

**CORROSION INHIBITION BY RESIN-CONDUCTING POLYMER BASED
COPOLYMER AND COMPOSITES COATINGS**

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Programme : Polymer Science & Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**REÇİNE-İLETKEN POLİMER ESASLI KOPOLİMER VE KOMPOZİT
KAPLAMALAR İLE KOROZYON ÖNLENMESİ**

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ABBREVIATIONS

AC	: Alternative Current
ACN	: Acetonitrile
Al	: Aluminum
CAN	: Ceric amonium nitrate
B_a	: Cathodic Tafel Slope
B_c	: Anodic Tafel Slope
CAN	: Ceric amonium nitrate
CF	: Cyclohexanone-Formaldehyde
CP	: Conducting Polymer
DC	: Direct Current
E_{corr}	: Corrosion Potential
EIS	: Electrochemical Impedance Spectroscopy
Ew.	: Equivalent Weight
f_b	: Break Point Frequency
FTIR	: Fourier Transform Infrared
I_{corr}	: Corrosion Current
LPR	: Linear Polarization Resistance
H₂SO₄	: Sulphuric Acid
PCz	: Polycarbazole
PDMS	: Poly Dimethyl Siloxane
PPy	: Polypyrrole
PS	: Potentiostatic
R_p	: Polarization Resistance

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CORROSION INHIBITION BY RESIN-CONDUCTING POLYMER BASED COPOLYMER AND COMPOSITES COATINGS

SUMMARY

Steel, copper and aluminum are industrially important metals. However, corrosion of them causes enormous lost and several problems. Protection of these industrial metal are very important both economically and dangerous situations that they might cause.

Innovations in polymeric materials allow to use of these materials in corrosion inhibition. Protective coatings generally contain three component; binders, pigments and solvents. Resins are one kind of binders that use in industry. Modern coating technologies require development of high performance materials. Composites are the important class in high performance material. Recently the use of solvent are limited due to volatile component emission rules and thatsway minumum solvent containing or water based systems are preferred.

In this study the effect of polymeric coatings on the corrosion inhibition of aluminum was investigated. Conducting polymers (polypyrrole (PPy), polycarbazole (PCz)), two block copolymers of Py with silicon tegomers (PDMS) (DN4 and DN6), and copolymer of Cz with PDMS (DN1_1) were used as polymeric coatings. PPy and PCz homopolymers were coated electrochemically on Al electrode surface and their performance compared with copolymers.

In order to improve the performance of homopolymers they were used together with cyclohexanone-formaldehyde resin (CF). They dispersed homogeneously in the resin and coated on Al electrode surface and investigated comparatively with unmodified CF.

Electrodes were coated from different solution that contain different amoun of polymer. These solutions added dropwise on electrode surface and different number of layer coated on electrode surface. Corrosion behavior of the polymeric coating was investigated by polarization measurements and electrochemical impedance spectroscopy (EIS) measurements in 1M H₂SO₄ by time. The optimum condition were determined for each coating.

All results suggest that thick coatings show high protection on the surface for fresh coatings. However thinner coatings have better efficiency by increasing exposure time.

The best performance for DN4 were obtained for DN4-1-4 which means a coating obtained from the most diluted solution with four layer. For DN6 copolymer the best one is DN6-1-2. For longer exposure time DN4 which has lower molecular weight

seems more efficient than DN6. DN1.1-1-2 seems the optimum condition for DN1_1 block copolymer.

PPy and PCz modified CF coatings durable material in the acidic medium and they have excellent adhesion and protection for aluminium. Their efficiency is much better than the DN4, DN6 and DN1_1 coatings.

Generally it can be concluded that corrosion protection of PPy and PCz homopolymer coatings can be improved either by copolymerization with silicon tegomer or with dispersing them in a well adherent resin such as CF.

REÇİNE-İLETKEN POLİMER ESASLI KOPOLİMER VE KOMPOZİT KAPLAMALAR İLE KOROZYON ÖNLENMESİ

ÖZET

Çelik, bakır ve alüminyum endüstriyel olarak önemli metallerdir. Ancak korozyonları büyük kayıplara ve tehlikelere sebep olmaktadır. Yol açtıkları ekonomik kayıplar ve tehlikeler dolayısıyla endüstriyel olarak önemli olan bu endüstriyel metallerin korozyonunun önlenmesi çok önemlidir.

Polimerik malzemeler, gelişimleriyle birlikte korozyon korumasında kullanılabilir hale gelmişlerdir. Koruyucu kaplamalar genellikle üç bileşen içerirler; bağlayıcı, pigmentler ve çözücüler. Reçineler bağlayıcıların bir türüdür ve endüstride yaygın kullanılırlar. Modern kaplama teknolojileri yüksek performanslı malzemelerin geliştirilmesine yol açtı ve kompozitler bu tür malzemelerin önemli bir bölümüdür. Son zamanlarda çözücülerin kullanımı uçucuların salınımıyla ilgili bazı düzenlemeler nedeniyle sınırlandırılmıştır bu yüzden, çok düşük miktarda çözücü içeriğine sahip veya su bazlı sistemler tercih edilir.

Bu çalışmada polimerik kaplamaların alüminyumun korozyonunu önlemedeki etkileri incelenmiştir. İletken polimer olarak (polipirol (PPy), polikarbazol (PCz)), silikon tegomer (PDMS) ile pirol (Py) den oluşan iki blok kopolimer (DN4 ve DN6) ve silikon tegomer (PDMS) ile karbazol (Cz) blok kopolimerleri kaplamalarda kullanıldı. Pirol(PPy) ve karbazol(Cz) homopolimerleri alüminyum yüzeyine elektrokimyasal olarak kaplanarak, performansları yukarıda adı geçen kopolimerler ile karşılaştırılmıştır.

Elektrotlar farklı miktarlarda polymer içeriğine sahip çözeltiler kullanılarak kaplandılar. Bu çözeltiler elektrot yüzeyine damlatılarak kaplamalar yapılmış oldu ve farklı katman sayıları elektrotlar yüzeyine kaplanmıştır. Polimerik kaplamaların 1 M H₂SO₄ içerisindeki korozyon davranışları, polarizasyon ölçümleri ve elektrokimyasal empedans spektrumu (EIS) ölçümleri kullanılarak elde edilmiştir. Her kaplama için optimum koşullar belirlenmiştir.

Bütün sonuçlar, asidik ortama ilk daldırıldıklarında kalın olan kaplamaların daha yüksek bir korumaya sahip olduklarını ancak artan zamanla, korozyona uzun süre maruz kalan kaplamalarda ince kaplamaların daha iyi bir performans ortaya koyduğunu göstermiştir.

DN4 grubu için en iyi korozyon koruması DN4-1-4 sağlanmıştır ve DN4-1-4 bu grup içerisindeki en düşük konsantrasyonlu kaplamadır ve 4 katman halinde yüzeye uygulanmıştır. DN6-1-2 ise DN6 grubu içerisindeki, korozyona en dayanıklı olan kaplamadır. DN4, DN6 dan daha düşük moleköl ağırlığına sahiptir ve uzun süre asite maruz kaldıklarında DN6 dan daha etkilidir. DN1_1-1-2 ise DN1_1 grubunun en verimli kaplamasıdır.

PPy ve PCz ile modifiye edilen CF kaplamaları dayanıklı malzemelerdir ve asit içerisinde mükemmel yapışma ve koruma özelliklerine sahiptirler ve DN4, DN6, DN1_1 ürünlerinden daha etkilidirler.

Sonuç olarak PPy ve PCz homopolimerlerinin korozyon koruması, silikon tegomer ile oluşturulacak blok kopolimerleri veya CF reçinesi içerisinde dağıtılarak yapılan karışımları ile geliştirilebilir.

1. INTRODUCTION

Corrosion is defined in different ways, but the usual interpretation of the term is “an attack on a metallic material by reaction with its environment”. Polymer coatings have long been studied for their possible use in anticorrosive applications[1-11].

Corrosion of metallic materials can be divided into three main groups :

1. Wet corrosion, where the corrosive environment is water with dissolved species. The liquid is an electrolyte and the process is typically electrochemical.
2. Corrosion in other fluids such as fused salts and molten metals.
3. Dry corrosion, where the corrosive environment is a dry gas. Dry corrosion is also frequently called chemical corrosion and the best-known example is hightemperature corrosion.

In general, the development of modern society and industry has led to a stronger demand for engineers with specialized knowledge in corrosion. There are a number of reasons for this:

- a) The application of new materials requires new corrosion knowledge.
- b) Industrial production has led to pollution, acidification and increased corrosivity of water and the atmosphere.
- c) Stronger materials, thinner cross-sections and more accurate calculation of dimensions make it relatively more expensive to add a corrosion allowance to the thickness.
- d) The widespread use of welding has increased the number of corrosion problems.
- e) The development of industrial sectors like nuclear power production and offshore oil and gas extraction has required stricter rules and control.
- f) Considering the future, it should be noticed that most methods for alternative energy production will involve corrosion problems.

The ability of conducting polymer coatings to protect metal surfaces has led to growing interest, particularly in the last 3–4 years, to synthesis these coatings on iron, aluminum and their alloys in order to assess the corrosion protection that they afford. However, very few studies have been carried out on the corrosion protection of copper by conducting polymer coatings, despite the use of this material in wide range of technological applications[12].

The cost of corrosion in industrialized countries has been estimated to be about 3–4% of the gross national product. It has been further estimated that about 20% of this loss could have been saved by better use of existing knowledge in corrosion protection, design etc. In other words, there is a demand for applied research, education, information, transfer of knowledge and technology, and technical development. Teaching, where considerable emphasis is placed on the connections between practical problems and basic scientific principles, is considered to be of vital importance.

Corrosion and corrosion prevention is more interdisciplinary than most subjects in engineering. Consequently, mastery of corrosion means that it is necessary to have insight into physical chemistry and electrochemistry, electronics/electrical techniques, physical metallurgy, the chemical, mechanical and processing properties of materials, fluid dynamics, the design of steel structures and machines, joining technology, and the materials market situation. These areas of knowledge constitute the foundation upon which corrosion technology is built [13].

2. RECOGNIZING THE FORMS OF CORROSION

2.1 Recognizing Corrosion

Group I: Identifiable by visual inspection;

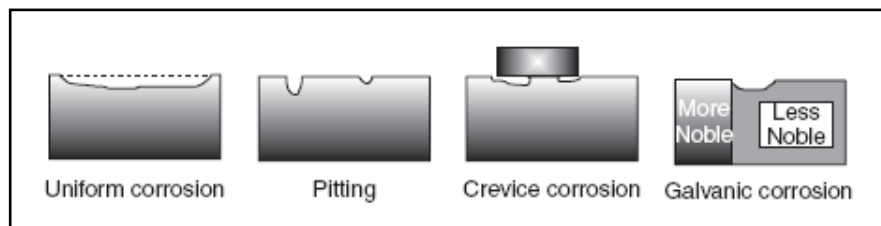


Figure 2.1: Forms of uniform corrosion, pitting, crevice corrosion, and galvanic corrosion.

Group II: Identifiable with special inspection tools;

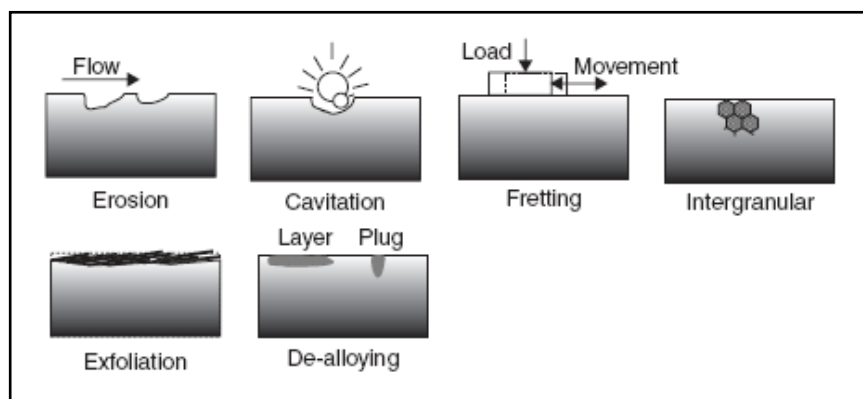


Figure 2.2: Forms of erosion, cavitation, fretting, intergranular, exfoliation, and de-alloying corrosions.

Group III: Identifiable by microscopic examination;

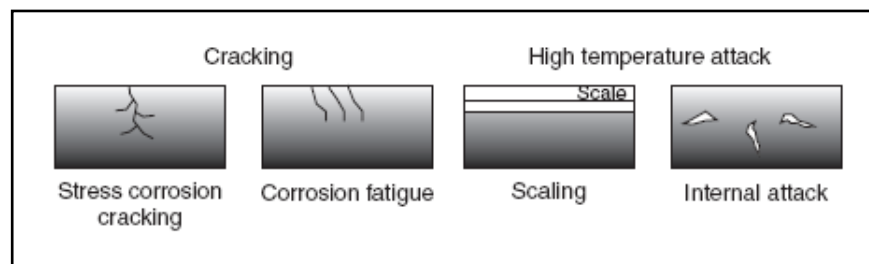


Figure 2.3: Forms of stress corrosion cracking, corrosion fatigue, scaling, and internal attack.

Group I: Corrosion problems readily identifiable by visual examination.

1. Uniform corrosion is characterized by an even, regular loss of metal from the corroding surface.
2. Localized corrosion during which all or most of the metal loss occurs at discrete areas. In this scheme crevice corrosion is said to be a particular form of pitting usually due to localized differences in the environment (pitting crevice).
3. Galvanic corrosion occasioned by electrical contact between dissimilar conductors in an electrolyte.

Group II: Corrosion damage that may require supplementary means of examination for identification.

4. Velocity effects include erosion–corrosion, a form of attack caused by high velocity flow; cavitation caused at even higher flow by the collapse of bubbles formed at areas of low pressure in a flowing stream; and fretting that is caused by vibratory relative motion of two surfaces in close contact under load (erosion–corrosion, cavitation, fretting).
5. Intergranular corrosion at the grain boundaries in the metal structure (*intergranular, exfoliation*).
6. Dealloying corrosion due to the selective dissolution of one component of an alloy.

Group III: Corrosion specimens for these types should usually be verified by microscopy of one kind or another.

7. Cracking phenomena includes corrosion fatigue, a mechanical phenomenon enhanced by nonspecific corrosive environments, and environmental racking, in which a brittle failure is induced in an otherwise ductile material under tensile stress in an environment specific for the alloy system (*stress corrosion cracking, fatigue*).
8. High-temperature corrosion (*scaling, internal attack*).
9. Microbial effects caused by certain types of bacteria or microbes when their metabolism produces corrosive species in an otherwise innocuous environment, or when they produce deposits which can lead to corrosion attack.

Many of the forms in the previous list are more families or multiple forms of corrosion damage. It is obvious that pitting and crevice corrosion, for example, are quite distinct in how they occur, have very dissimilar triggering mechanisms, and would be prevented by totally different methods [14].

2.2 Pitting Corrosion

Probably the most common type of localized corrosion is pitting, in which small volumes of metal are removed by corrosion from certain areas on the surface to produce craters or pits that may culminate in complete perforation of a pipe or vessel wall. Pitting corrosion may occur on a metal surface in a stagnant or slow-moving liquid. It may also be the first step in crevice corrosion, poultice corrosion, and many of the corrosion cells.

Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict, and design against. A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system. Only a small amount of metal is corroded, but perforations can lead to costly repair of expensive equipment.

Pitting cavities may fill with corrosion products and form caps over the pit cavities sometimes creating nodules or tubercles. While the shapes of pits vary widely. They are usually roughly saucer-shaped, conical, or hemispherical for steel and many associated alloys.

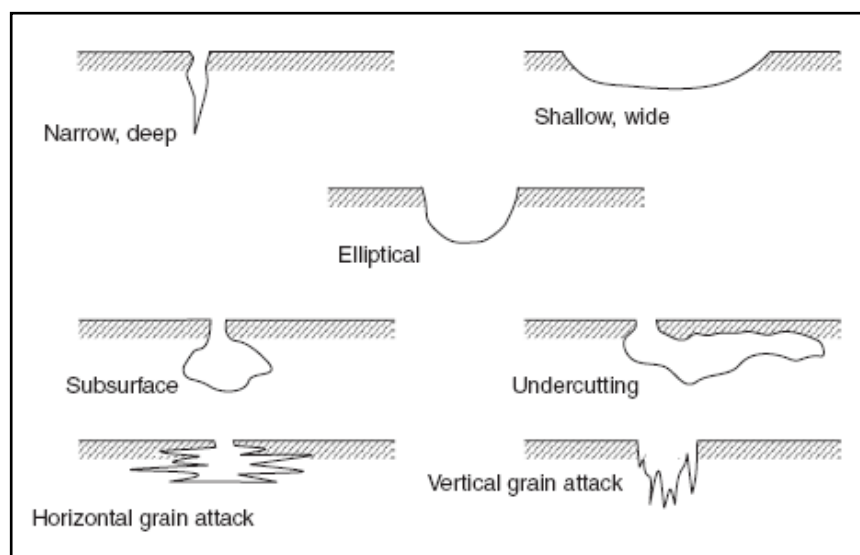


Figure 2.4: Typical cross-sectional shapes of corrosion pits.

The following are some factors contributing to initiation and propagation of pitting corrosion:

- Localized chemical or mechanical damage to a protective oxide film

Water chemistry factors that can cause breakdown of a passive film such as acidity, low dissolved oxygen concentrations which tend to render a protective oxide film less stable and high chloride concentrations

- Localized damage to or poor application of a protective coating
- The presence of nonuniformities in the metal structure of the component, for example, nonmetallic inclusions [14].

2.2.1 Penetration mechanism

The penetration mechanism requires transfer of the aggressive anions through the passive layer to the metal-oxide interface, where they cause further specific action. The high electrical field strength and a high defect concentration within the presumably severely disordered structure of the passivating oxide layer may explain this transfer.

2.2.2 Film breaking mechanism

The occurrence of fissures within the passive layer is a possible explanation for the observations mentioned last, especially for a nonstationary state of the passive layer. A sudden change of the electrode potential even in a negative direction will cause stresses within the film. Chemical changes or electrostriction is a reasonable explanation.

2.2.3 Adsorption mechanism

The adsorption mechanism for pit nucleation starts with the formation of surface complexes that are transferred to the electrolyte much faster than uncomplexed Fe^{2+} ions.

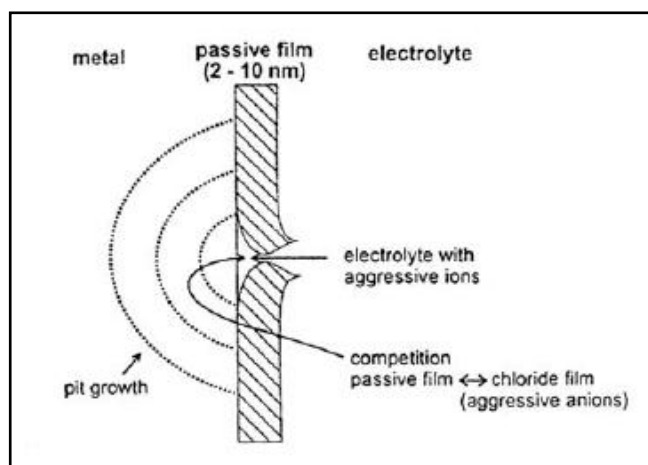


Figure 2.5: Film breaking mechanism and related competing processes.

Electrochemical and surface analytical methods for the study of passive layers and their breakdown have been very successful in the past, and closer insight into the effective mechanisms has been achieved. STM and SFM (Scanning Force Microscopy) will give valuable information about the nucleation and very early stages of growth of corrosion pits. The application of these methods for fundamental studies of pitting corrosion has just started. Further investigations using these methods and extension to other metals will broaden the experience and knowledge and will give better insight into the mechanisms of this technologically important type of corrosion [15].

2.3 Crevice Corrosion

Crevice corrosion is a localized type of corrosion occurring within or adjacent to narrow gaps or openings formed by metal-to-metal or metal-to-nonmetal contact. It results from local differences in oxygen concentrations, associated deposits on the metal surface, gaskets, lap joints, or crevices under bolts or around rivet heads, where small amounts of liquid can collect and become stagnant [16].

Crevices may be produced by design or accident. Crevices caused by design occur at gaskets, flanges, rubber O-rings, washers, bolt holes, rolled tube ends, threaded joints, riveted seams, overlapping screen wires, lap joints, beneath coatings (filiform corrosion) or insulation (poultice corrosion), and anywhere close-fitting surfaces are present.

Resistance to crevice corrosion can vary from one alloy-environment system to another. Although crevice corrosion affects both active and passive metals, the attack is often more severe for passive alloys, particularly those in the stainless steel group. Breakdown of the passive film within a restricted geometry leads to rapid metal loss and penetration of the metal in that area.

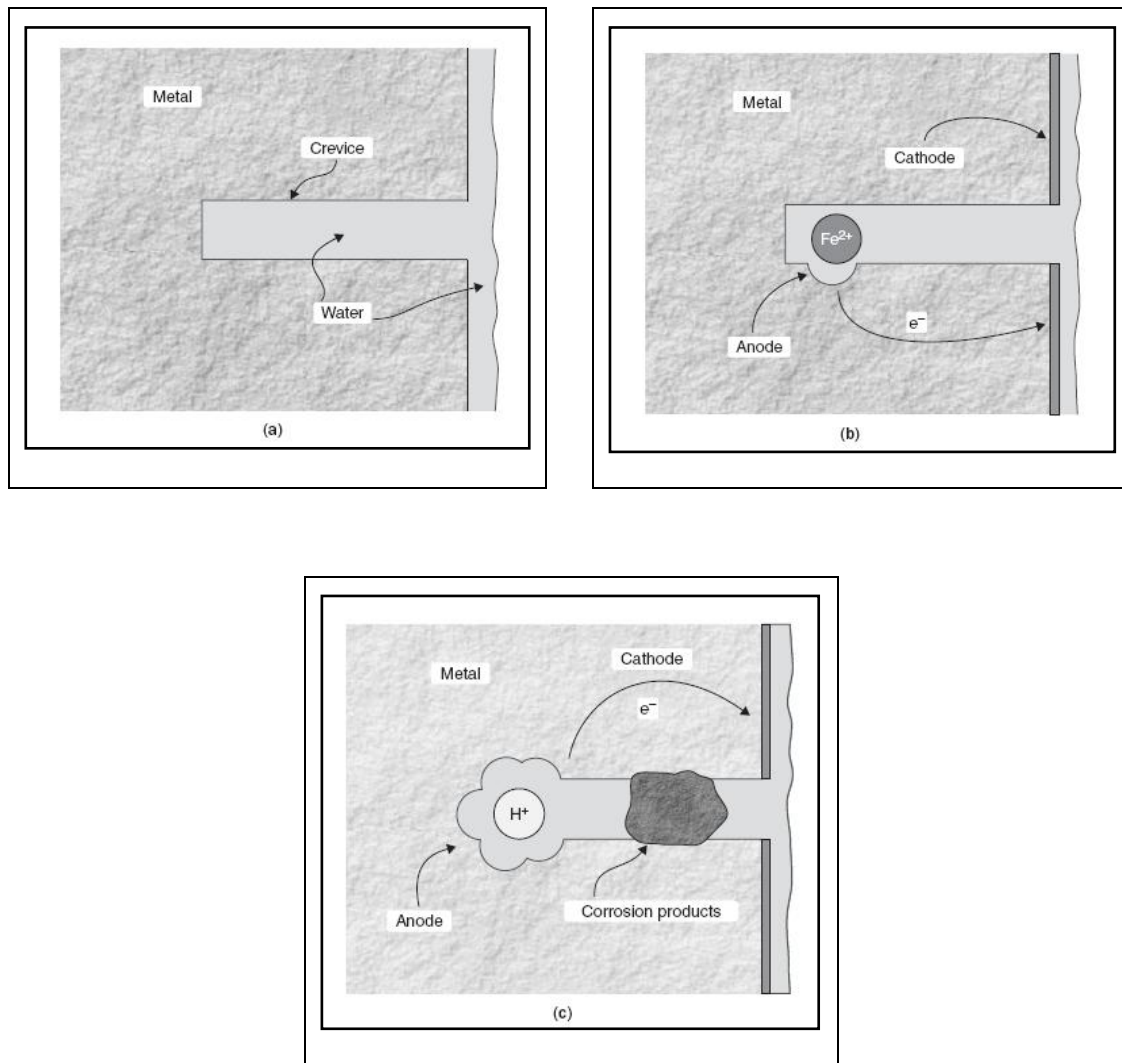


Figure 2.6: Schematic description of the stages of a crevice formation: (a) first stage; (b) second stage; (c) third stage.

Crevice corrosion can be prevented or reduced through improved design to avoid crevices, regular cleaning to remove deposits, by selecting a more corrosion-resistant material, and by coating carbon steel or cast iron components with epoxy or other field-applied or factoryapplied organic coatings [17].

