's curve for all sample we notice from this fig the corrosion rate decrease after coating by nanofibers. It is seen from the polarization curve Fig. 5a that the anodic show very huge passive region, because the formation of aluminum oxide film . This oxide film gains stout with increasing the applied voltage to -717.2 mV vs. In addition to increasing the voltage to the less negative values led to a rapidly increasing of the output current of aluminum, where the passive and thick oxide film secession occurred. This is because not only the potential step but also the pitting corrosion of aluminum. At this condition, the dissolution of aluminum proceeds as follows. [11]
M = M^{+3} + 3e^-
M = Al

The chloride ions attack the weak parts of the oxide film and access the metal surface to form a metal chloride soluble complex that leave to the solution which cause pitting corrosion of metal. [11]

\[ \text{M}_3^{+} + 4\text{Cl}^- = \text{MCl}_4 \]

It is also seen from Fig. 5 b&c and Table 1 that the PA coating on aluminum surface decreased the values of \( j_{\text{corr}} \) and \( K_{\text{corr}} \) which lead to increase the values of RP. Furthermore, the PA coated aluminum electrodes showed less negative values for E\text{Corr}. This indicates that PA nanofiber coatings highly prevent the dissolution aluminum via uniform and pitting corrosion in the chloride test solution and the protection efficiency in the order PA under (34kV) > PA (under 24kV).

**Figure 6:** Tafel’s corrosion curves a. Uncoated Aluminum b. Al coated by PA-6 nanofibers under 24 kV c. Al coated by PA-6 nanofibers under 34 kV

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_{\text{corr}} )</th>
<th>( I_{\text{corr}} )</th>
<th>( j_{\text{corr}} = \frac{I_{\text{corr}}}{A} )</th>
<th>( b_a )</th>
<th>( b_c )</th>
<th>C.R mils/year</th>
</tr>
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<tbody>
<tr>
<td>Al surface</td>
<td>-717.2</td>
<td>6.56 ( \mu )A</td>
<td>1.312 ( \mu )A/cm(^2)</td>
<td>10.1</td>
<td>-509</td>
<td>10</td>
</tr>
<tr>
<td>Al + PA nanofibers coating under 24 kV</td>
<td>-721.2</td>
<td>3.29 nA</td>
<td>0.00065</td>
<td>14.2</td>
<td>-956.3</td>
<td>0.066</td>
</tr>
<tr>
<td>Al + PA nanofibers coating under 34 kV</td>
<td>-721</td>
<td>2.97 nA</td>
<td>0.00059</td>
<td>14</td>
<td>-547</td>
<td>0.060</td>
</tr>
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</table>

**Table 2:** show the results of corrosion test

4. Conclusion

We conclude from this search the PA electruspune nanofibers is very efficiency for protective the metal surface from corrosion , also the increasing of high voltage for preparation to electrosun nanofibers lead to increase the corrosion resistance of metal surface .

Acknowledgement

The authors extend their appreciation to the Technology university / Nano technology research center and Babylon University / Material engineering collage for perform this search.

References


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Author(s) biography

Prof. Dr. Balkees M. Al dabbagh: professor of materials science and technology of composite materials at the University of Technology/ Dep. Of applied Sciences/ Materials Science Branch. She performed hundreds of applied research in the field of modern technology and materials, especially the nanotechnology field, supervised dozens of postgraduate students in various fields including the use of nanomaterials in modern technologies such as prevention and protection in all its forms.

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