2.4 Galvanic Corrosion

This form of corrosion is sometimes referred to as dissimilar metal corrosion, and is found in unusual places, often causing professionals the most headaches. Galvanic corrosion is often experienced in older homes where modern copper piping is connected to the older existing carbon steel lines. The coupling of the carbon steel to the copper causes the carbon steel to corrode. The galvanic series of metals provides details of how galvanic current will flow between two metals and which metal will corrode when they are in contact or near each other and an electrolyte is present.

When two different metallic materials are electrically connected and placed in a conductive solution (electrolyte), an electric potential exists. This potential difference will provide a stronger driving force for the dissolution of the less noble (more electrically negative) material. It will also reduce the tendency for the more noble metal to dissolve. Precious metals gold and platinum are at the higher potential (more noble or cathodic) end of the series (protected end), while zinc and magnesium are at the lower potential (less noble or anodic) end. It is this principle that forms the scientific basis for using such materials as zinc to sacrificially protect the stainless steel drive shaft on a pleasure boat [18].

When joining two dissimilar metals together, galvanic corrosion can be prevented by insulating the two metals from each other. For example, when bolting flanges of dissimilar metals together, plastic washers can be used to separate the two metals [19].

2.5 Intergranular Corrosion

Intergranular corrosion is a form of localized attack in which a narrow path is corroded out preferentially along the grain boundaries of a metal. It often initiates on the surface and proceeds by local cell action in the immediate vicinity of a grain boundary. Although the detailed mechanism of intergranular corrosion varies with each metal system, its physical appearance at the microscopic level is quite similar for most systems. The effects of this form of attack on mechanical properties may be extremely harmful [14].

If pure zinc-aluminum alloys are exposed to temperatures in excess of (70°C) under wet or damp conditions, intergranular corrosion might take place. The use of these alloys should be restricted to temperatures below (170°C) [20].

2.6 Dealloying Corrosion

Dealloying, also referred to as selective leaching or parting corrosion, is a corrosion process in which the more active metal is selectively removed from an alloy, leaving behind a porous weak deposit of the more noble metal. Specific categories of dealloying often carry the name of the dissolved element. For example, the preferential leaching of zinc from brass is called dezincification. If aluminum is removed, the process is called dealuminification, and so forth. In the case of gray iron, dealloying is called graphitic corrosion.

In the dealloying process, typically one of two mechanisms occurs: alloy dissolution and replating of the cathodic element or selective dissolution of an anodic alloy constituent. In either case, the metal is left spongy and porous and loses much of its strength, hardness, and ductility.

Dezincification can be prevented by alloy substitution. Brasses with copper contents of 85% or more resist dezincification. Some alloying elements also inhibit dezincification (e.g., brasses containing 1% tin). Where dezincification is a problem, red brass, commercial bronze, inhibited admiralty metal, and inhibited brass can be successfully used [17].

2.7 Hydrogen-Induced Cracking

The HIC mechanism has not yet fully established. Various factors are believed to contribute to unlocking the lattice of the metal, such as hydrogen pressure at the crack tip, the competition of hydrogen atoms for the lattice-bonding electrons, easier plastic flow of dislocations in the metal at the crack tip in the presence of hydrogen, and the formation of certain metal hydrides in the alloy [14].

2.8 Hydrogen Blistering

Hydrogen blistering literally means the formation of surface bulges resembling a blister. The generation of hydrogen gas in voids or other defect sites located near the

surface can lead to such a condition. The blisters often rupture, producing surface cracks. Internal hydrogen blistering along grain boundaries (fissures) can lead to hydrogen-induced stepwise cracking.

Hydrogen blistering is encountered mostly during acid pickling operations. Corrosion-generated hydrogen causes blistering of steel in oil well equipment and petroleum storage and refining equipment [16].

2.9 Erosion Corrosion

When there is a relative movement between a corrosive fluid and a metallic material immersed in it, the material surface is in many cases exposed to mechanical wear effects leading to increased corrosion, which we usually call erosion corrosion.

Erosion corrosion may be accompanied by pure mechanical erosion, by which solid particles in the fluid may tear out particles from the material itself and cause plastic deformation, which may make the metal even more active. Erosion corrosion can be divided into two types :

- a) Impingement corrosion, often occurring in systems with two-phase or multiphase flow, particularly where the flow is forced to change direction. Numerous impacts from liquid drops in a gas stream, or particles or gas bubbles in a liquid flow lead to pits with a direction pattern. In cases with solid particles, where corrosion products are removed and the surface locally activated.
- b) Turbulence corrosion, which occurs in areas with particularly strong turbulence such as the inlet end of heat exchanger tubes [13].

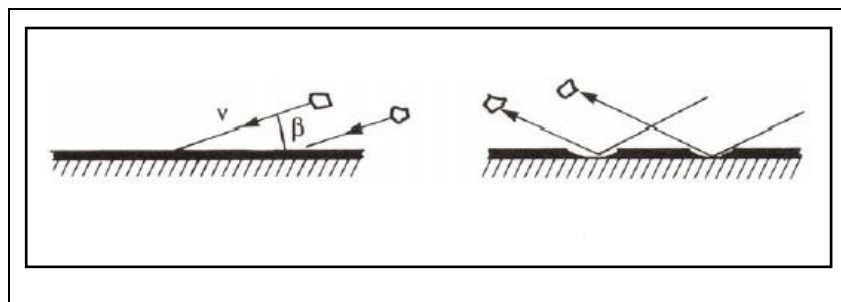


Figure 2.7: Impacts from solid particles in a liquid flow causing removal of corrosion products from the surface (erosion corrosion).

Erosion corrosion may be considered at the design stage when a wider range of options is available to prevent its occurrence than if it occurs after the item of plant has been built [21].

3. CORROSION PREVENTION

3.1 Principles of Prevention

Five different main principles can be used to prevent corrosion:

1. Appropriate materials selection
2. Change of environment
3. Suitable design
4. Electrochemical, i.e. cathodic and anodic protection
5. Application of coatings

The choice between these possibilities is usually based upon economic considerations, but in many cases aspects such as appearance, environment and safety must also be taken care of. Two or more of the five principles are commonly used at the same time.

3.2 Corrosion Protection by Coatings

Through the application of coatings, corrosion is prevented by one of the following three main mechanisms or by combination of two of them:

- i) Barrier effect, where any contact between the corrosive medium and the metallic material is prevented.
- ii) Cathodic protection, where the coating material acts as a sacrificial anode.
- iii) Inhibition/passivation, including cases of anodic protection.

When other protective strategies are inappropriate or uneconomic, active metals must be protected by applied coatings. The most familiar coatings are paints, a term covering various organic media, usually based on alkyd and epoxy resins, applied as liquids which subsequently polymerize to hard coatings. They range from the oil-based, air-drying paints applied by brush used for civil engineering structures, to

thermosetting media dispersed in water for application by electrodeposition to manufactured products, including motor vehicle bodies. Alternatively, a vulnerable but inexpensive metal can be protected by a thin coating of an expensive resistant metal, usually applied by electrodeposition. One example is the tin coating on steel food cans; another is the nickel/chromium system applied to steel where corrosion resistance combined with aesthetic appeal is required, as in bright trim on motor vehicles and domestic equipment. An important special use of a protective metal coating is the layer of pure aluminum mechanically bonded to aluminum aircraft alloys, which are strong but vulnerable to corrosion [22]. The research of increased stiffness, but low-density material is a key point for several industries especially for aerospace, since structural weight reduction is a very efficient means of improving aircraft performance. The research of more advanced materials with high specific properties is therefore mandatory for such industry. Li–Al alloys are among the candidate materials because the addition of lithium to aluminium reduces the overall alloy's weight (1 wt.% Li added to Al reduces the density by 3%) and increases the elastic modulus. Furthermore, fatigue crack resistance in Al–Li alloys is high; allowing the use of such alloy as important structural material. In contrast to new materials systems such as fibre-reinforced composites, Li–Al alloys do not require large capital investments in new fabricating facilities, resulting in being more cost effective than composites in some applications. However, these materials exhibit poor corrosion resistance, suffering several types of degradation (exfoliation, pitting, intergranular and intersubgranular corrosion, etc.) that strongly limits their usage in hostile environments [23].

The corrosion protection in conventional coatings was generally achieved with the use of inhibitors such as metallic pigments, metal oxides and salts at relatively high volume concentrations. Due to the strict environmental regulations on the use of heavy metal containing paints, the new class of primers based on polyaniline (PANI) have received much attraction. Significant advancements have been made in utilizing inherently conducting polymers in the formulation of corrosion resistant coatings to eliminate the requirement of toxic inhibitors. The advantages of intrinsically conducting polymers over conventional inhibitors are their low density, thermal and chemical stability. Electropolymerised coatings of polyaniline, polypyrrole, polythiophene and polyindole on steel have found to offer good corrosion protection.

Oil based alkyds are perhaps the most widely used industrial protective coating material by virtue of their ease of application, relatively low cost, color stability, and good weather ability in most atmospheric environments. Therefore, it is reasonable to assume that coating formulators would seek to improve properties of the drying oil alkyd by modification with conducting polymer. These modifications are expected to enhance the corrosion-protective properties thereby making the material cost effective. Hence, taking into consideration the economic and environmental significance of the utilization of sustainable resource based raw materials for the development of polymers so as to replace the polymers derived from petrochemicals, the present study reports the corrosion-protective performance of soy oil alkyd coatings using different loadings of PANI (0.5 wt%, 1.5 wt% and 2.5 wt%). The coatings were evaluated for their physico-mechanical properties, corrosion-protective efficiency as well as corrosion potential studies. The morphology of the corroded specimens (coated and uncoated) were analyzed by SEM studies. [24]

3.2.1 Metallic coatings

Metal coatings are applied by dipping, electroplating, spraying, cementation, and diffusion. The selection of a coating process for a specific application depends on several factors, including the corrosion resistance that is required, the anticipated lifetime of the coated material, the number of parts being produced, the production rate that is required, and environmental considerations.

All coatings provide barrier protection; that is, they provide a barrier between the corrosive environment and the metal substrate; however, all commercially prepared metal coatings are porous to some degree. Furthermore, coatings tend to become damaged during shipment or in use. Therefore, galvanic action at the base of a pore or scratch becomes an important factor in determining coating performance. From the corrosion standpoint, metal coatings can be divided into two classes, namely, noble coatings, which provide only barrier protection, and sacrificial coatings, which, in addition to barrier protection, also provide cathodic protection.[25]

3.2.2 Inorganic coatings

Inorganic coatings can be produced by chemical action, with or without electrical assistance, and include numerous classes of materials, among them the hydraulic cements that can set underwater, ceramics and clays, glass, carbon, silicates, and

others. Some treatments to produce inorganic coatings can change the surface layer of a metal into a protective film of metallic oxide or compound that has better corrosion resistance than the natural oxide film and provides an effective base or key for supplementary protection such as paints. In some instances, these treatments can also be a preparatory step prior to painting.[14]

3.2.3 Organic coatings

Organic coatings are widely used to protect metal surfaces from corrosion. The effectiveness of such coatings is dependent not only on the properties of the coatings, that are related to the polymeric network and possible flaws in this network, but also on the character of the metal substrate, the surface pretreatment, and the application procedures. Therefore, when considering the application of a coating, it is necessary to take into account the properties of the entire system.

Organic coatings provide protection either by the formation of a barrier action from the layer or from active corrosion inhibition provided by pigments in the coating. In actual practice, the barrier properties are limited because all organic coatings are permeable to water and oxygen to some extent. The average transmission rate of water through a coating is about 10–100 times larger than the water consumption rate of a freely flowing surface, and in normal outdoor conditions, an organic coating is saturated with water at least half of its service life. For the remainder of the time, it contains a quantity of water comparable in its behavior to an atmosphere of high humidity.

Corrosion of a substrate beneath an organic coating is an electrochemical process that follows the same principles as corrosion of an uncoated substrate. It differs from crevice corrosion because the reactants often reach the substrate through a solid. In addition, during the early stages of corrosion, small volumes of liquid are present, resulting in extreme values of pH and ion concentrations.[26]

3.2.3.1 Conductive polymer coatings

In recent years conducting polymers with conjugated double bonds have attracted considerable interest for the developing of many advanced materials [27-32]. In the last years, a great interest has been paid to the electrodeposition of conducting polymers onto active metals due principally to their use as anti-corrosion coatings. At

least for different configurations to apply conductive polymer coatings have been reported: (i) as a coatings alone; (ii) as a primer coating with a conventional topcoat; (iii) blended with a conventional polymer coating; and (iv) as an additive to modify a conventional organic coating[marine paint-armelin]. Several authors have reported significant results in the synthesis of polypyrrole (PPy) onto reactive metals such as Al. The influence of pH on the electropolymerisation of Py onto Al electrodes was explained considering that the passive layer formed might be able to inhibit the dissolution of the metal without blocking the access of the monomer and its further oxidation. No film formation was observed in neutral and weakly alkaline solutions because the oxide passivates the electrode and hinders the process of polymerisation[33].

A noticeable enhancement of protection of ferrous materials against corrosion using conducting polymers as coatings has been demonstrated and several mechanisms have been described to explain this protection. It has been proposed an anodic galvanic protection mechanism which considers that the film in its conductive state acts as an efficient oxidiser to maintain the metal in the passive state. It has also been proposed that the conducting polymer serves to mediate the anodic current between the passivated surface and oxygen reduction on the polymer film[34]. conductive polymers confer active protection by exchanging electrons with the metallic substrate. Protection is afforded by the oxidation or passivation of the metal, shifting the corrosion potential towards more positive values and modifying the oxygen reduction reaction[35]. PPy first suppresses corrosion but its proton-conducting property does not stop the decomposition of the surface passive layer under the PPy layer with protons. The dissolution of iron under the PPy film causes cracking of the PPy layer on the surface. From the SEM micrographs, PPy first covers the Fe (II)-oxalate crystals. As the time of electrolysis is prolonged, the natural morphology of PPy can be obtained. The PPy layer protects mild steel both in 3% NaCl and 0.1 M NaOH. At the same time, due to the property of proton conductivity, the PPy layer does not protect mild steel from corrosion in acidic solutions[36].

The poor solubility of PPy (related to its conjugated structure) and its specific mechanical properties limit its applicability as a coating. Several studies in which these properties of polypyrrole are modified by adding functional groups to the PPy

ring. The use of large anions instead of oxalate ions has a significant effect on the deposition rate of polypyrrole.

The uptake of electrolyte by the porous polypyrrole coatings is probably most important. It explains why the protection time of samples investigated is low. Water between the coating and the metal causes delamination. The protection time of the dual layer coatings can be improved by using other large anions and refined process conditions. Another interesting possibility is attempting to seal the polypyrrole pores. This may be achieved by making composite coatings of (modified) polypyrrole and one or more environmentally friendly oxides[37].

4. CORROSION TESTING

Corrosion testing is an important step in the process of materials selection. It is necessary to carry out corrosion tests on materials of interest in the anticipated environments such as immersion, buried, or atmosphere or industrial in nature. [38]

4.1 Non Electrochemical Testing

Weight lost, pitting and crevice rate, stress-strain time, resistance measurements, surface measurements, different analytical measurements are the main non-electrochemical test methods.

4.2 Electrochemical Testing

Corrosion of metallic substances is an electrochemical process. An alternate approach to field or other accelerated tests in understanding and predicting metallic corrosion is the use of electrochemical parameters/ tests. Electrochemical tests often complement other test methods by providing kinetic and mechanistic data that would be otherwise difficult to obtain. Electrochemical tests are typically grouped as direct current (dc) or alternating current (ac) methods based on the type of perturbation signal that is applied in making the measurements. A number of investigators have used dc and ac electrochemical methods to study the performance and the quality of protective coatings, including passive films on metallic substrates, and to evaluate the effectiveness of various surface pretreatments[17].

4.2.1 Tafel extrapolation method

The Tafel extrapolation method is based on the mixed-potential theory, which is illustrated in Figure 4.1. The dashed lines represent the anodic and cathodic components of the mixed electrodes involved in the corrosion process, the intersecting point of which corresponds to i_{corr} and E_{corr} . When a corroding specimen is polarized by the applied current, usually cathodic, the experimental polarization curve originates at E_{corr} and at high current densities becomes linear on

a semilogarithmic plot. This linear portion coincides with the extended reduction curve as shown by the bold line in the figure. It is evident that an extrapolation of the linear portion of the experimental curve will intersect the E_{corr} horizontal at the point that corresponds to i_{corr} .

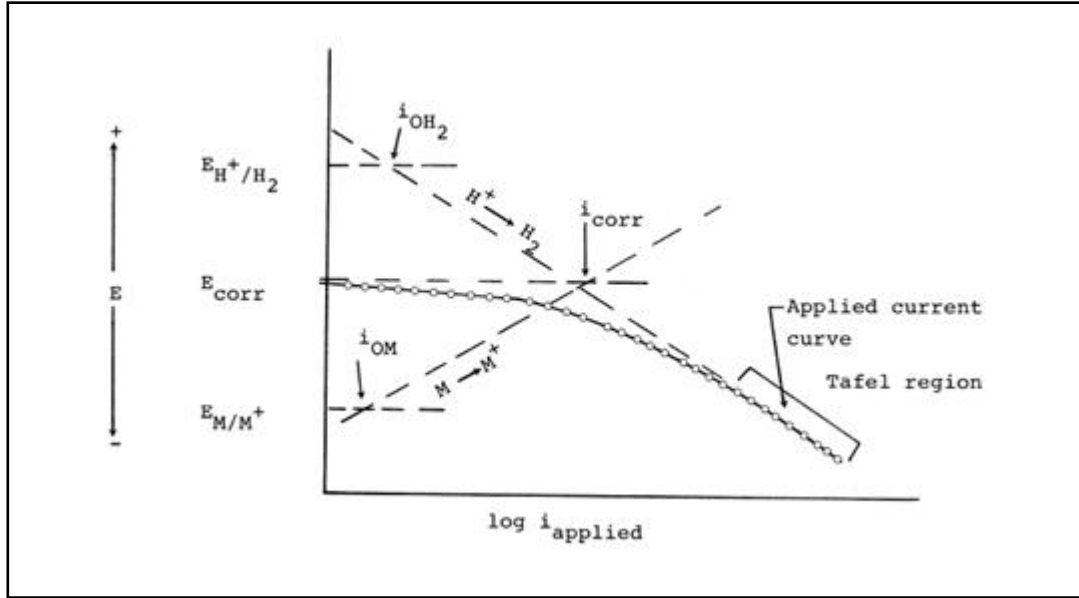


Figure 4.1: Tafel extrapolation method of corrosion rate measurement through cathodic polarization.

This method is rapid. However, the linear portion should extend over a considerable length, not less than one order of magnitude, to ensure accuracy in extrapolation. Where more than one reduction process is prevailing, the linearity is also affected. These disadvantages are largely overcome in the linear polarization method.

4.2.2 Linear polarization method

Within 10 mV more noble or more active than the corrosion potential, the applied current density is a linear function of the electrode potential. This is shown in Figure 4.2. The slope of the linear polarization curve is given by

$$\frac{\Delta E}{\Delta i_{app}} = \frac{\beta_a \beta_c}{2.3(i_{corr})(\beta_a + \beta_c)} \quad (4.1)$$

where β_a and β_c are the Tafel slopes for anodic and cathodic reactors, respectively. The slope is in the unit of ohms and is referred to as the polarization resistance R_p . This method is also known as the polarization resistance method. Although the linearity of the curve deviates at higher over voltages, the slope of the curve at the

origin is independent of the degree of linearity. The slope of the linear curve is inversely proportional to the corrosion current i_{corr}

Assuming $\beta_a = \beta_c = 0.12V$

$$\frac{\Delta E}{\Delta i_{app}} = \frac{\beta_a 0.026}{i_{corr}} \quad (4.2)$$

From this equation the corrosion rate can be calculated without knowledge of the kinetic parameters. This principle is utilized in commercial instruments designed for corrosion rate measurement. These instruments are based on galvanic circuitry and have two-electrode or three-electrode configurations [39].

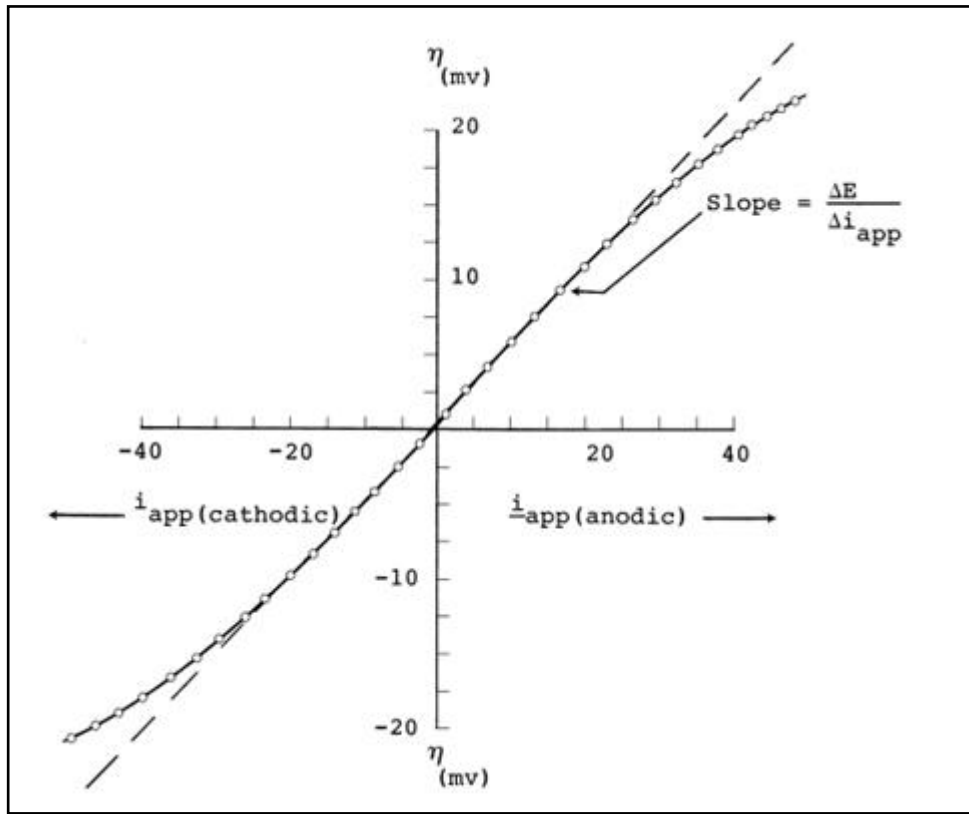


Figure 4.2: Applied-current linear polarization curve for corrosion rate measurement.

4.2.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) has been shown to be a powerful technique in the evolution of the performance and degradation of commonly used coating systems. The general approach usually includes two steps: first, recording of the impedance spectra in a wide frequency range (10^5 Hz to 10^{-3} Hz) as a function of the exposure time to the corrosive environment and, second, analyzing EIS data based on an equivalent circuit model. The performance of the coating is evaluated

according to magnitudes of the parameters in the equivalent circuit and their changes with exposure time. This procedure usually is time consuming and requires appropriate computer software[40].

The expression for $Z(\omega)$ composed of a real and an imaginary part. If the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis of a chart, we get a “Nyquist Plot” see Figure 4.3. Notice that in this plot the Y-axis is negative and that each point on the Nyquist Plot is the impedance at one frequency. Figure 4.3 has been annotated to show that low frequency data are on the right side of the plot and higher frequencies are on the left.

On the Nyquist Plot the impedance can be represented as a vector (arrow) of length $|Z|$. The angle between this vector and the X-axis, commonly called the “phase angle”, is Φ ($=\arg Z$).

Nyquist Plots have one major shortcoming. When you look at any data point on the plot, you cannot tell what frequency was used to record that point.

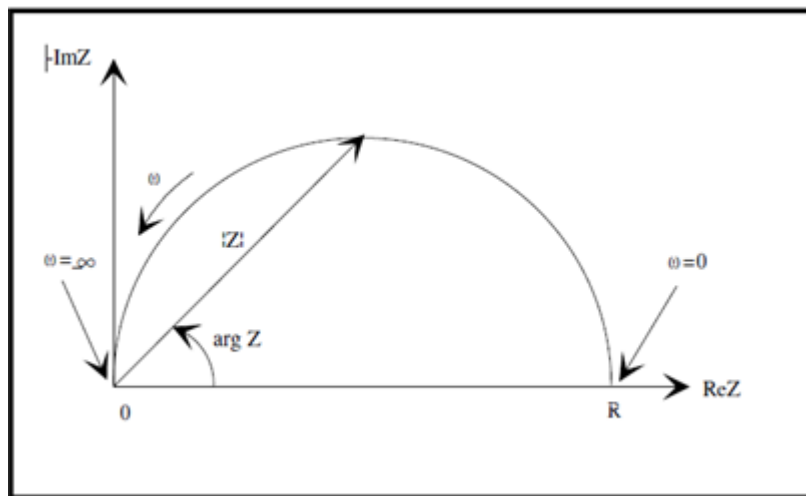


Figure 4.3: Nyquist Plot with impedance vector.

Another popular presentation method is the Bode Plot. The impedance is plotted with log frequency on the X-axis and both the absolute values of the impedance ($|Z| = Z_0$) and the phase-shift on the Y-axis.

The Bode Plot for the electric circuit of Figure 4 is shown in Figure 4.4. Unlike the Nyquist Plot, the Bode Plot does show frequency information[41].

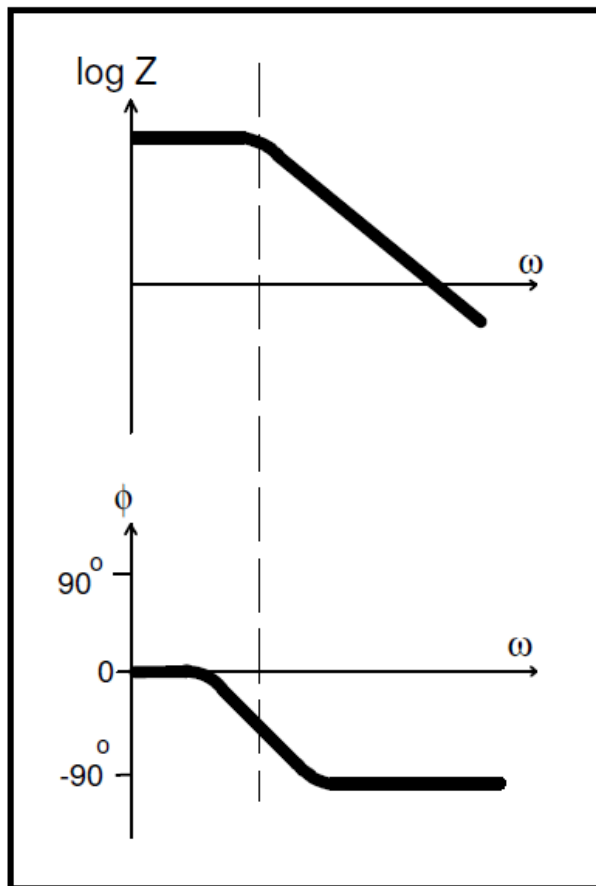


Figure 4.4: Bode Plot with one time constant.

5. EXPERIMENTAL WORK

5.1 Equipment

Electrochemical experiments were carried out in a 3-electrode cell which has platinum as counter electrode, silver as reference electrode, and coated Al as working electrode. Electropolymerization measurements were obtained by CV, corrosion behavior of the polymeric coating was investigated by Tafel Extrapolation and EIS measurements on Gamry 5.30 Model Potentiostat. Scan rate was selected 5mV/sec. coated electrodes during the polarization measurements. Impedance measurement of the frequency range 10mHz-1MHz. was taken as a basis, where the alternating current signal of 10 mV were applied. Polymers were analyzed by FT-IR reflectance spectrophotometer (PerkinElmer, Spectrum One; with a Universal ATR attachment with a diamond and ZnSe crystal C790951).

5.2 Chemicals

Chemicals Acetonitrile (CH_3CN) was provided from Merck, Sulphuric acid (H_2SO_4) (Merck), Acetone ($\text{C}_3\text{H}_6\text{O}$) (Fluka), N,N-Dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$) (Merck), Carbazole Monomer ($\text{C}_{12}\text{H}_9\text{N}$) (BDH), Pyrrole Monomer ($\text{C}_4\text{H}_5\text{N}$) (Fluka), Toluene (C_7H_8) (Merck), Sodium Perchlorate (NaClO_4) (Sigma-Aldrich), Ceric Ammonium Nitrate (CAN) ($\text{H}_8\text{N}_8\text{CeO}_{18}$) (Aldrich), Sodium Hydroxide (NaOH) (Merck), Nitric Acid (HNO_3) (Merck), [PPy_b-(DH.PDMS)]-DN4, [PPy_b-(DH.PDMS)]-DN6, [PCz_b-(DH.PDMS)]-DN1_1 block copolymers were synthesized by Assoc.Prof. Dr. Nilgün Kızılcın [42]. All chemicals were analytical grade and no further purification was employed.

5.3 Electrodes

Electrodes have cylindrical shape and their diameter is 5 mm. Electrodes were placed in glass tubes which prohibit connection between the substrate and the other electrodes such as silver and platinum wire, and they were stucked by using two

component epoxy resin. That epoxy material durable inside the acidic medium and also denying the solution to enter between glass tube and substrate. Electrodes have 0.196 cm^2 surface area and that constant area expose to acidic medium. Aluminum electrodes contaminate (%w/w) 0.40 Fe, 0.30 Si, 0.05 Cu, 0.20-0.60 Mn, 2.70-3.70 Mg, 0.20 Zn, 0.20 Ti, 0.30 Cr.

5.4 Coatings

5.4.1 Copolymer coatings

Different amount of [PPy_b_(DH.PDMS)] (**DN4**) dissolved in DMF : acetone (1/10 v/v) (0,1 ml DMF - 1 ml acetone), [PPy_b_(DH.PDMS)] (**DN6**) dissolved in DMF : acetone (2/15 v/v) (0,2 ml DMF – 1,5 ml acetone) and [PCz_b_(DH.PDMS)]- (**DN1_1**) dissolved in 1 ml acetone. The sequential multilayer deposition was carried out by dropping coating solution onto aluminum substrate at different amount . After deposition of each layer the substrate is allowed to dry and finally the coated substrate left in vacuum oven at 60°C for 12 hours until complete dryness. The coating and abbreviation are listed in Table 5.1, Table 5.2, Table 5.3. Last two number represent the stock concentration and number of layers. For example DN6-1-2 means the coating obtained from a stock solution of 0.01g/ml with two layer.

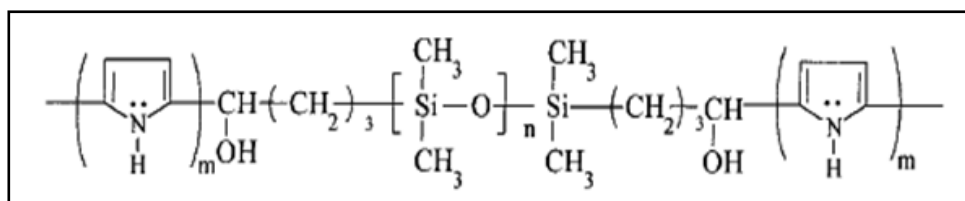


Figure 5.1: Structure of the DN4 - [PPy_b_(DH.PDMS)] and DN6 - [PPy_b_(DH.PDMS)].



Figure 5.2: Structure of the DN1_1 - [PCz_b_(DH.PDMS)].

Table 5.1: Polymer concentrations, polymer amount, thickness and number of layer for [PCz_b_(DH.PDMS)]-DN1_1 coatings.

Coating	Concentration(g/ml) ^a	Amount(g) ^b	Layer	Thickness(μm)
DN1_1-1-2	0.01	0,000084	2	0,112
DN1_1-1-3	0.01	0,000126	3	0,167
DN1_1-1-4	0.01	0,000168	4	0,223
DN1_1-1-5	0.01	0,000210	5	0,279
DN1_1-2-2	0.025	0,000210	2	0,279
DN1_1-2-3	0.025	0,000315	3	0,418
DN1_1-2-4	0.025	0,000420	4	0,557
DN1_1-2-5	0.025	0,000525	5	0,697
DN1_1-3-2	0.04	0,000336	2	0,446
DN1_1-3-3	0.04	0,000504	3	0,669
DN1_1-3-4	0.04	0,000672	4	0,892
DN1_1-3-5	0.04	0,000084	5	1,115

^a Concentration of stock solution; ^b The amount of polymer that the coating contain

Table 5.2: Polymer concentrations, polymer amount, thickness and number of layer for [PPy_b_(DH.PDMS)]-DN4 coatings.

Coating	Concentration(g/ml) ^a	Amount(g) ^b	Layer	Thickness(μm)
DN4-1-2	0.006	0,000084	2	0,112
DN4-1-3	0.006	0,000126	3	0,167
DN4-1-4	0.006	0,000168	4	0,223
DN4-1-5	0.006	0,000210	5	0,279
DN4-2-2	0.009	0,000126	2	0,167
DN4-2-3	0.009	0,000189	3	0,251
DN4-2-4	0.009	0,000252	4	0,334
DN4-2-5	0.009	0,000315	5	0,418
DN4-3-2	0.012	0,000168	2	0,223
DN4-3-3	0.012	0,000252	3	0,334
DN4-3-4	0.012	0,000336	4	0,446
DN4-3-5	0.012	0,000420	5	0,557
DN4-4-2	0.018	0,000252	2	0,334
DN4-4-3	0.018	0,000378	3	0,502
DN4-4-4	0.018	0,000504	4	0,669
DN4-4-5	0.018	0,000630	5	0,836
DN4-5-2	0.024	0,000336	2	0,446
DN4-5-3	0.024	0,000504	3	0,669
DN4-5-4	0.024	0,000672	4	0,892
DN4-5-5	0.024	0,000840	5	1,115

^a Concentration of stock solution; ^b The amount of polymer that the coating contain

Table 5.3: Polymer concentrations, polymer amount, thickness and number of layer for [PPy_b_(DH.PDMS)]-DN6 coatings.

Coating	Concentration(g/ml) ^a	Amount(g) ^b	Layer	Thickness(μm)
DN6-1-2	0.01	0,000084	2	0,112
DN6-1-3	0.01	0,000126	3	0,167
DN6-1-4	0.01	0,000168	4	0,223
DN6-1-5	0.01	0,000210	5	0,279
DN6-2-1	0.025	0,000105	1	0,139
DN6-2-2	0.025	0,000210	2	0,279
DN6-2-3	0.025	0,000315	3	0,418
DN6-2-4	0.025	0,000420	4	0,557
DN6-2-5	0.025	0,000525	5	0,697
DN6-3-1	0.04	0,000168	1	0,223
DN6-3-2	0.04	0,000336	2	0,446
DN6-3-3	0.04	0,000504	3	0,669
DN6-3-4	0.04	0,000672	4	0,892
DN6-3-5	0.04	0,000840	5	1,115

^a Concentration of stock solution; ^b The amount of polymer that the coating contain

5.4.2 Conducting polymer containing organic coatings

In recent years, conducting polymers (CPs) can be successfully used as anticorrosive additive to modify the formulation of conventional organic coatings (paints) [43], the most important benefit of this technology being that a very low concentration of conducting polymer is needed.

There is an increasing interest on the use of CP to protect reactive metals against corrosion [44]. At least four different configurations to apply CP coatings have been reported:

- (i) as a coatings alone;
- (ii) as a primer coating with a conventional topcoat;
- (iii) blended with a conventional polymer coating; and
- (iv) as an additive to modify a conventional organic coating.

In this study we applied two of these configuration coating alone as homopolymer and silicone containing copolymers and additive to modifiye a conventional organic coating.

In this study, for this purpose, a small concentration (8% w/w) of PPy and PCz homopolymer obtained by chemical polymerization were properly dispersed in a cyclohexanone-formaldehyde resin (CF) containing acetone and DMF by using homogenizator and they coated on electrode surface by dipping methods. This will allow a reliable comparison between the anticorrosive properties of PPy and PCz. The aim of these assays is to check if CPs, in this case PPy and PCz, are so or even more effective against corrosion than conventional inorganic pigments in order to replace them and to compare the performance with PPy and PCz containing silicone tegomer copolymer coatings. The corrosion assays performed in this work consisted on cyclic short term exposures of coated Al electrodes to accelerated ageing conditions in 1M H₂SO₄ solution at room temperature.

5.4.3 Homopolymer coatings

For comparison polypyrrole and polycarbazole homopolymers also coated on Al substrate by electrochemical method. The electropolymerizations which were taken by using chronoamperometry scan were carried out with 0.1 M Cz and 0,1M Py in 0.1 M NaClO₄ containing solution in the range of 2V constant potential and 2,3V constant potential, respectively. All electrochemical experiments were performed in a 3-electrode cell, working electrode aluminum (A=0.196 cm²), counter electrode Pt spiral and reference electrode is Ag wire. Than the electrode potentials were calibrated according to Ag/AgCl.

The corrosion behaviors of the resulting polymeric films are tested by anodic and cathodic polarization curves and EIS measurements in 1M H₂SO₄ solution.

6. RESULTS AND DISCUSSION

Al electrodes was coated with there different copolymers ([PPy_b_(DH.PDMS)], [PCz_b_(DH.PDMS)], PPy / DH.PDMS , PCz / DH.PDMS) by dipping methods from their solutions. In order to determine the optimum coating conditions different solutions that contain different amount of polymer were prepared. From these solution polymer was coated by dropwise layer by layer. The detail about coating was given in Table 5.1, Table 5.2, Table 5.3.

A small concentration of PPy and PCz homopolymer obtained by chemical polymerization were also dispersed in a cyclohexanone-formaldehyde resin (CF) containing acetone and DMF and they coated on electrode surface by dipping methods. The corrosion protection efficiency of organic coating modified by the addition of these conducting polymers was also tested.

Every coated films are tested by anodic and cathodic polarization curves and EIS measurements. For monitoring the stability of polymeric films, the corrosion electrodes was left in corrosion medium (1M H₂SO₄) for different time periods.

From polarization curves, corrosion currents (I_{corr}), corrosion potentials (E_{corr}), anodic and cathodic Tafel slopes (B_a , B_c), obtained by Tafel extrapolation method.

Corrosion rates in the more useful units of rate of penetration, such as milli-inch per year was also calculated:

$$\text{Corrosion Rate (mpy)} = (0.13 i_{\text{cor}} \text{ EW}) / d$$

$$i_{\text{corr}} = \text{corrosion current density } (\mu\text{A cm}^{-2}).$$

$$\text{E.W} = \text{equivalent weight of the corroding species, (g).}$$

$$d = \text{density of the corroding species, (g/cm}^3\text{).}$$

$$\text{mpy} = \text{milli-inches per year}$$

When electrode was corroded, the capacitive area expanded to lower frequency range. Capacitance-resistance transition frequency (f_b) results changing with time are examined by Mansfeld and his group and they acquired knowledge about the

stability of the coating [45]. From Bode diagram and Nyquist diagram f_b and R_p values of coated electrodes were obtained and plotted against time.

Although a notable effort has been devoted to investigate the corrosion inhibition provided by PANi, the research involving other CPs is very scarce, being restricted to a few PPy and almost none PCz. In this study Al electrodes are coated with PCz and PPy homopolymers electrochemically. The results obtained using conducting polymers (PCz and PPy) have been compared with those obtained for pyrrole and carbazole containing silicone tegomer coatings (DN6, DN4 and DN1_1) and also PCz and PPy modified CF coatings.

6.1 DN4 Coated Aluminum

Polarization curves obtained for DN4-1-4 coated Al at different exposure time were given in Figure 6.1. Corrosion values calculated from these curves and summarized in Table 6.1. Changes in corrosion potentials (E_{corr}) with exposure time stabilized after one hour Figure 6.2. As it can be seen corrosion potentials are shifted to more anodic potential and corrosion currents are decreased when coated electrode left in corrosion medium and the polymer coating protects aluminium metal against corrosion in contact with aggressive acidic solutions.

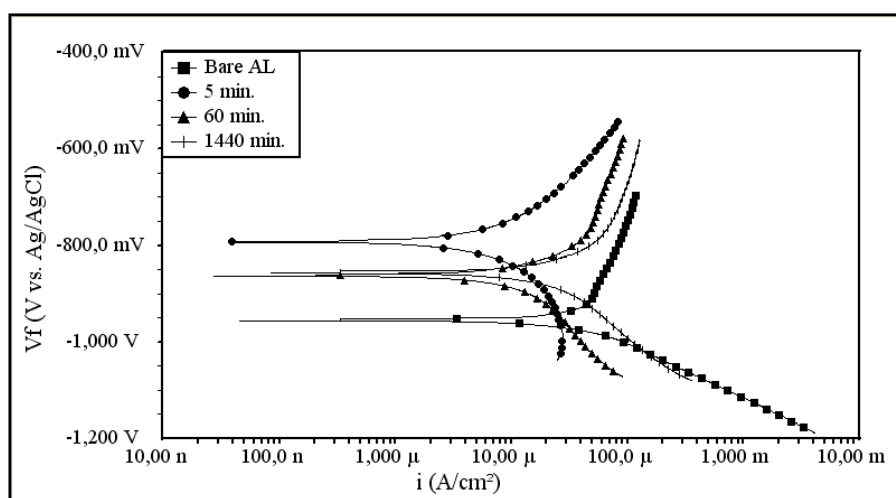
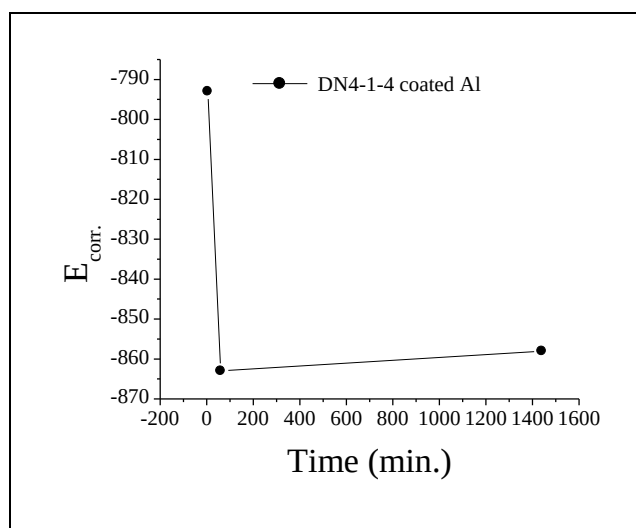


Figure 6.1: Polarization curves of DN4-1-4 coated Al left in 1 M H_2SO_4 .

Table 6.1: Corrosion values of DN4-1-4 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μ A/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	13,90	-793,0	0,2946	0,3176	5,947	98,5
60	82,00	-863,0	0,4782	553,3*10 ³	35,21	91,5
1440	136,0	-858,0	1,813	0,6029	58,23	85,9
Bare	969,0	-931,0	0.373	0,125	415,8	-

**Figure 6.2:** Time dependence of E_{corr.} values for DN4-1-4coated Al electrode.

The effects of the type of coating and the parameters of the coating on the impedance spectra can be well characterized by comparing the spectra measured after soaking in corrosion medium. Bode and Nyquist diagram of DN4 coated from a solution of 0.01 g/ml at 4 layer (DN4 1-4) were given in Figure 6.3, Figure 6.4 Changes in f_b and R_p values of coated electrodes obtained from these diagrams are given in Figure 6.5 and 6.6, respectively.

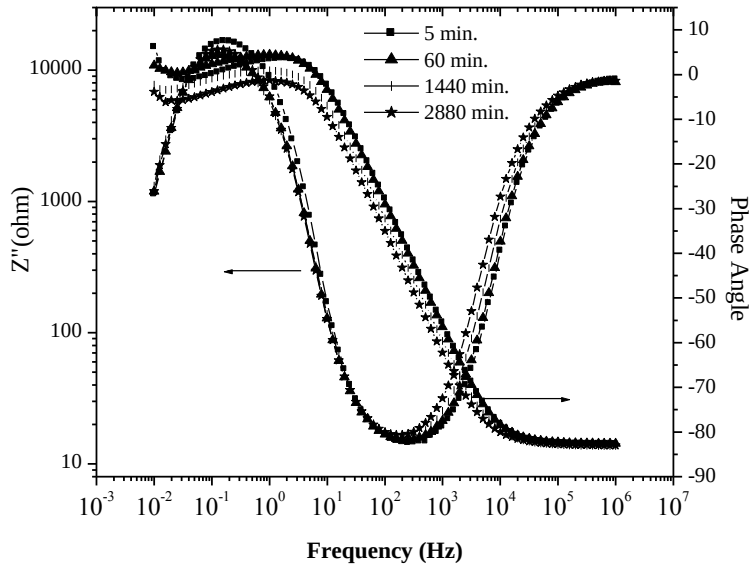


Figure 6.3: Bode diagrams of DN4-1-4 coated Al electrode.

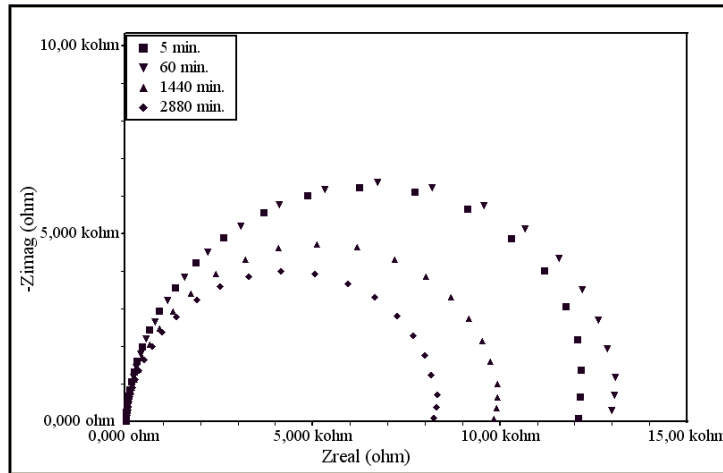


Figure 6.4: Nyquist diagrams of values for DN4-1-4 coated Al electrode.

Break-point frequencies, f_b values are expected to increase when the corrosion take place [46]. In our cases for DN4-1-4 coated Al electrode, f_b values decrease with time Fig 6.5. This result indicate stabilization of coating.

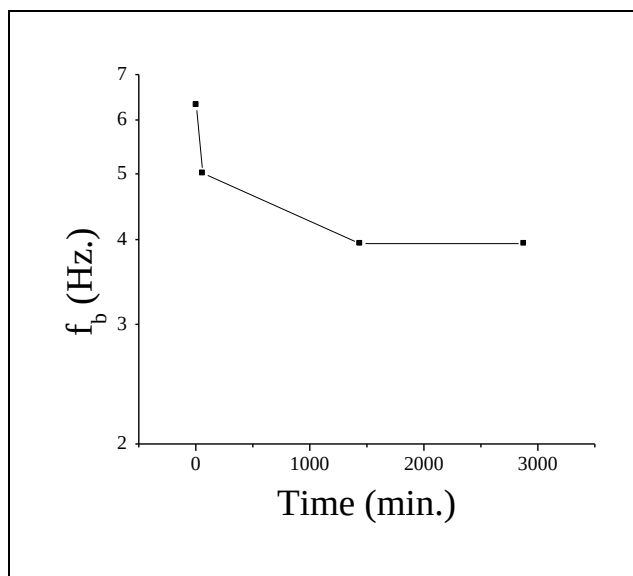


Figure 6.5 : Time dependence of f_b values for DN4-1-4 coated Al electrode.

R_p values of coated electrodes expected to increase as compare to bare electrode and it is desired to stay unchanged when the electrode left in corrosion medium.

R_p values of DN4-1-4 coated Al electrode first increase from 12 kohm to 13 kohm after one hour and then start to decrease Figure 6.6. However this decrease is not higher than 31% and we can assume that DN4-1-4 coating stay stable during 3000 min.

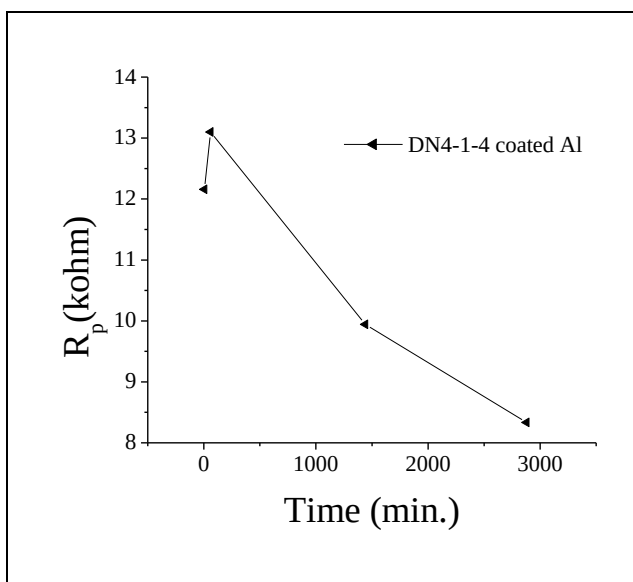


Figure 6.6: Time dependence of R_p values for DN4-1-4 coated Al electrode.

Similarly polarization curves and Bode diagrams of other DN4 coated Al electrode from solution with different concentration and having different layers were given in Fig 6.7, Fig 6.9, Fig 6.11, Fig 6.16, Fig 6.18, Fig 6.20 and Fig 6.8, Fig 6.10, Fig 6.12,

Fig 6.17, Fig 6.19, Fig 6.21, respectively. Corrosion values obtained from polarization curves summarized in Table 6.2, Table 6.3, Table 6.4, Table 6.5, Table 6.6, Table 6.7.

In all cases corrosion potentials shifted to noble direction according to bare electrode which indicating an anodic protection. Changes in E_{corr} values of coated electrode with exposure time shows that their values sharply decrease at first and it become almost constant after one hour Figure 6.2, Figure 6.13, Figure 6.22. For DN4-2 group the most noble potential belongs to coating obtained with 4 layer (DN4-2-4) and the lowest value obtained for DN4-2-2. This result suggest that increase in thickness gives an anodic shift of potential. However there is a critical value for thickness. Beyond this thickness, the loss of adhesion between the coating and aluminum substrate occur and the coating leaves the aluminum surface. So the corrosion potentials start to shift in cathodic direction. For DN4-2 group, it seems this happen after 5 layer coating.

Increase in Tafel slopes (B_a and B_c) also indicate passivation of electrode with a resistive coating layer Table 6.2, Table 6.3, Table 6.4.

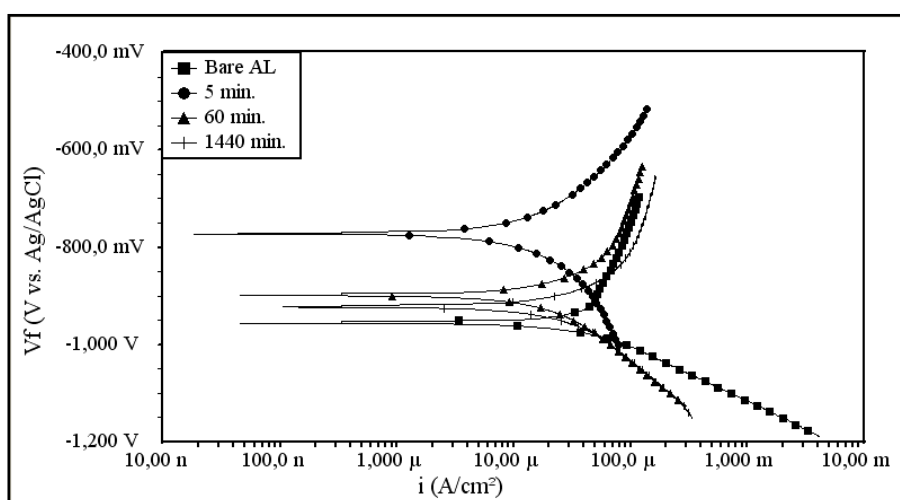


Figure 6.7: Polarization curves of DN4-2-3 coated Al left in 1 M H_2SO_4 .

Table 6.2: Corrosion values of DN4-2-3 coated Al left in 1 M H_2SO_4 .

Time (minute)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV)	B_a (V/decade)	B_c (V/decade)	CR (mpy)	IE%
5	42,10	-772,0	0,4514	0,6064	18,06	95,6
60	119,0	-900,0	1,545	0,5652	50,88	87,7
1440	192,0	-923,0	1,884	0,6745	82,65	80,1
Bare	969,0	-931,0	0.373	0,125	415,8	-

R_p and f_b values calculated from Bode and Nyquist diagrams and plotted against time. f_b values of DN4_2 group seem stable after one hour exposure in corrosion medium Figure 6.14. R_p values have similar trends and support the conclusion that DN4_2 coatings minimize the tendency for loss of adhesion through undercutting corrosion or blistering Fig 6.15. For the other DN4 coatings (DN_3, DN_4 and DN_5) f_b values are almost stable Figure 6.23.

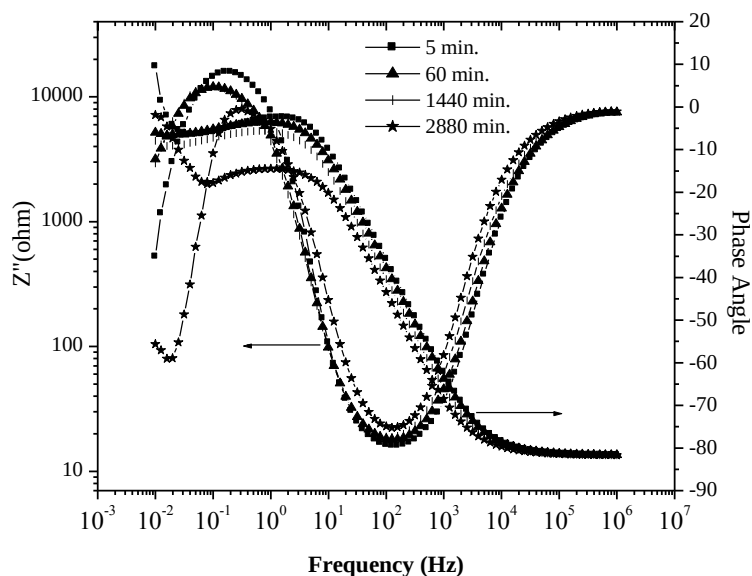


Figure 6.8: Bode diagrams of DN4-2-3 coated Al electrode.

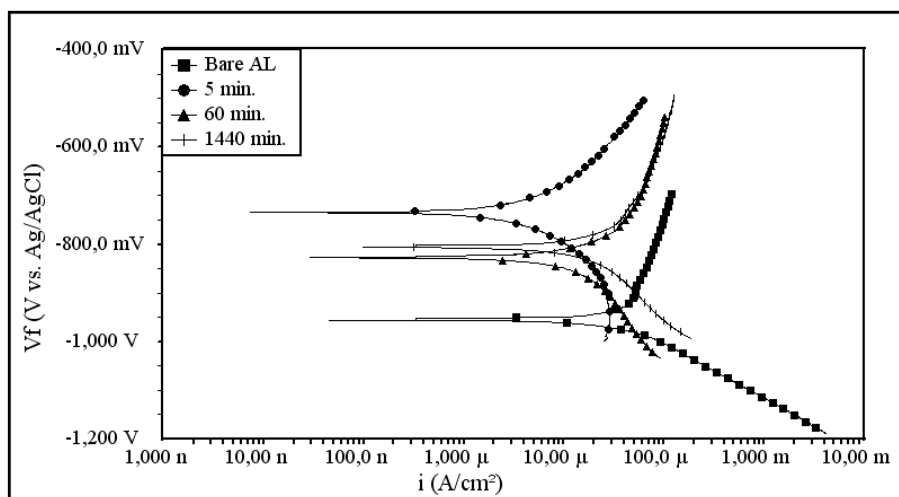


Figure 6.9: Polarization curves of DN4-2-4 coated Al left in 1M H_2SO_4 .

Table 6.3: Corrosion values of DN4-2-4 coated Al left in 1M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	6,280	-735,0	0,1922	0,1995	2,697	99,3
60	114,0	-828,0	0,6013	3,253*10 ⁹	48,80	88,2
1440	258,0	-805,0	0,9544	2418	111,0	73,3
Bare	969,0	-931,0	0.373	0,125	415,8	-

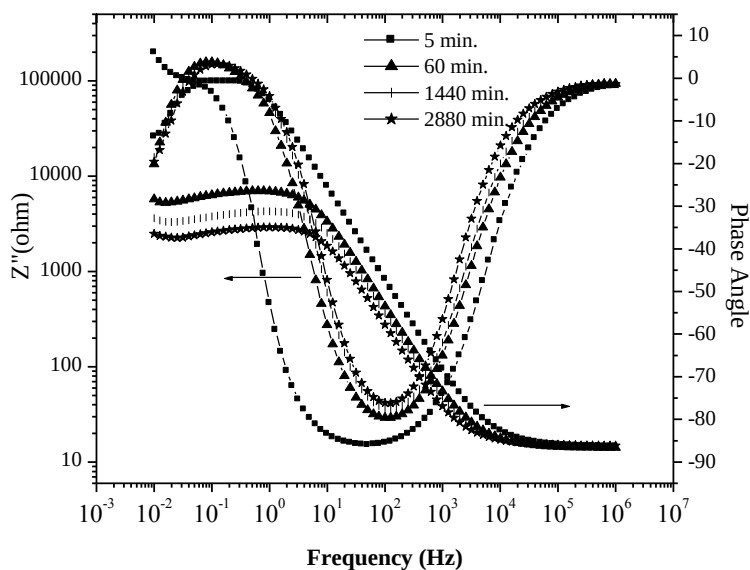


Figure 6.10: Bode diagrams of DN4-2-4 coated Al electrode.

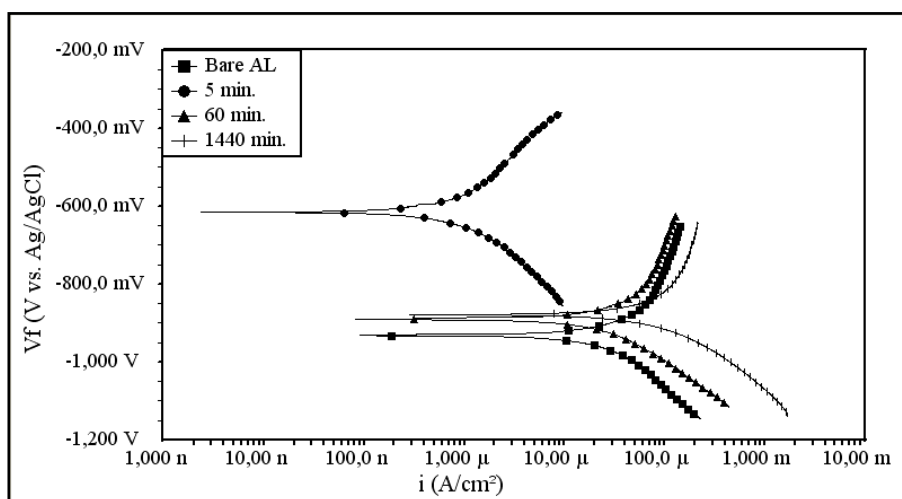


Figure 6.11: Polarization curves of DN4-2-5 coated Al left in 1M H₂SO₄.

Table 6.4: Corrosion values of DN4-2-5 coated Al left in 1M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	8,090	-615,0	876,2*10 ³	0,7863	3,472	99,1
60	217,0	-890,0	223,5*10 ⁶	0,6342	93,17	77,6
1440	251,0	-878,0	1,000*10 ¹⁵	0,2699	108,0	74,1
Bare	969,0	-931,0	0.373	0,125	415,8	-

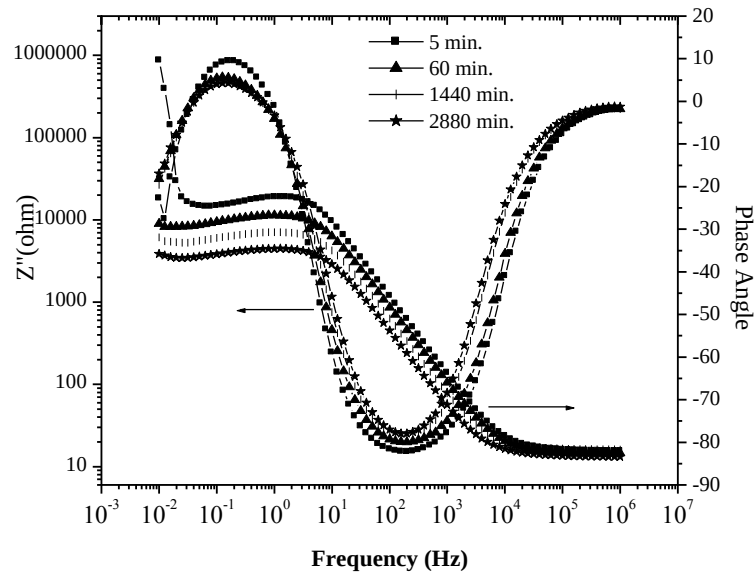


Figure 6.12: Bode diagrams of DN4-2-5 coated Al electrode.

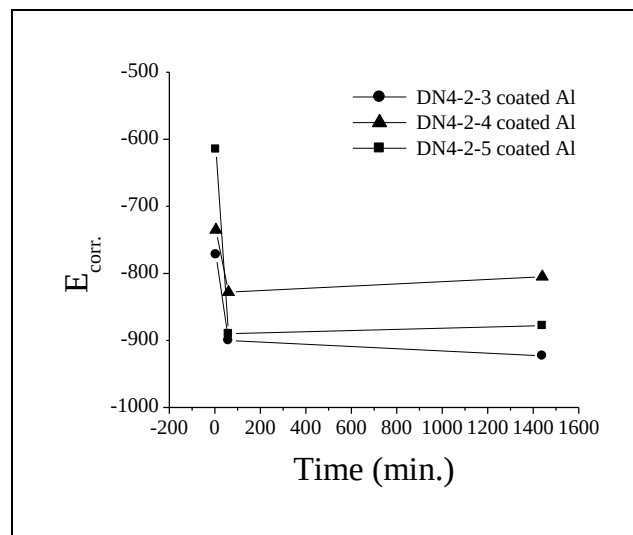


Figure 6.13: Time dependence of $E_{corr.}$ values for DN4-2-3, DN4-2-4, DN4-2-5 coatings.

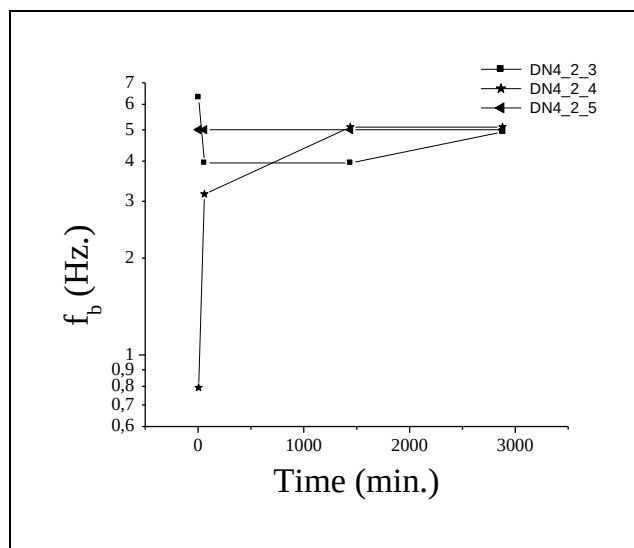


Figure 6.14 : Time dependence of f_b values for DN4-2-3, DN4-2-4, DN4-2-5 coatings.

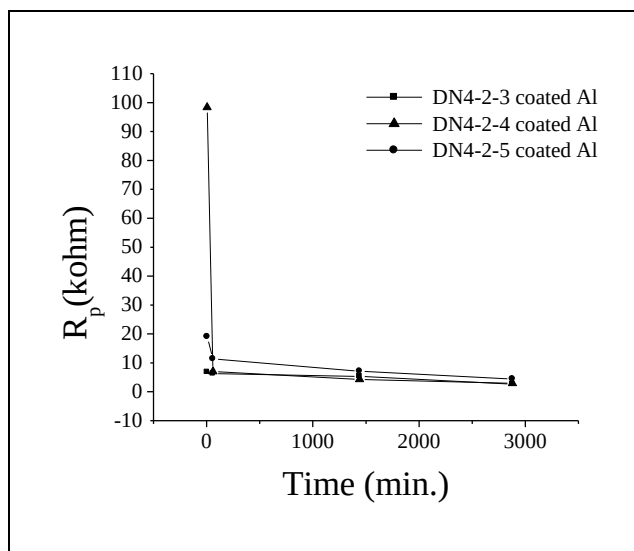


Figure 6.15: Time dependence of R_p values for DN4-2-3, DN4-2-4, DN4-2-5 coatings.

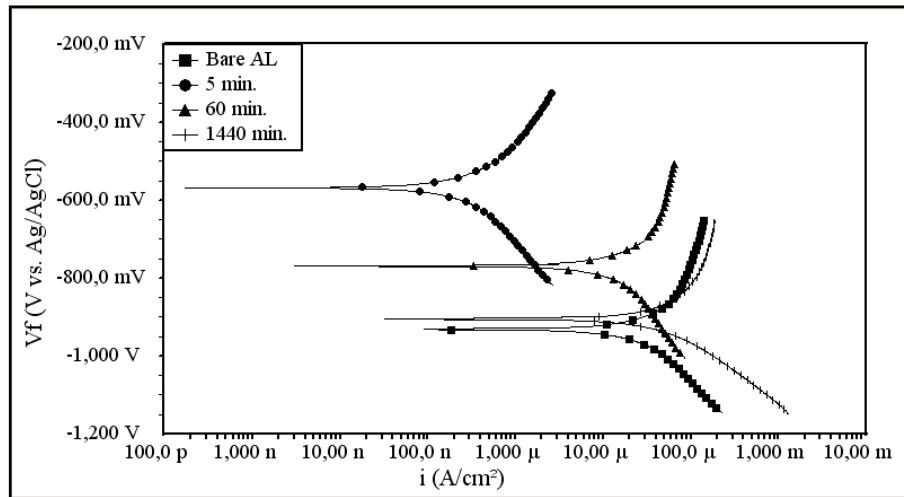


Figure 6.16: Polarization curves of DN4-3-4 coated Al left in 1 M H₂SO₄.

Table 6.5: Corrosion values of DN4-3-4 coated Al left in 1 M H₂SO₄.

Time (minute)	I_{corr} ($\mu A/cm^2$)	E_{corr} (mV)	B_a (V/decade)	B_c (V/decade)	CR (mpy)	IE %
5	3,160	-568,0	0,9327	$3,515 \cdot 10^6$	1,358	99,6
60	233,0	-769,0	1,486	$435,2 \cdot 10^3$	99,90	75,9
1440	265,0	-905,0	$852,6 \cdot 10^3$	0,4397	113,7	72,6
Bare	969,0	-931,0	0.373	0,125	415,8	-

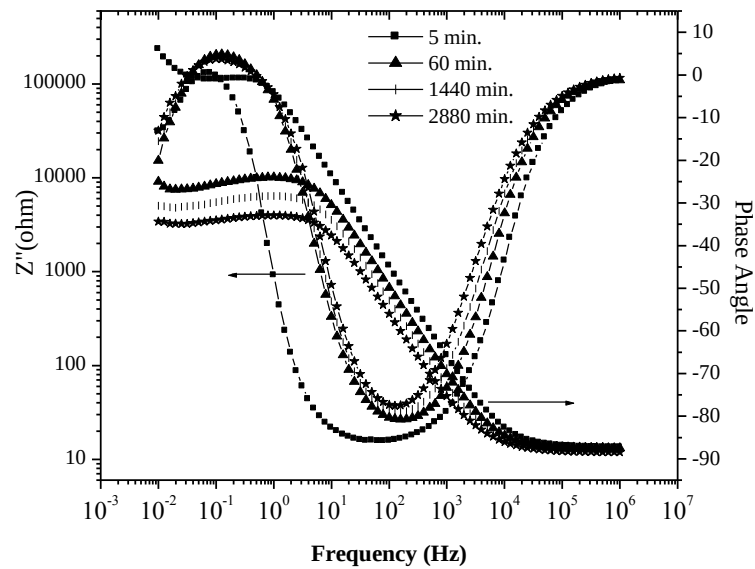


Figure 6.17: Bode diagrams of DN4-3-4 coated Al electrode.

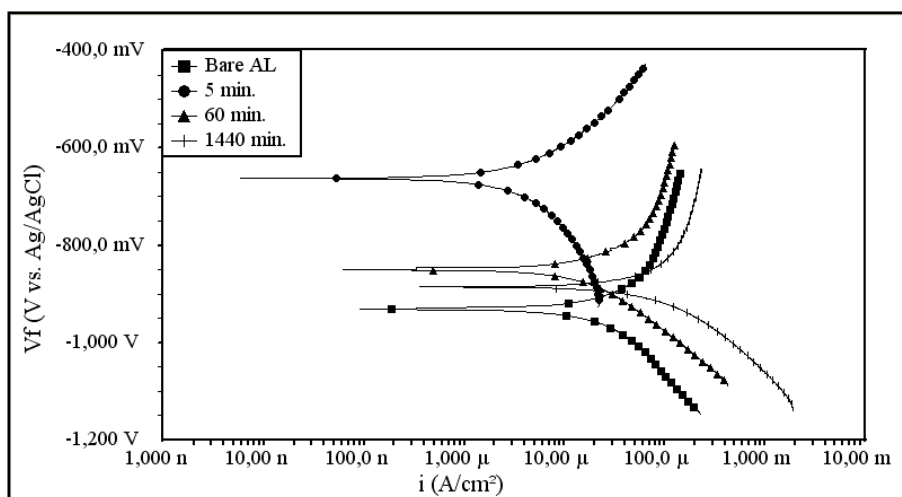


Figure 6.18: Polarization curves of DN4-4-4 coated Al left in 1 M H₂SO₄.

Table 6.6: Corrosion values of DN4-4-4 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	7,140	-663,0	0,2178	0,4395	3,067	99,2
60	208,0	-850,0	0,9102	3,947	89,13	78,5
1440	259,0	-885,0	1,000*10 ¹⁵	0,2515	111,0	73,2
Bare	969,0	-931,0	0.373	0,125	415,8	-

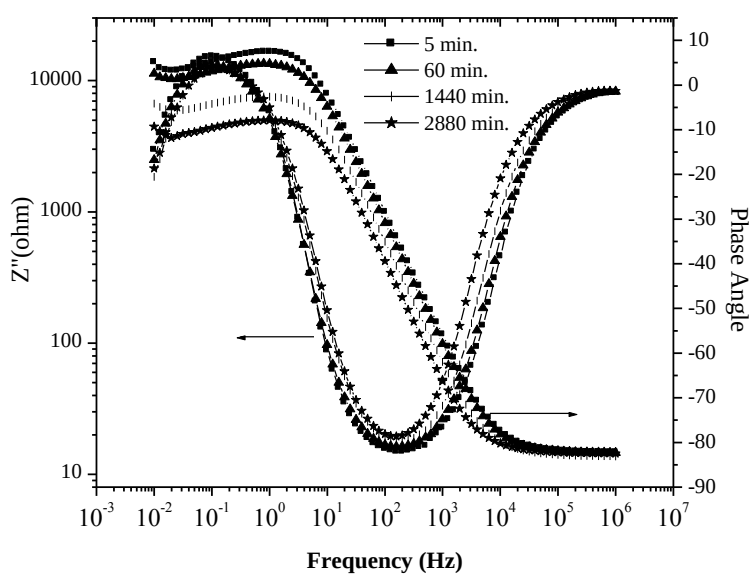


Figure 6.19: Bode diagrams of DN4-4-4 coated Al electrode.

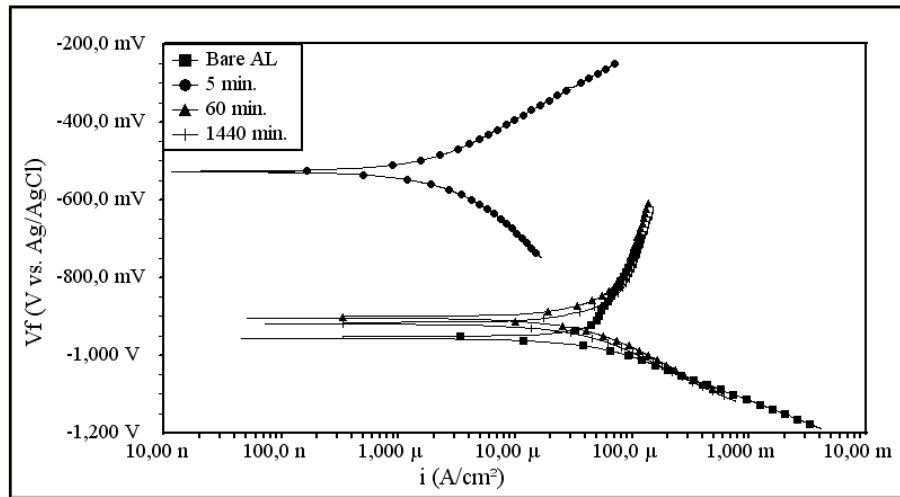


Figure 6.20: Polarization curves of DN4-5-4 coated Al left in 1 M H₂SO₄.

Table 6.7: Corrosion values of DN4-5-4 coated Al left in 1 M H₂SO₄.

Time (minute)	I_{corr} ($\mu A/cm^2$)	E_{corr} (mV)	B_a (V/decade)	B_c (V/decade)	CR (mpy)	IE %
5	3,650	-527,0	0,3185	0,2979	1,569	99,6
60	184,0	-903,0	$70,40 \cdot 10^6$	0,4010	78,90	81,0
1440	250,0	-918,0	$829,0 \cdot 10^3$	0,5013	107,2	74,2
Bare	969,0	-931,0	0.373	0,125	415,8	-

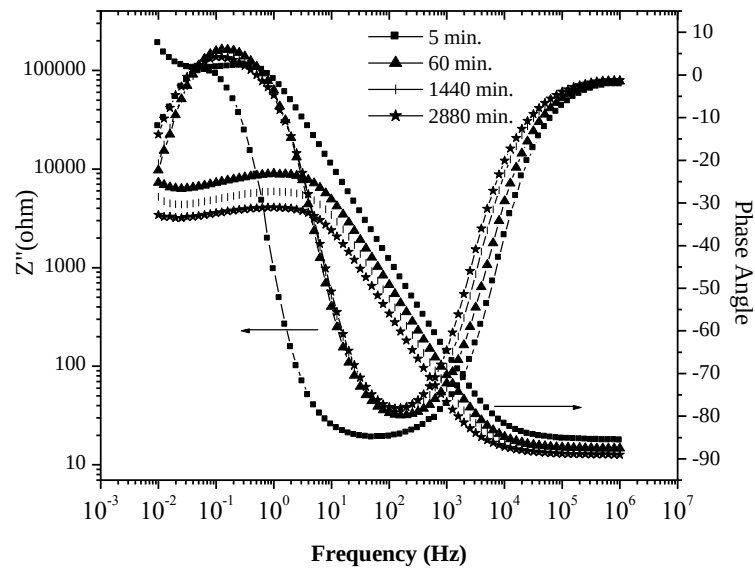


Figure 6.21: Bode diagrams of DN4-5-4 coated Al electrode.

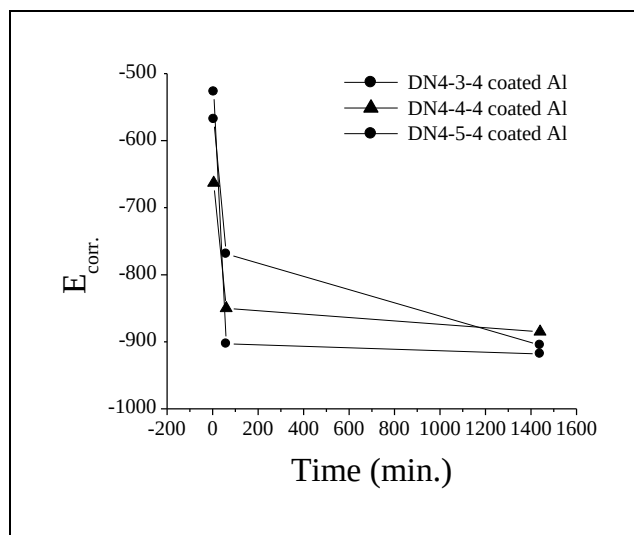


Figure 6.22: Time dependence of $E_{corr.}$ values for DN4-3-4, DN4-4-4, DN4-5-4 coatings.

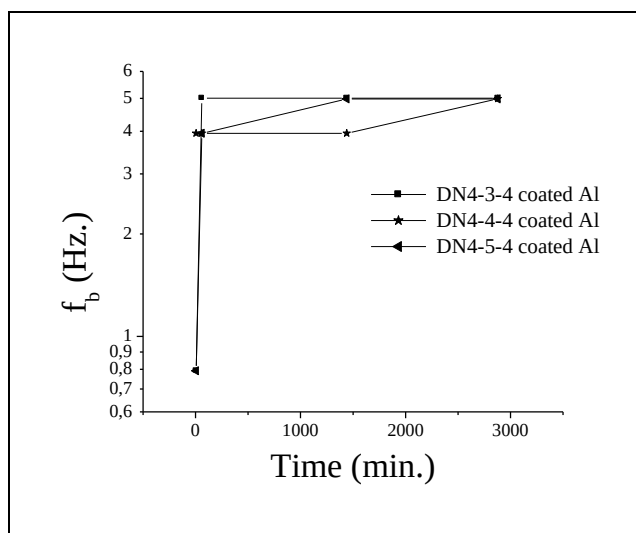


Figure 6.23 : Time dependence of f_b values for DN4-3-4, DN4-4-4, DN4-5-4 coatings.

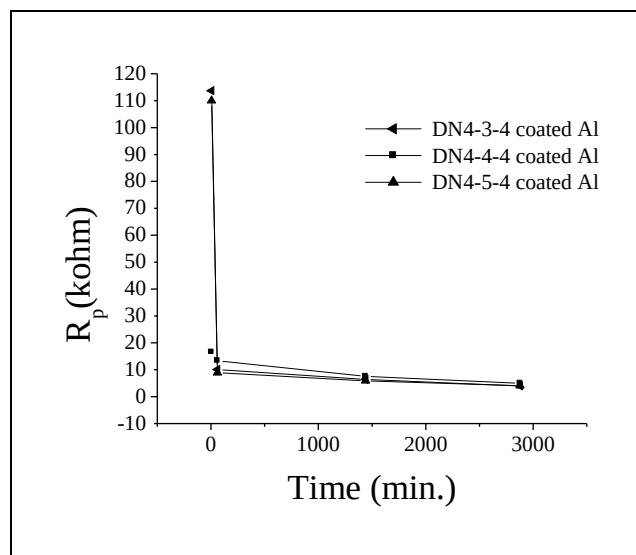


Figure 6.24: Time dependence of R_p values for DN4-3-4, DN4-4-4, DN4-5-4 coatings.

R_p values of DN4 electrodes coated from different solutions (DN4-1, DN4-2, DN4-3, DN4-4, DN4-5, Table 4.3) at same layer number were compared in accordance with exposure time Figure 6.25 and Figure 6.26.

For one hour exposure time coatings obtained from solution 1 (DN4-1; 0.06g/ml) and 4 (DN4-4; 0.018g/ml) has highest R_p values suggested the most resistive coatings Fig.6.25. If the concentration of coating solution increased further (DN4-5, 0.024 g/ml), lower R_p values observed from DN4-4. Increase in thickness of due to increase in concentration of coating solution causes some delamination in corrosion environment.

After 48 hours coated obtained the diluted coating solution (DN4-1) has the highest R_p values and this results indicated that this coating is more stable than the others Figure 6.26.

R_p result for different coating and different exposure time shows that the thickness and the concentration of solution is important for the protection efficiency of coating and coating obtained diluted solutions are more stable for longer exposure time.

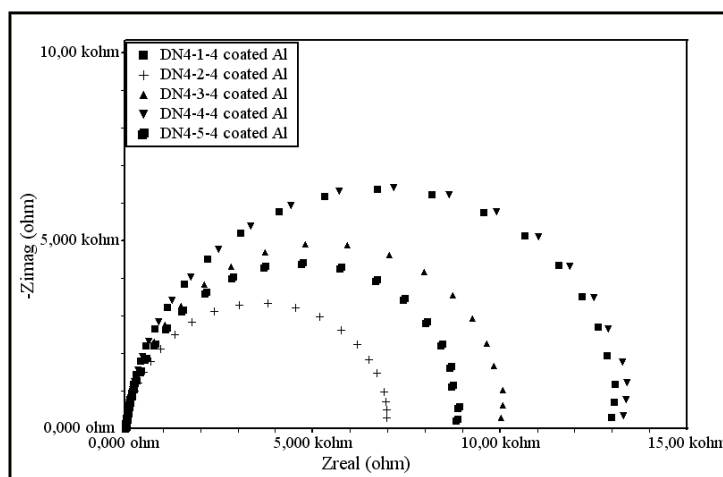


Figure 6.25: Nyquist diagrams of values for DN4-1-4, DN4-2-4, DN4-3-4, DN4-4-4, DN4-5-4 coated Al electrodes. (1 hour).

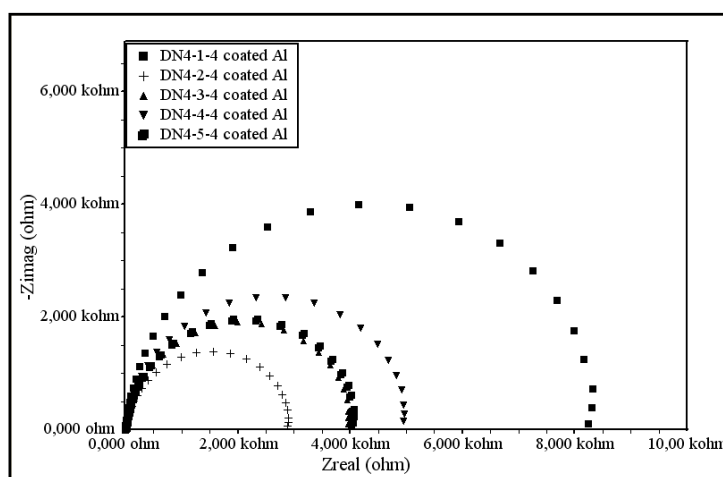


Figure 6.26: Nyquist diagrams of values for DN4-1-4, DN4-2-4, DN4-3-4, DN4-4-4, DN4-5-4 coated Al electrodes. (48 hour).

Changes in corrosion current values for DN4 coated electrodes were plotted against to layer numbers for different exposure time Figure 6.27, Figure 6.28, Figure 6.29, Figure 6.30, Figure 6.31. Minimum corrosion current desired for better protection. So results suggest that for DN4-1, DN4-2, DN4-3, DN4-4, DN4-5; 3-4 layer, 2 layer, 2 layer, 2 layer and 2 layer are favorable, respectively.

The concentration of the DN4_1 is the least (0.01g/ml), each layer will be thin and this allow to apply a multilayer coating without delamination. Although the lower current values obtained for 2 layer coating for higher concentrations (DN4_3, DN4_4 and DN4_5), it is possible to apply 3-4 layer with DN4_1. At higher concentration and at multilayer coatings, thickness increases and this causes delamination of the coatings.

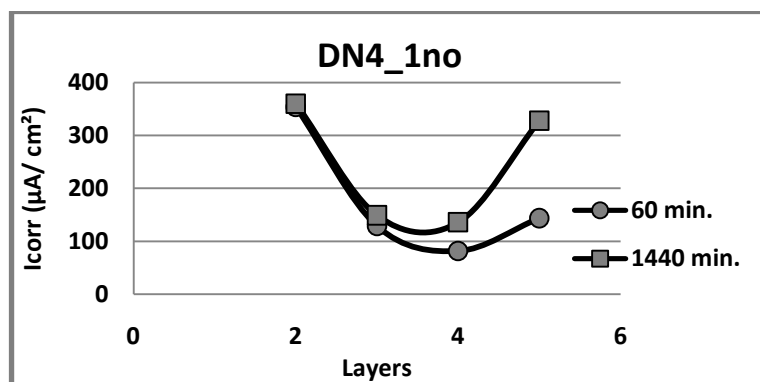


Figure 6.27: Changes of i_{corr} values for DN4-1 coated Al electrodes.

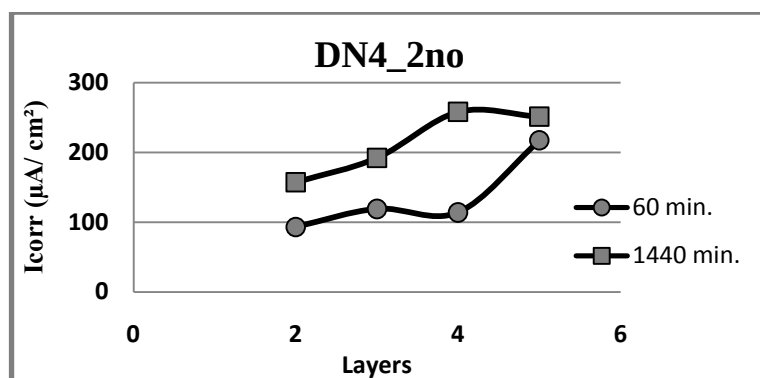


Figure 6.28: Changes of i_{corr} values for DN4-2 coated Al electrodes.

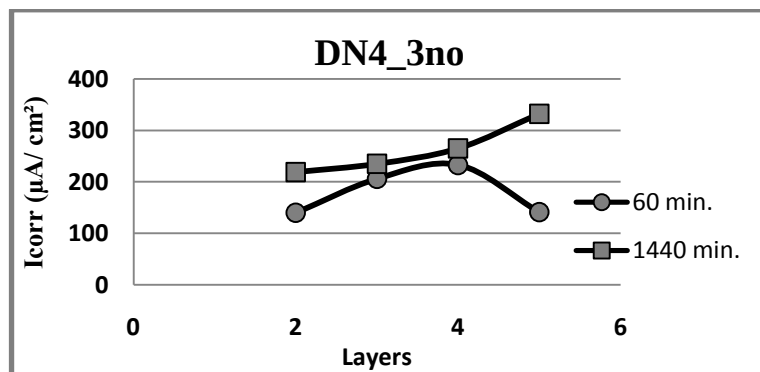


Figure 6.29: Changes of i_{corr} values for DN4-3 coated Al electrodes.

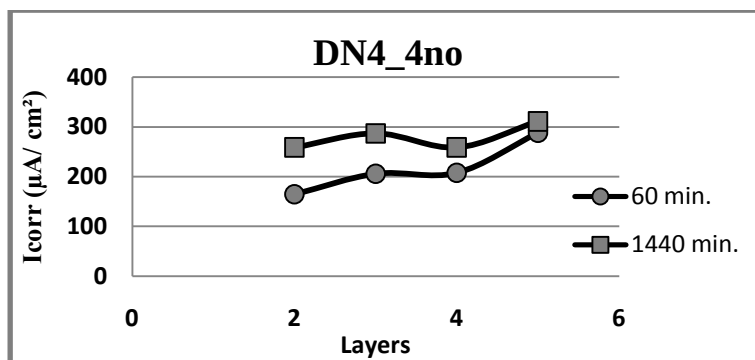


Figure 6.30: Changes of i_{corr} values for DN4-4 coated Al electrodes.

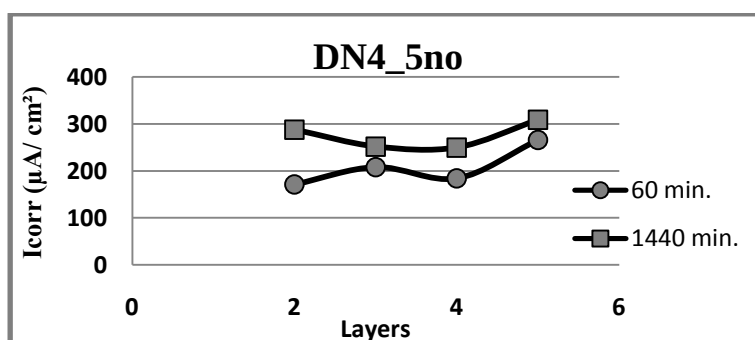


Figure 6.31: Changes of i_{corr} values for DN4-5 coated Al electrodes.

DN4 and DN6 both pyrrole and polydimethylsiloxane containing copolymers. Only difference between them is the amount of oxidant used during the synthesis [42]. Oxidant concentration used for DN6 is lower than DN4 and this only effect the molecular weigh of reuslting polymer. We would like to see the effect of molecular weight on the protection efficiency of coating.

6.2 DN6 Coated Aliminum

Similarly DN6 was coated from different solution with different layer and thickness on Al electrode Table 5.3. The performance of coatings were tested with polarization curves and EIS measurements Figures 6.32, Figures 6.35, Figures 6.37, Figures 6.39, Figures 6.45, Figures 6.47, Figures 6.50, Figures 6.55, Figures 6.57, Figures 6.59 and Figures 6.33, Figures 6.36, Figures 6.38, Figures 6.41, Figures 6.46, Figures 6.49, Figures 6.51, Figures 6.56, Figures 6.58, Figures 6.61.

Corrosion values calculated from polarization curves by Tafel extrapolation are summarized in Table 6.8, Table 6.9, Table 6.10, Table 6.11, Table 6.12, Table 6.13, Table 6.14, Table 6.15, Table 6.16, Table 6.17. As it can be seen from tables corrosion current significantly decreased in accordance with the bare electrode. Percentage inhibition (IE%) values were calculated from the following equation:

$$IE\% = \frac{i_{corr(bare)} - i_{corr(t)}}{i_{corr(bare)}} \times 100 \quad (6.1)$$

For DN6-1 group the highest inhibition efficiency for fresh coating were obtained for DN6-1-4 and DN6-1-5. The concentration of DN6_1 is less (0.01g/ml). As the number of layer increase the protection of the coating increase. After 1440 min IE values of thinner coating (DN6-1-2 and DN6-1-3) become more efficient due to delamination of thicker ones ((DN6-1-4 and DN6-1-5). It can be concluded that for DN6-1 group DN6-1-2 and DN6-1-3 coatings seems more efficient for longer period left in corrosion medium Figure 6.40.

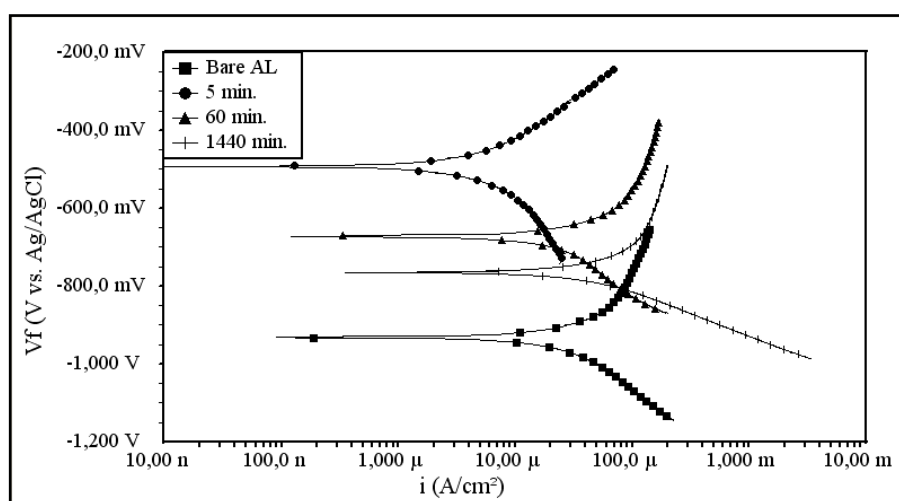


Figure 6.32: Polarization curves of DN6-1-2 coated Al left in 1 M H₂SO₄.

Table 6.8: Corrosion values of DN6-1-2 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE%
5	12,00	-492,0	0,3416	621,2*10 ⁹	5,142	98,7
60	126,0	-672,0	0,3692	643,5*10 ³	54,29	87,0
1440	172,0	-765,0	2,064	0,2576	74,05	82,3
Bare	969,0	-931,0	0.373	0,125	415,8	-

Bode and Nyquist diagram of DN6-1-2 coated electrode were given in Figure 6.33 and 6.34 respectively. Diameter of semicircle related to R_p values of coated surface and semicircle with higher diameter obtained for coating left in corrosion medium for 1 hour Fig 6.34. Although R_p values decrease with exposure time, these decrease are very small and it can be assume that DN6-1-2 coated Al electrode stay almost stable for 2880 min in corrosion medium.

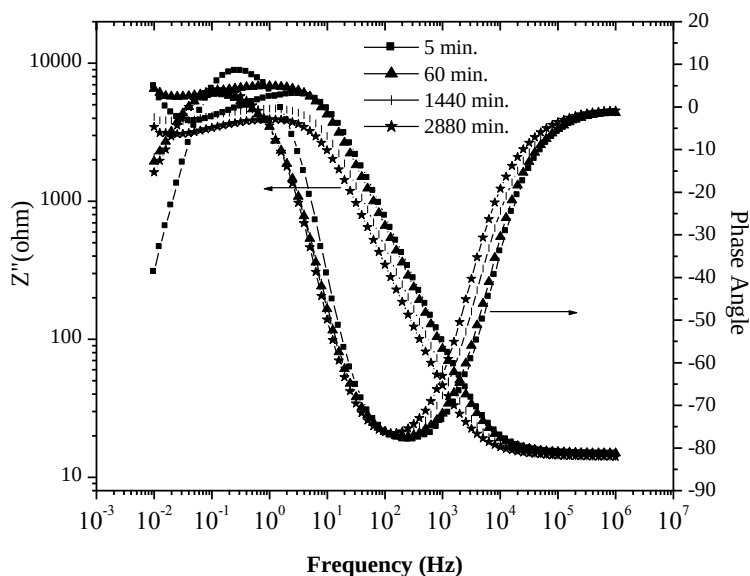


Figure 6.33: Bode diagrams of DN6-1-2 coated Al electrode.

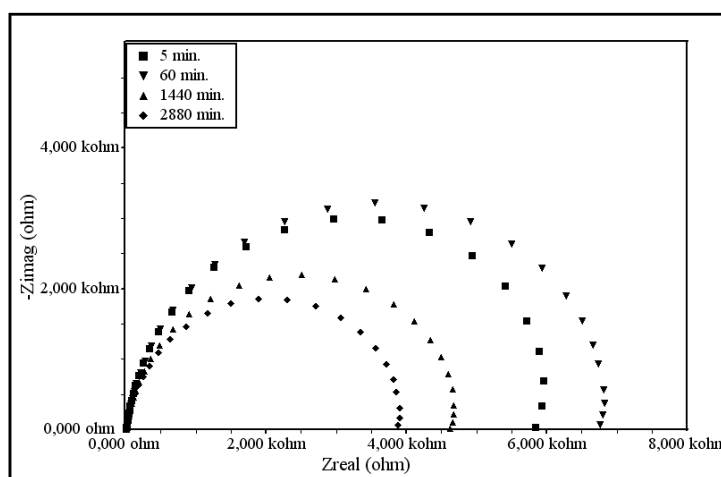


Figure 6.34: Nyquist diagrams of values for DN6-1-2 coated Al electrode.

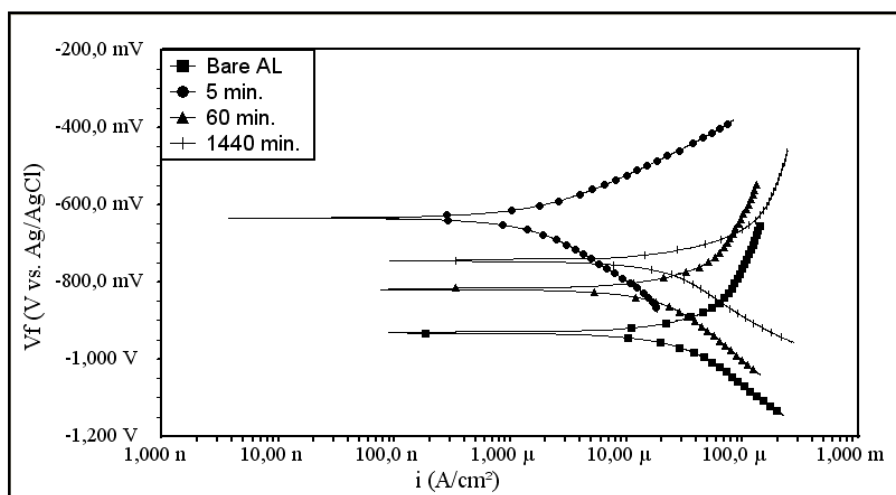


Figure 6.35: Polarization curves of DN6-1-3 coated Al left in 1 M H₂SO₄.

Table 6.9: Corrosion values of DN6-1-3 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	1,980	-634,0	0,1497	0,2503	0,849	99,8
60	141,0	-818,0	0,5728	653,8*10 ⁶	60,75	85,4
1440	181,0	-746,0	0,4899	1,000*10 ¹⁵	77,70	81,3
Bare	969,0	-931,0	0,373	0,125	415,8	-

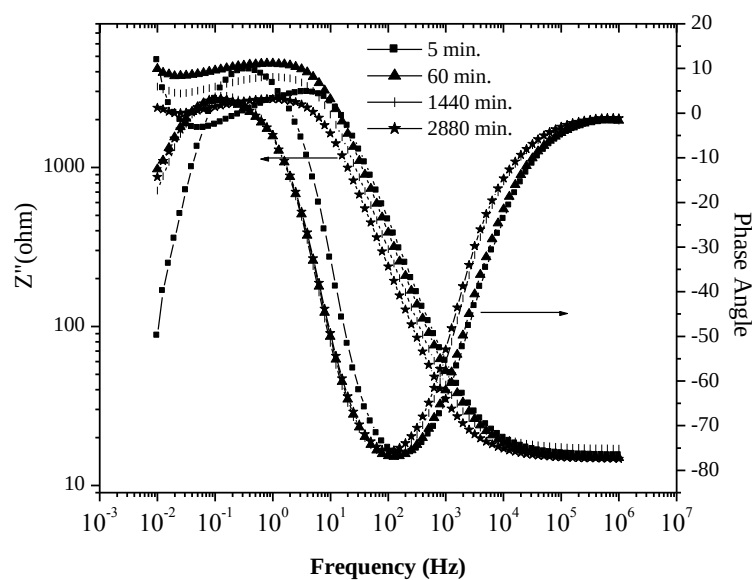


Figure 6.36: Bode diagrams of DN6-1-3 coated Al electrode.

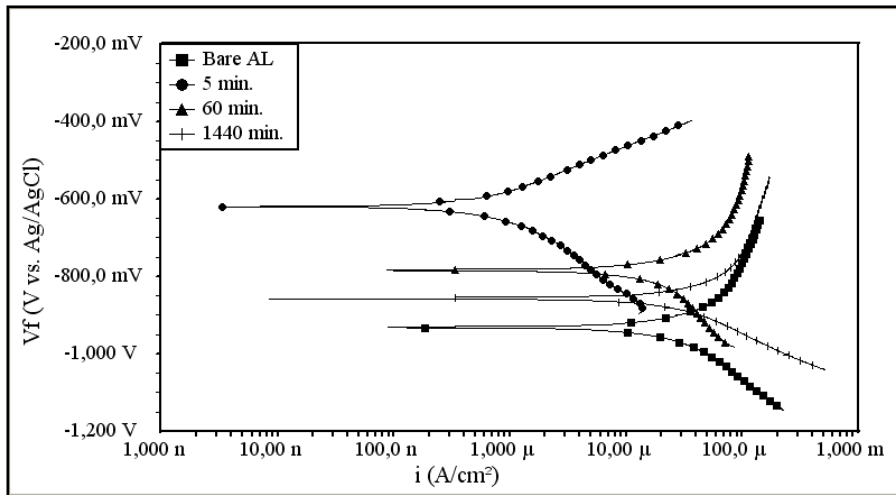


Figure 6.37: Polarization curves of DN6-1-4 coated Al left in 1 M H₂SO₄.

Table 6.10: Corrosion values of DN6-1-4 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	1,080	-619,0	0,1982	0,2245	0,463	99,9
60	164,0	-784,0	0,7254	1,121*10 ⁶	70,21	83,1
1440	259,0	-858,0	725,6*10 ⁶	0,6071	111,3	73,3
Bare	969,0	-931,0	0.373	0,125	415,8	-

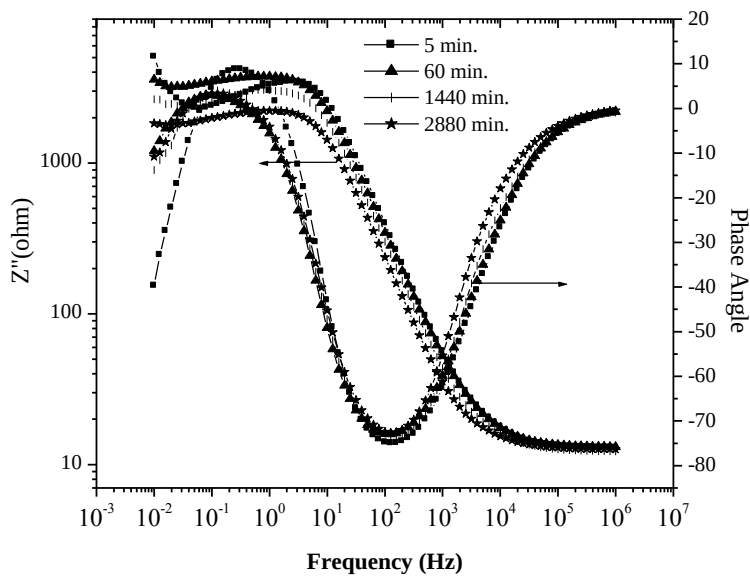


Figure 6.38: Bode diagrams of DN6-1-4 coated Al electrode.

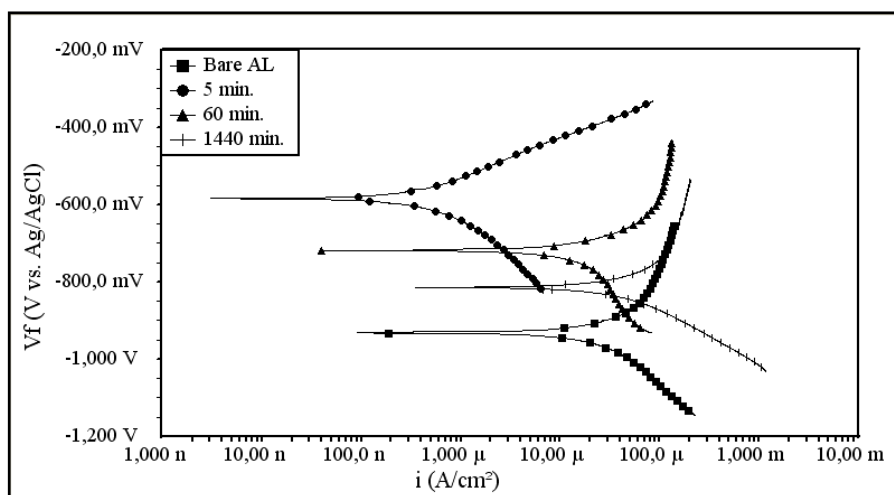


Figure 6.39: Polarization curves of DN6-1-5 coated Al left in 1 M H₂SO₄.

Table 6.11: Corrosion values of DN6-1-5 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	0,722*10 ⁻³	-583,0	0,1753	0,2209	0,310	99,9
60	198,0	-720,0	0,8274	6,180*10 ¹²	85,11	79,6
1440	294,0	-815,0	26,24*10 ⁶	0,4420	126,0	69,7
Bare	969,0	-931,0	0.373	0,125	415,8	-

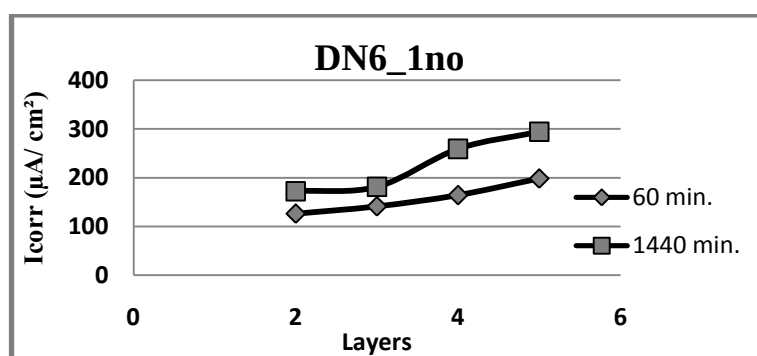


Figure 6.40: Changes of i_{corr} values for DN6-1 coated Al electrodes.

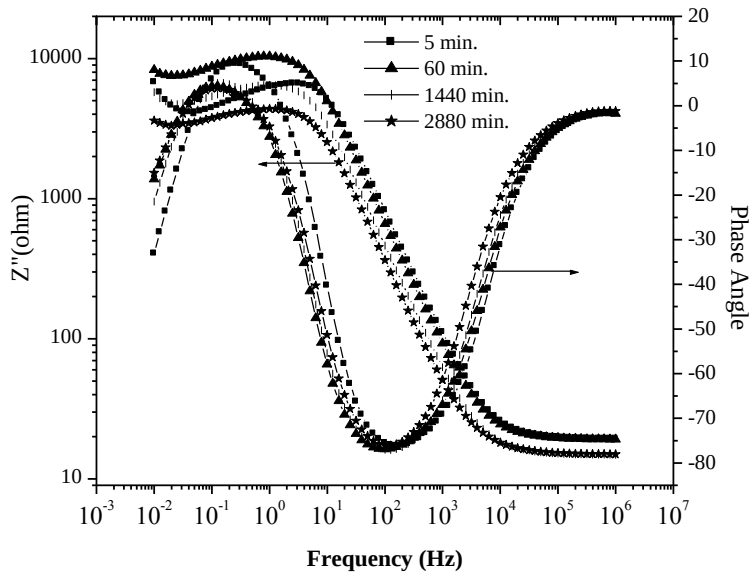


Figure 6.41: Bode diagrams of DN6-1-5 coated Al electrode.

E_{corr} values of DN6-1 group stabilize after 1 hour Figure 6.42. Thinner layer coatings (DN6-1-2 and DN6-1-3) have more anodic values and changes in their values as compare to beginning are less than the thicker ones (DN6-1-2 and DN6-1-3).

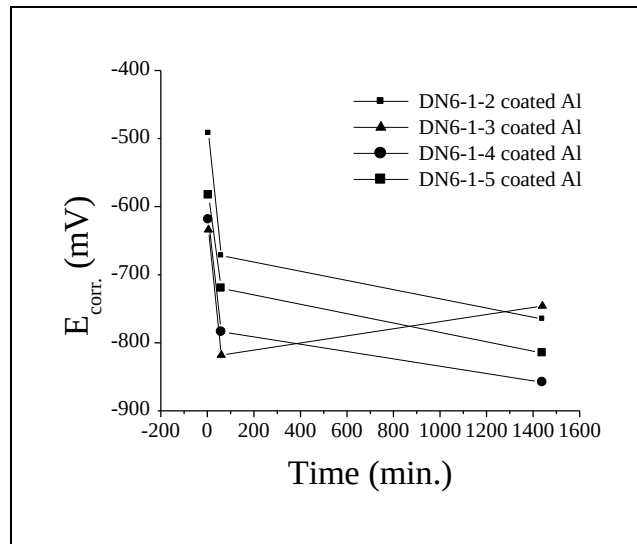


Figure 6.42: Time dependence of E_{corr} values for DN6-1-2, DN6-1-3, DN6-1-4, DN6-1-5 coatings.

Break-point frequencies (f_b) of DN6-1 coated Al electrodes decrease at first and then become almost constant for all coatings Figure 6.43. This result suggest a well adherent and protective coatings.

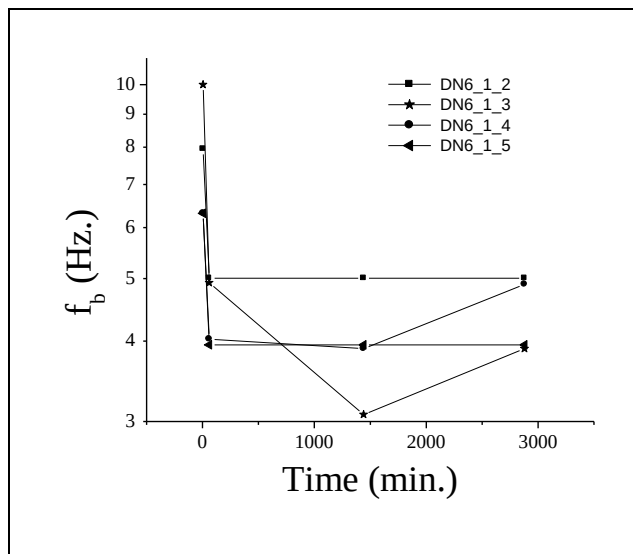


Figure 6.43 : Time dependence of f_b values for DN6-1-2, DN6-1-3, DN6-1-4, DN6-1-5 coatings.

Changes in R_p values of DN6-1 coated electrodes are very small supporting the results obtained from i_{corr} and f_b values Figure 6.44.

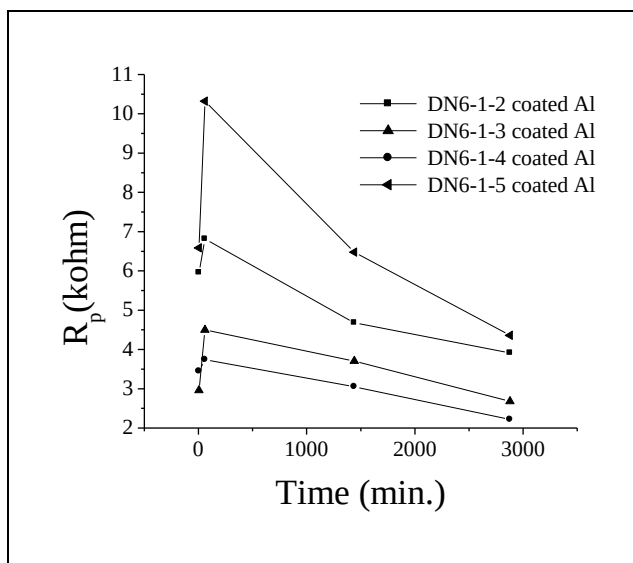


Figure 6.44: Time dependence of R_p values for DN6-1-2, DN6-1-3, DN6-1-4, DN6-1-5 coatings.

The polymer (DN6) concentration is increased and electrode was coated similarly to DN6-1 group. The polarization measurement and EIS results obtained for DN6-2 coated electrodes were given in Figure 6.45, Figure 6.47, Figure 6.50 and Figure 6.46, Figure 6.49, Figure 6.51.

For DN6-2 group the highest inhibition efficiency for fresh coating was obtained for DN6-2-4. As the number of layer increase the protection efficiency of the coating increase. After 1440 min IE values of thinner coating (DN6-2-2 and DN6-2-3) become more efficient due to delamination of thicker ones (DN6-2-4) Table 6.12, Table 6.13 Table 6.14. All results summarized in Figure 6.48 and thinner coatings seems more efficient.

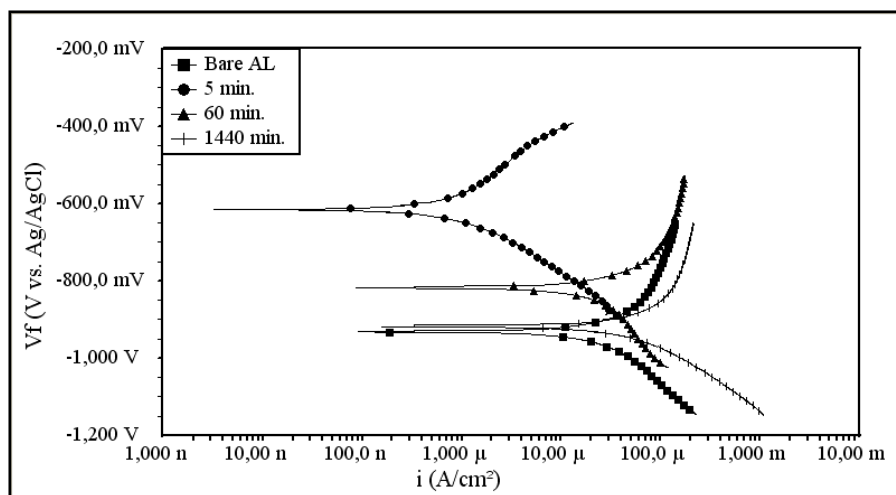


Figure 6.45: Polarization curves of DN6-2-1 coated Al left in 1 M H₂SO₄.

Table 6.12: Corrosion values of DN6-2-1 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μ A/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	1,530	-615,0	0,3936	0,1964	0,658	98,8
60	121,0	-818,0	0,3777	$1,000 \cdot 10^{15}$	51,81	87,0
1440	160,0	-918,0	1,283	0,2828	68,74	82,3
Bare	969,0	-931,0	0.373	0,125	415,8	-

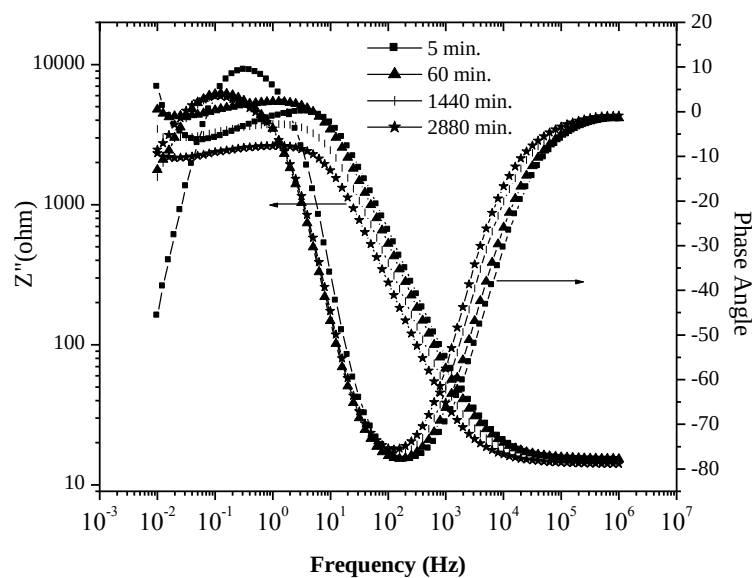


Figure 6.46: Bode diagrams of DN6-2-1 coated Al electrode.

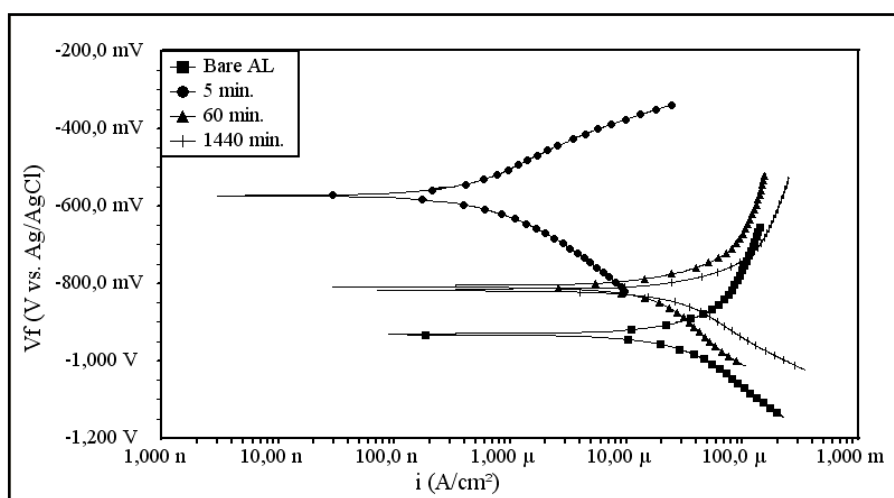


Figure 6.47: Polarization curves of DN6-2-2 coated Al left in 1 M H₂SO₄.

Table 6.13: Corrosion values of DN6-2-2 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	0,634	-572,0	0,2245	0,1757	0,272	99,8
60	146,0	-809,0	0,6461	1,000*10 ¹⁵	62,83	85,4
1440	181,0	-818,0	0,4298	380,9*10 ⁶	77,58	81,3
Bare	969,0	-931,0	0.373	0,125	415,8	-

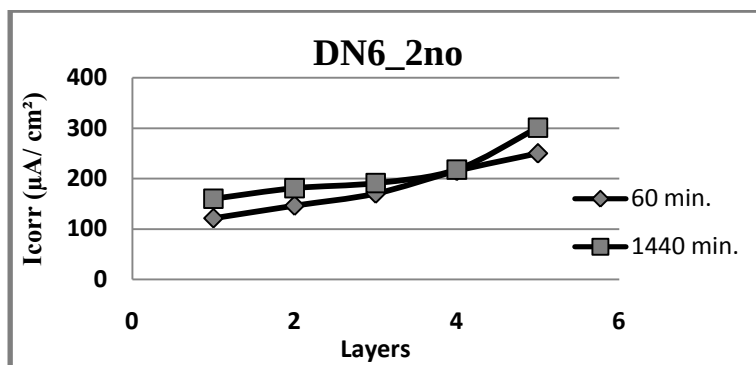


Figure 6.48: Changes of i_{corr} values for DN6-2 coated Al electrodes.

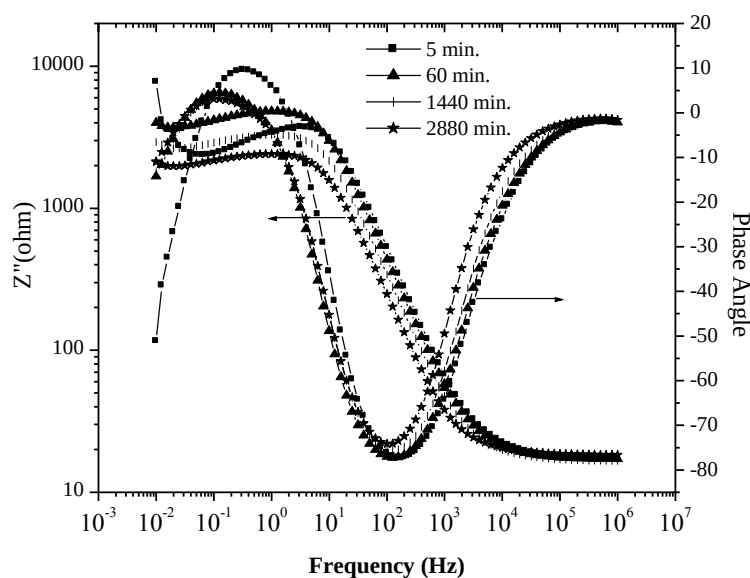


Figure 6.49: Bode diagrams of DN6-2-2 coated Al electrode.

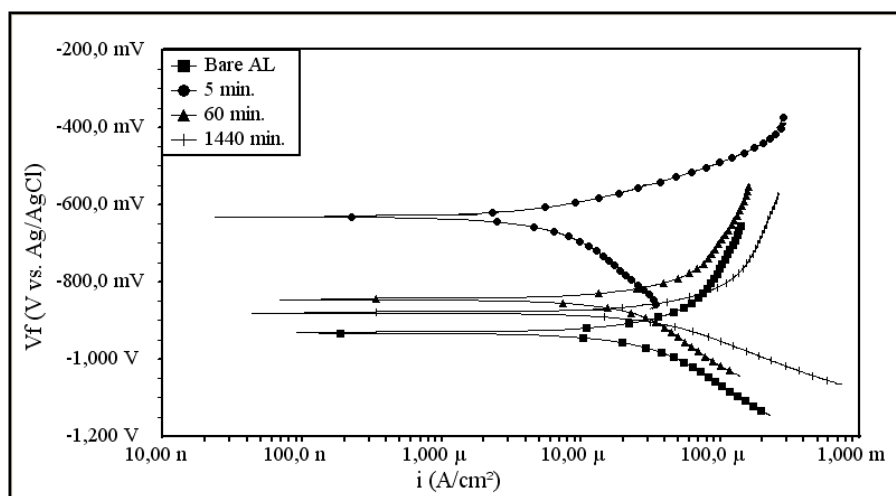


Figure 6.50: Polarization curves of DN6-2-3 coated Al left in 1 M H_2SO_4 .

Table 6.14: Corrosion values of DN6-2-3 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	8,100	-631,0	0,1295	0,3518	3,477	99,9
60	170,0	-845,0	0,5960	134,1*10 ³	72,78	83,1
1440	191,0	-879,0	1,182	0,4343	82,08	73,3
Bare	969,0	-931,0	0.373	0,125	415,8	-

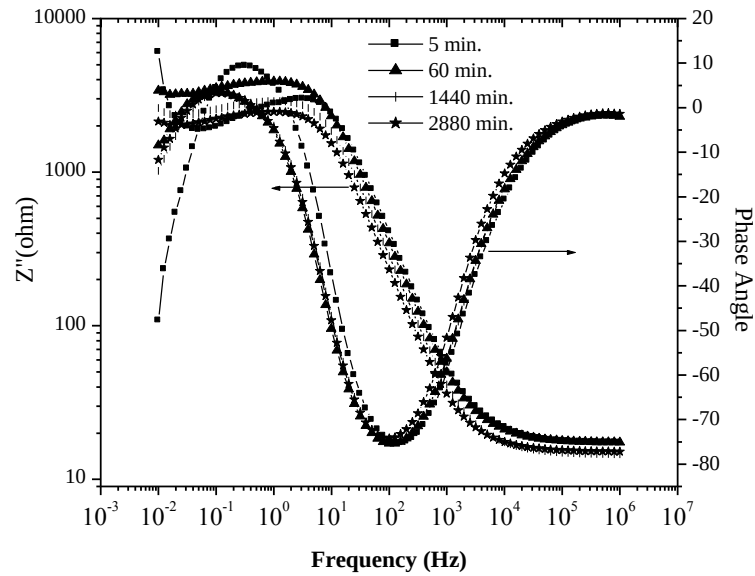


Figure 6.51: Bode diagrams of DN6-2-3 coated Al electrode.

E_{corr} values of DN6-2 coated aluminum continue to decrease in one hour and then they stabilized Figure 6.52.

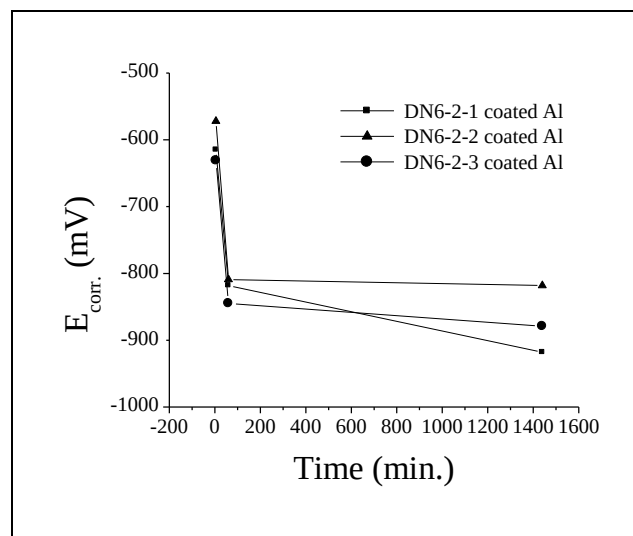


Figure 6.52: Time dependence of E_{corr.} values for DN6-2-1, DN6-2-2, DN6-2-3 coatings.

f_b and R_p values of DN6-2 coated electrodes obtained from Bode and Nyquist diagrams Figure 6.53 and Figure 6.54. At the beginning f_b values decrease and R_p values increase showing an effective protection. By time there is small changes in these values indicating a stable coating.

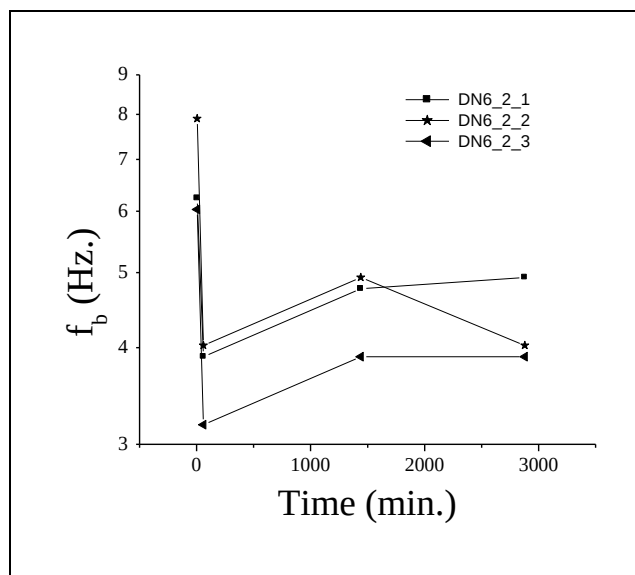


Figure 6.53 : Time dependence of f_b values for DN6-2-1, DN6-2-2, DN6-2-3 coatings.

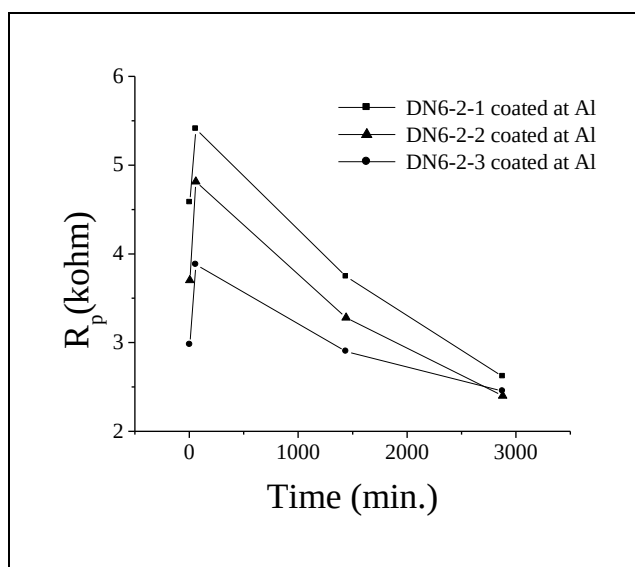


Figure 6.54: Time dependence of R_p values for DN6-2-1, DN6-2-2, DN6-2-3 coatings.

Concentration of polymer (DN6) increased again and similarly to DN6-1 and DN6-2 group coating were applied and polarization curves and EIS test performed to investigate corrosion behavior of (DN6-3) coatings Figure 6.55, Figure 6.57, Figure 6.59 and Figure 6.56, Figure 6.58, Figure 6.61.

Changes in corrosion currents were followed with time at different thickness. Similar results to DN6-1 and DN6-2 group were obtained for DN6-3 group coatings Table 6.15, 6.16, 6.17 and Figure 6.60, thinner coating are more effective at longer exposure time due to blister formation for thicker coating.

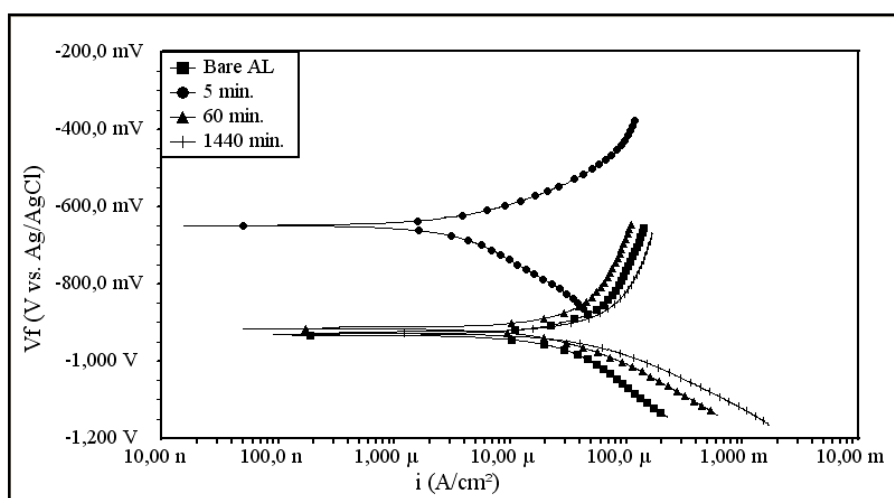


Figure 6.55: Polarization curves of DN6-3-1 coated Al left in 1 M H₂SO₄.

Table 6.15: Corrosion values of DN6-3-1 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	4,430	-648,0	0,1221	0,2368	1,902	99,5
60	130,0	-914,0	670,7	0,3945	56,03	86,6
1440	186,0	-927,0	1,000*10 ¹⁵	0,3188	80,01	80,8
Bare	969,0	-931,0	0.373	0,125	415,8	-

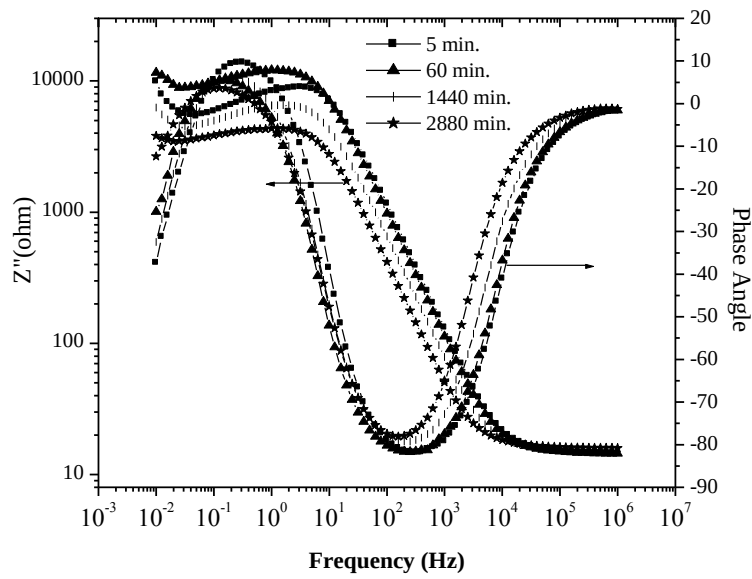


Figure 6.56: Bode diagrams of DN6-3-1 coated Al electrode.

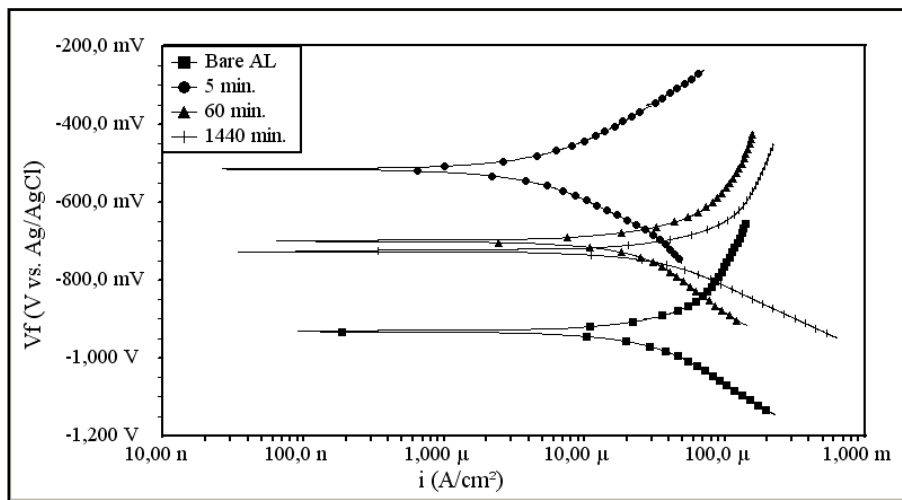


Figure 6.57: Polarization curves of DN6-3-2 coated Al left in 1 M H₂SO₄.

Table 6.16: Corrosion values of DN6-3-2 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	6,410	-515,0	0,2338	0,2489	2,754	99,4
60	159,0	-700,0	0,5636	1,000*10 ¹⁵	68,17	83,6
1440	213,0	-726,0	0,8378	0,8263	91,31	78,0
Bare	969,0	-931,0	0.373	0,125	415,8	-

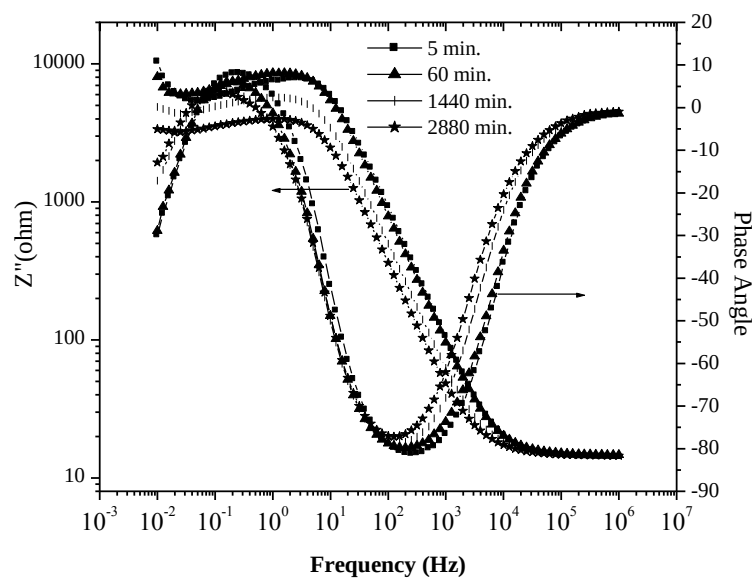


Figure 6.58: Bode diagrams of DN6-3-2 coated Al electrode.

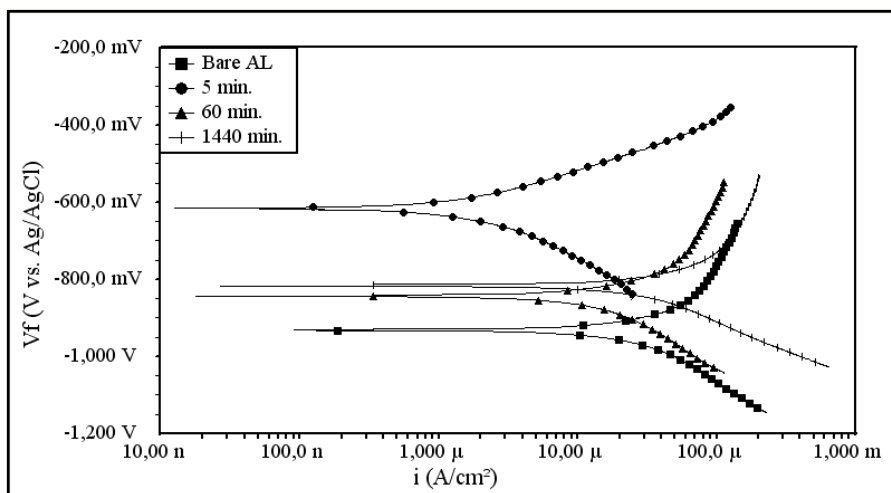


Figure 6.59: Polarization curves of DN6-3-3 coated Al left in 1 M H₂SO₄.

Table 6.17: Corrosion values of DN6-3-3 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	1,940	-615,0	0,1384	0,1719	0,833	99,8
60	189,0	-844,0	0,9253	989,2*10 ⁶	81,20	80,5
1440	348,0	-817,0	0,9733	2,913	149,2	64,1
Bare	969,0	-931,0	0.373	0,125	415,8	-

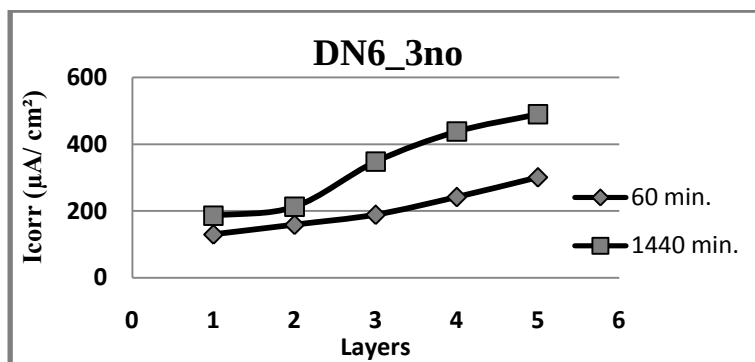


Figure 6.60: Changes of i_{corr} values for DN6-3 coated Al electrodes.

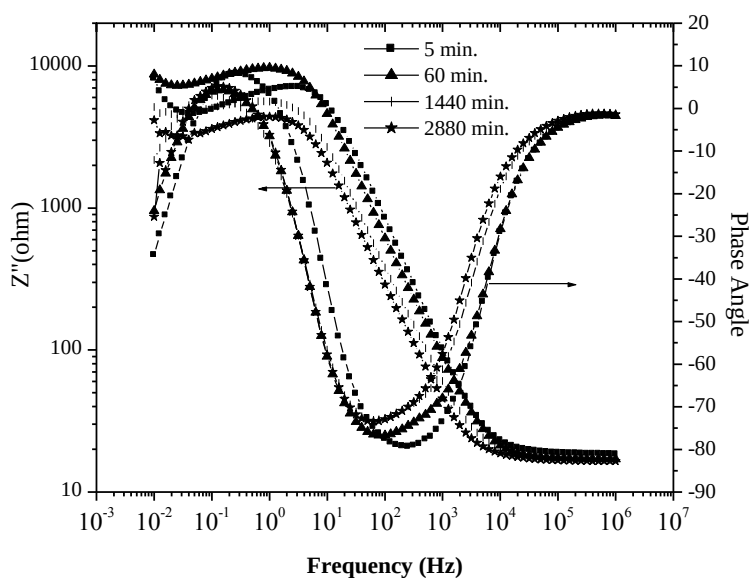


Figure 6.61: Bode diagrams of DN6-3-3 coated Al electrode.

E_{corr} values of DN6-3 coated aluminum electrodes are also become stable after one hour and the changes in the values for DN6-3-2 is less than the others Figure 6.62.

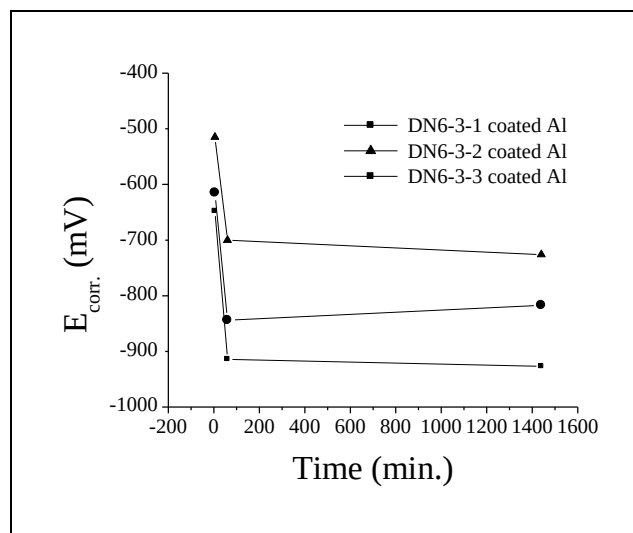


Figure 6.62: Time dependence of $E_{\text{corr.}}$ values for DN6-3-1, DN6-3-2, DN6-3-3 coatings.

Changes in f_b and R_p values of DN6-3 coated Al electrodes are very small Figure 6.63 and Figure 6.64. So these results also support the conclusion that DN6 is effective coating to protect the aluminum from acidic corrosion.

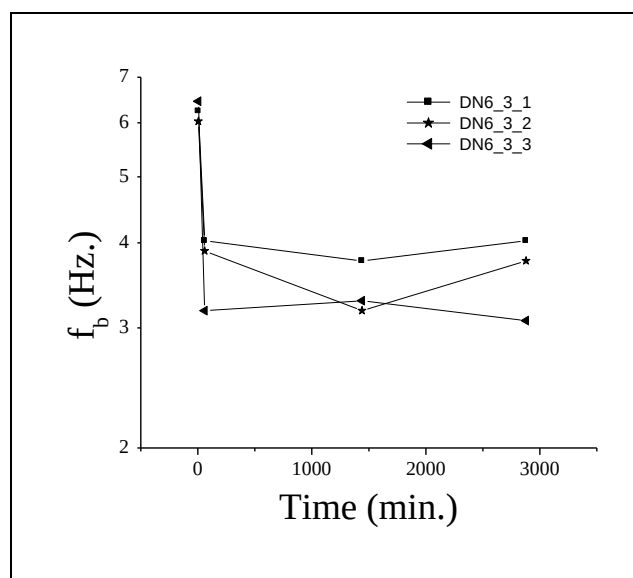


Figure 6.63 : Time dependence of f_b values for DN6-3-1, DN6-3-2, DN6-3-3 coatings.

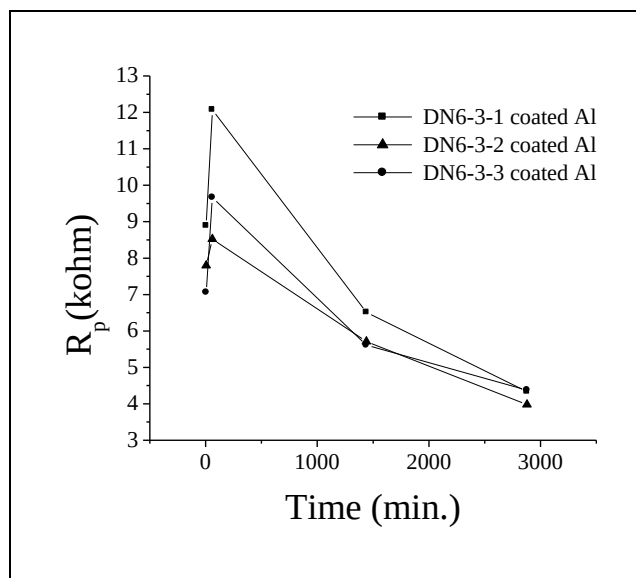


Figure 6.64: Time dependence of R_p values for DN6-3-1, DN6-3-2, DN6-3-3 coatings.

Nyquist diagram of DN6 coated electrodes obtain from different coating solutions DN6-1, DN6-2, DN6-3 Table 5.3 at same layer (2 layer) was compared for 1 hour and 48 hour exposure time Figure 6.65 and Figure 6.66. For one hour the coating obtained most concentrated solution (DN6-3) has the semicircle with the highest diameter which indicate the highest R_p values and the most resistive layer. For 48 hours exposure time, water uptake cause some decrease in R_p values and DN6-1 and DN6-3 show similar behavior. This result indicates that for longer time, thinner coating obtained from diluted solution might be as effective as thicker coating. The uptake of electrolyte by the porous coatings is probably most important. Water between the coating and the metal causes delamination. Thinner coated absorb water less than thicker one and this make coating more stable.

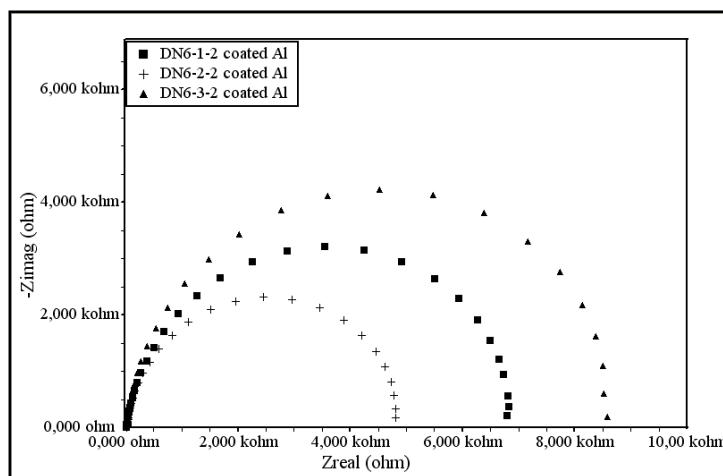


Figure 6.65: Nyquist diagrams of values for DN6-1-2, DN6-2-2, DN6-3-2 coated Al electrodes. (1hour).

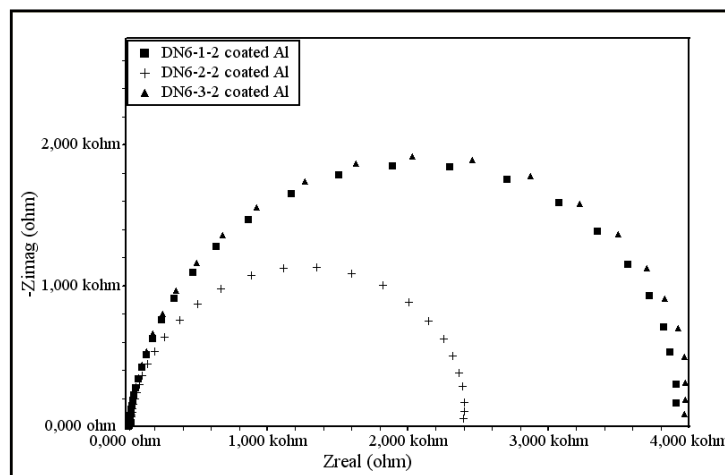


Figure 6.66: Nyquist diagrams of values for DN6-1-2, DN6-2-2, DN6-3-2 coated Al electrodes. (48 hour).

Comparison between the DN6 and DN4 coated electrodes in terms of changes in corrosion currents with time and layer number were given in Figure 6.69, Figure 6.72, Figure 6.73, Figure 6.74.

From these figure the following conclusion can be summarized:

For 60 min for DN4 coating obtained diluted solutions(1 no and 2 no) are effective with multilayer coating and 4 layer coating seems more favorable Figure 6.67, Figure 6.68, Figure 6.69. However for DN6 for all concentrations increase in layer number causes increase in currents.

For longer exposure time same behavior was observed both for DN6 and DN4 Figure 6.70, Figure 6.71, Figure 6.72.

The only difference in DN4 and DN6 is initiator concentration used in synthesis and it is lower in the case of DN6 which results a higher molecules weight copolymer. Since the molecular weight of DN6 expected to be higher than DN4, even the single layer system is effective for protection. The uptake of electrolyte for multilayer coating cause the delamination of thick coating more easily than thin single layer ones.

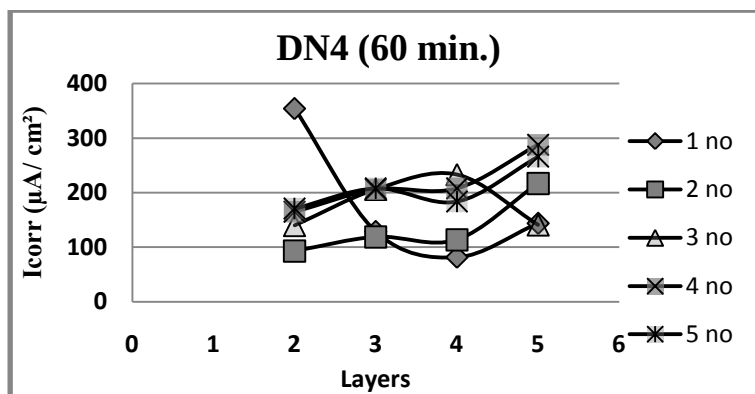


Figure 6.67: Changes of i_{corr} values for DN4 coated Al electrodes for 60 minutes.

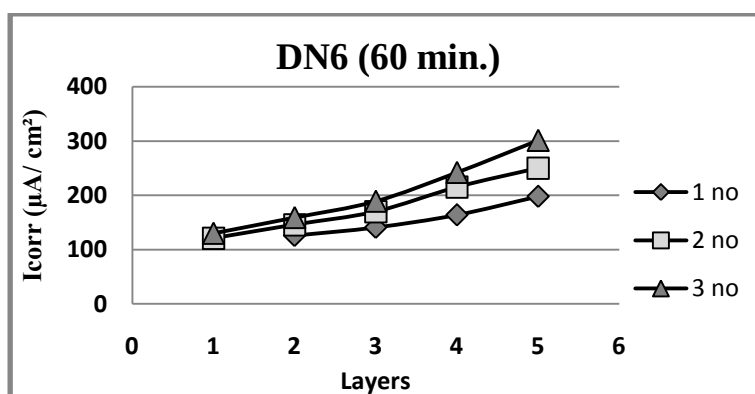


Figure 6.68: Changes of i_{corr} values for DN6 coated Al electrodes for 60 minutes.

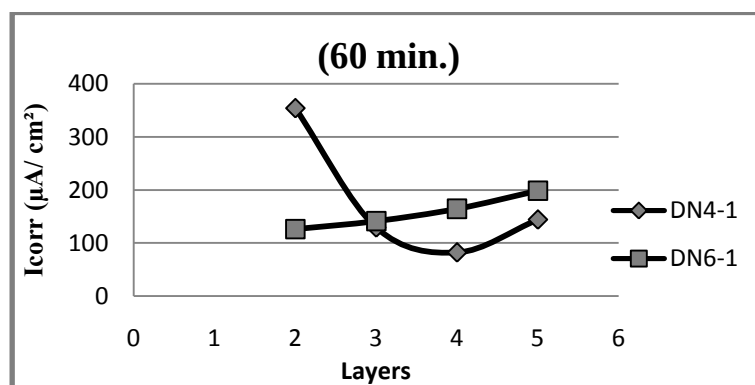


Figure 6.69: Changes of i_{corr} values for DN4-1, DN6-1 coated Al electrodes for 60 minutes.

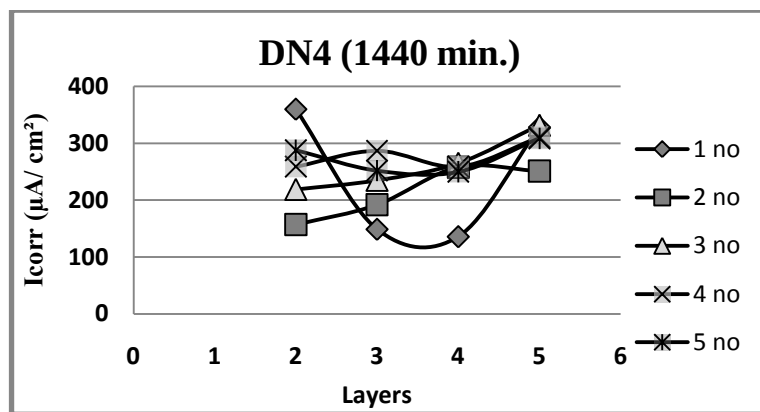


Figure 6.70: Changes of i_{corr} values for DN4 coated Al electrodes for 1440 minutes.

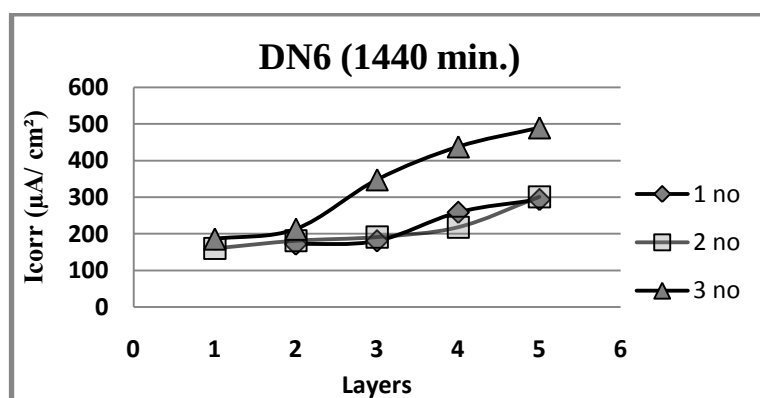


Figure 6.71: Changes of i_{corr} values for DN6 coated Al electrodes for 1440 minutes.

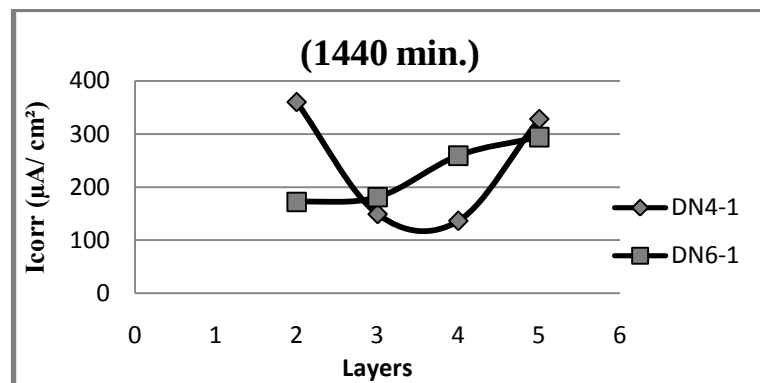


Figure 6.72: Changes of i_{corr} values for DN4-1, DN6-1 coated Al electrodes for 1440 minutes.

When DN4 and DN6 coating obtained from a solution that have same concentration for first 60 minute both have similar behavior. However for longer exposure time DN4 which has lower molecular weight seems more efficient than DN6 Figure 6.73, Figure 6.74.

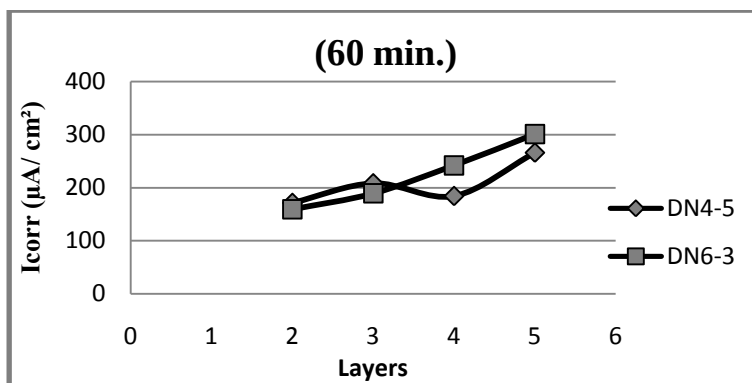


Figure 6.73: Changes of i_{corr} values for DN4-5, DN6-3 coated Al electrodes for 60 minutes.

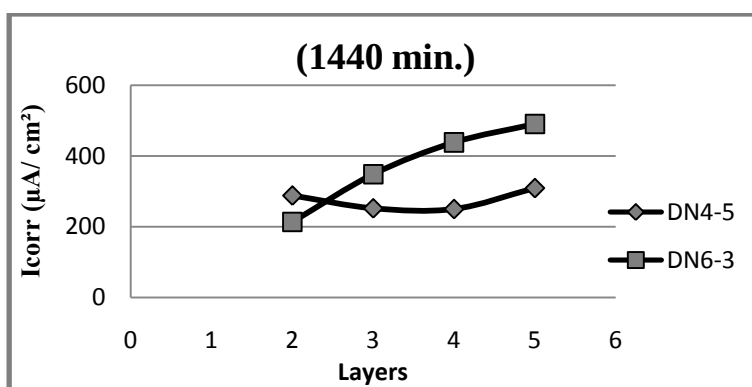


Figure 6.74: Changes of i_{corr} values for DN4-5, DN6-3 coated Al electrodes for 1440 minutes.

The uptake of electrolyte by the porous coatings is probably most important. It explains why the protection time of samples investigated is low. Water between the coating and the metal causes delamination.

The curves exhibit behavior that is somewhat similar to that of the single layer systems while the time to failure is significantly improved.

6.3 DN1_1 Coated Aluminum

Another copolymer (DN1-1) that have carbazole unit instead of pyrrole was coated and test similarly to DN4 and DN6 polymers. Anodic and cathodic polarization curves, corrosion data obtained from these curves Figure 6.75, Figure 6.78, Figure 6.84, Figure 6.86, Figure 6.92, Figure 6.94. Bode graphs were showed Figure 6.75, Figure 6.78, Figure 6.84, Figure 6.86, Figure 6.92, Figure 6.94 and Figure 6.76, Figure 6.79, Figure 6.85, Figure 6.87, Figure 6.93, Figure 6.95. Nyquist graphs were given Figure 6.77, Figure 6.100, Figure 6.101.

f_b and R_p values obtained from these graphs were given below for different coating having different layer numbers of DN1_1 coated electrodes Figure 6.82, Figure 6.90, Figure 6.98 and Figure 6.83, Figure 6.91, Figure 6.99.

I_{corr} , E_{corr} and IE values of DN1_1 group are given Table 6.18, Table 6.19, Table 6.20, Table 6.21, Table 6.22, Table 6.23.

When corrosion current values (i_{corr}) compared to bare electrode in can be seen that I_{corr} values significantly decreased for coated electrodes for all type of coatings Table 6.18, Table 6.19, Table 6.20, Table 6.21, Table 6.22, Table 6.23.

The uptake of electrolyte by the porous coatings is probably most important. Water between the coating and the metal causes delamination. Water uptake depends on the layer number that coating contains as well as thickness of coating. Here coatings obtained from three different solutions of polymer DN1_1-1, DN1_1-2, DN1_1-3. Details are given in Table 5.1. Changes in I_{corr} values for DN1_1-1 group depending on time and layer number were given in Figure 6.80. As the number of layer increase, higher corrosion currents were observed as the time of exposure increase. This happen due to water uptake and it explains why the protection time of samples investigated is low.

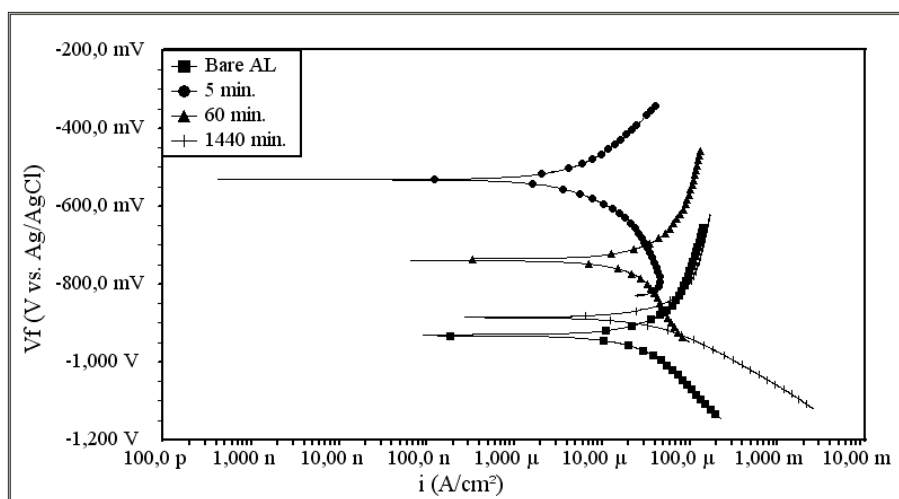


Figure 6.75: Polarization curves of DN1_1-1-2 coated Al left in 1M H₂SO₄.

Table 6.18: Corrosion values of DN1_1-1-2 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μ A/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	14,40	-531,0	0,5311	0,3603	6,166	98,5
60	172,0	-738,0	0,6538	73,61*10 ³	73,76	82,2
1440	205,0	-886,0	386,4*10 ⁶	0,3086	88,05	78,8
Bare	969,0	-931,0	0.373	0,125	415,8	-

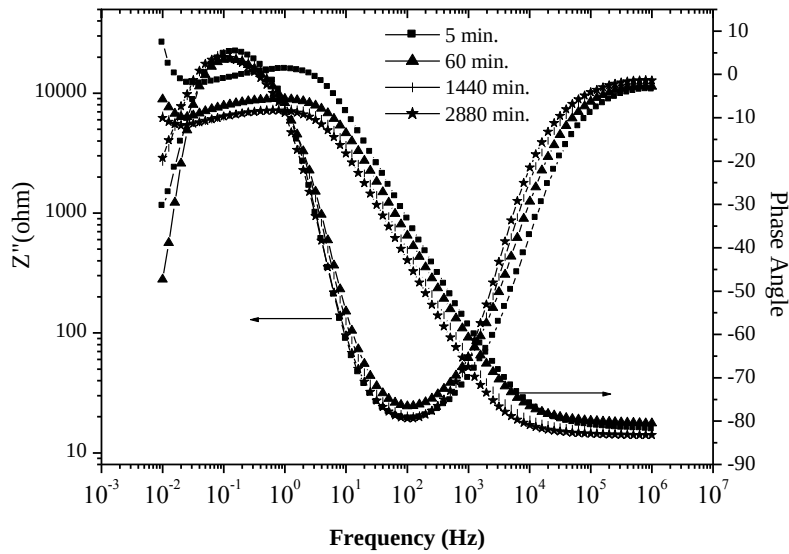


Figure 6.76: Bode diagrams of DN1_1-1-2 coated Al electrode.

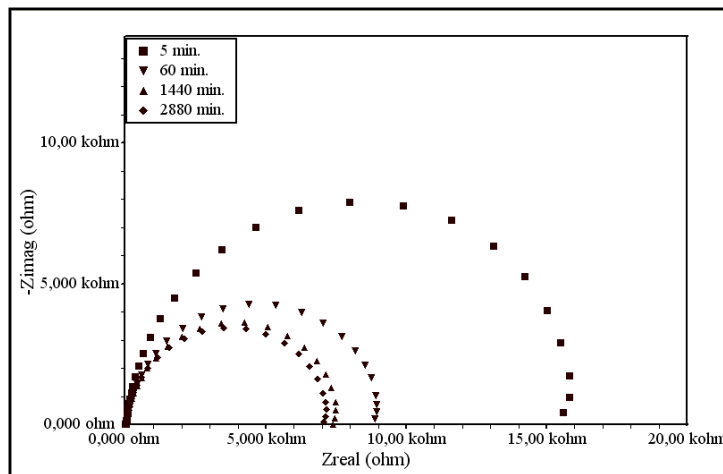


Figure 6.77: Nyquist diagrams of values for DN1_1-1-2 coated Al electrode.

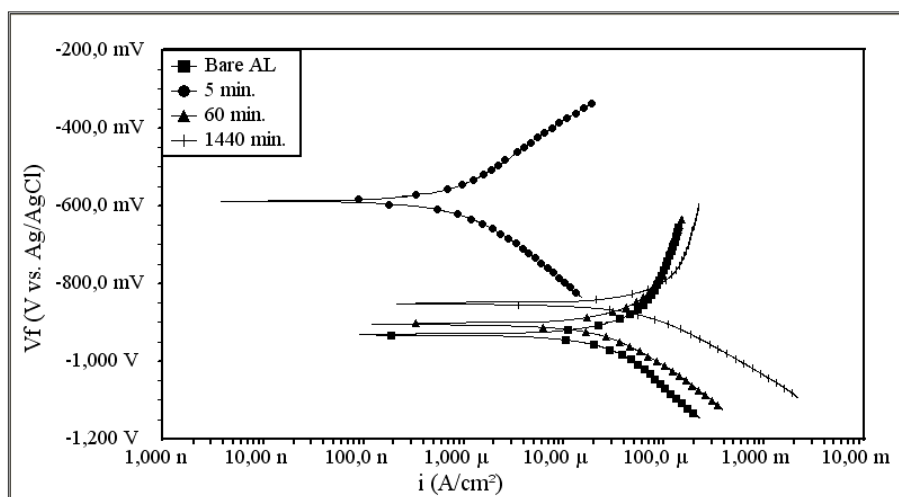


Figure 6.78: Polarization curves of DN1_1-1-3 coated Al left in 1 M H₂SO₄.

Table 6.19: Corrosion values of DN1_1-1-3 coated Al left in 1 M H₂SO₄.

Time (minute)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV)	B_a (V/decade)	B_c (V/decade)	CR (mpy)	IE %
5	1,430	-587,0	0,3203	0,2479	0,614	99,8
60	93,70	-905,0	0,5878	$458,8 \cdot 10^3$	40,25	90,3
1440	233,0	-852,0	2,217	0,3294	99,97	75,9
Bare	969,0	-931,0	0.373	0,125	415,8	-

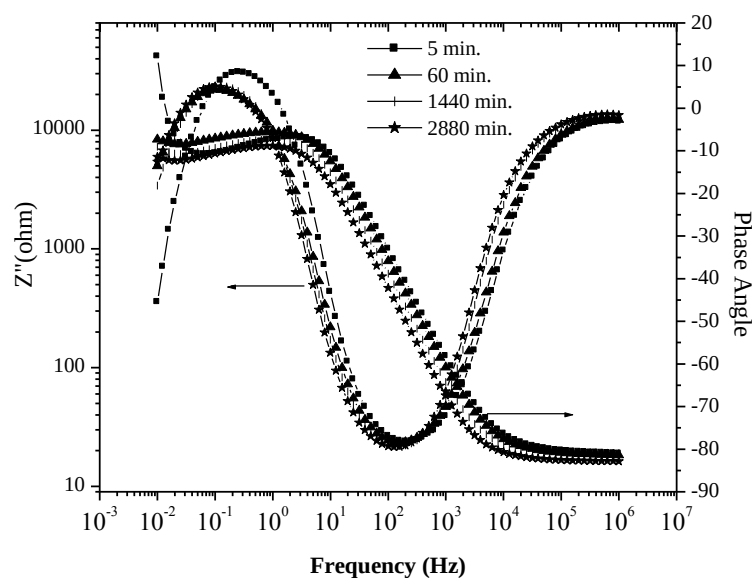


Figure 6.79: Bode diagrams of DN1_1-1-3 coated Al electrode.

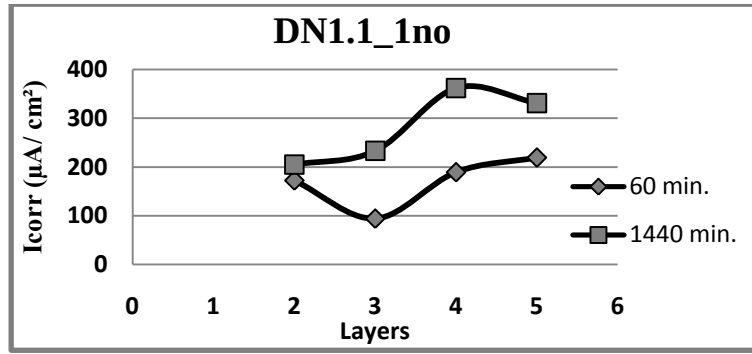


Figure 6.80: Changes of i_{corr} values for DN1.1-1 coated Al electrodes.

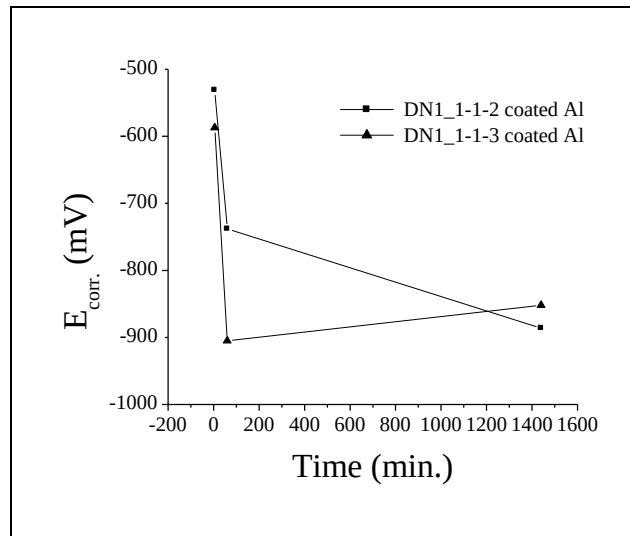


Figure 6.81: Time dependence of E_{corr} values for DN1_1-1-2, DN1_1-1-3 coatings.

Changes of E_{corr} values with time shows similar trends both for 2 and 3 layer coated Aluminum electrodes Figure 6.81. However decrease in E_{corr} value of fresh coating after one hour for 2 layer coated Al (DN1_1-1-2) is less 3 layer coated one (DN1_1-1-3).

Although breakpoint frequencies of DN1_1-1-2 and DN1_1-1-3 coatings have changes at first, they are almost stable during 3000 min exposure time Figure 6.82. These results suggest that damage of coating does not occur.

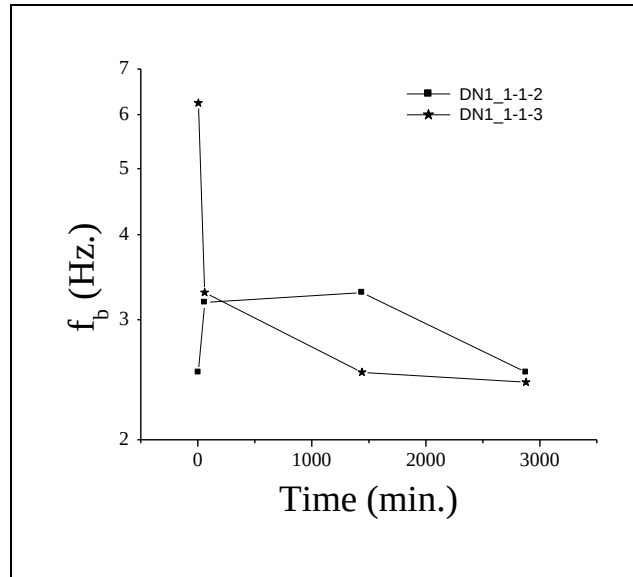


Figure 6.82 : Time dependence of f_b values for DN1_1-1-2, DN1_1-1-3 coatings.

As the disbonding of the coating occurs changes of polarization resistance, R_p , observed which related to delaminated area or delamination ratio. Here for DN1_1-1-2, DN1_1-1-3 coatings changes in R_p values are very small and supporting the conclusion that coatings are stable during 3000 min exposure time Fig 6.83.

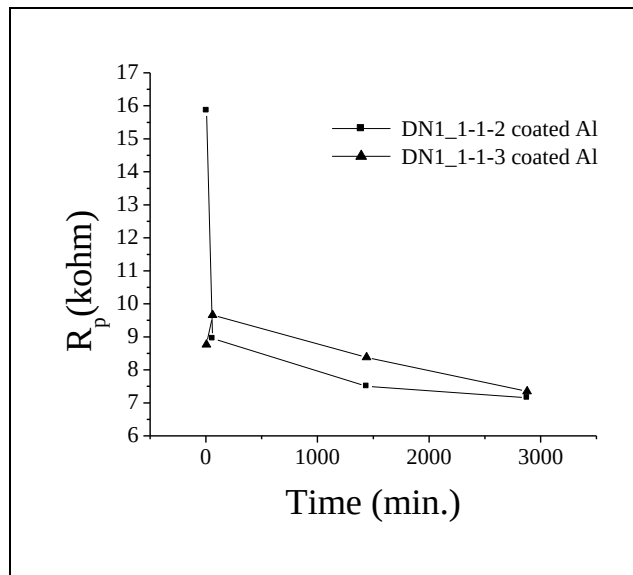


Figure 6.83: Time dependence of R_p values for DN1_1-1-2, DN1_1-1-3 coatings.

The results obtained from polarization and EIS measurements indicate that similarly to DN1_1-1 group coatings, DN1_1-2 which are obtained a more concentrated solutions of polymer, show good protection for aluminum electrode Figure 6.75, Figure 6.78, Figure 6.84, Figure 6.86 and Figure 6.76, Figure 6.79, Figure 6.85, Figure 6.87. In these group since the concentration is higher, thickness increase with layer number is higher than DN1_1-1 group. In this case one layer coating also seems effective for protection Figure 6.88.

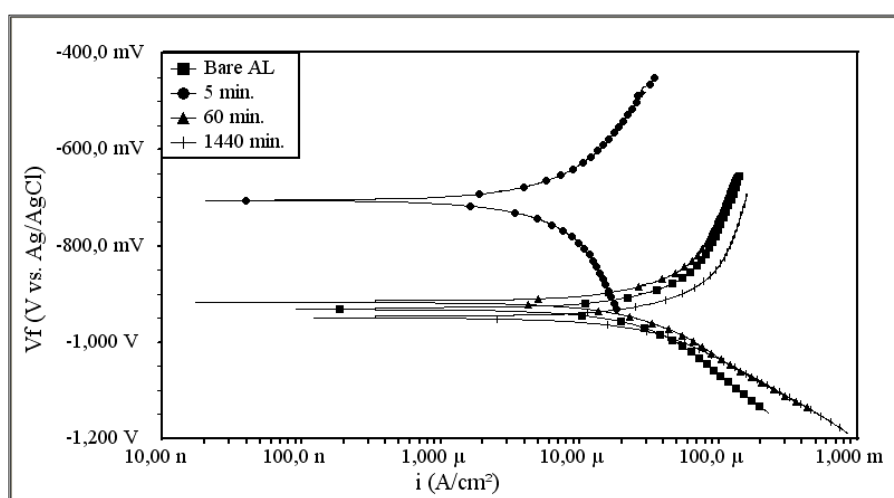


Figure 6.84: Polarization curves of DN1_1-2-2 coated Al left in 1 M H₂SO₄.

Table 6.20: Corrosion values of DN1_1-2-2 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE%
5	39,60	-705,0	0,7769	1,000*10 ¹⁵	17,02	95,9
60	265,0	-917,0	26,71*10 ⁶	0,8137	113,8	72,6
1440	294,0	-949,0	1,572*10 ³	0,6304	126,3	69,6
Bare	969,0	-931,0	0.373	0,125	415,8	-

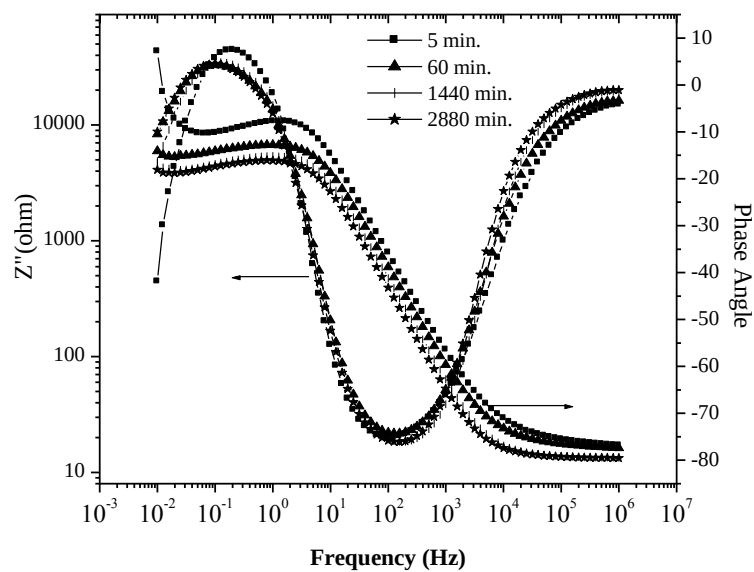


Figure 6.85: Bode diagrams of DN1_1-2-2 coated AL electrode.

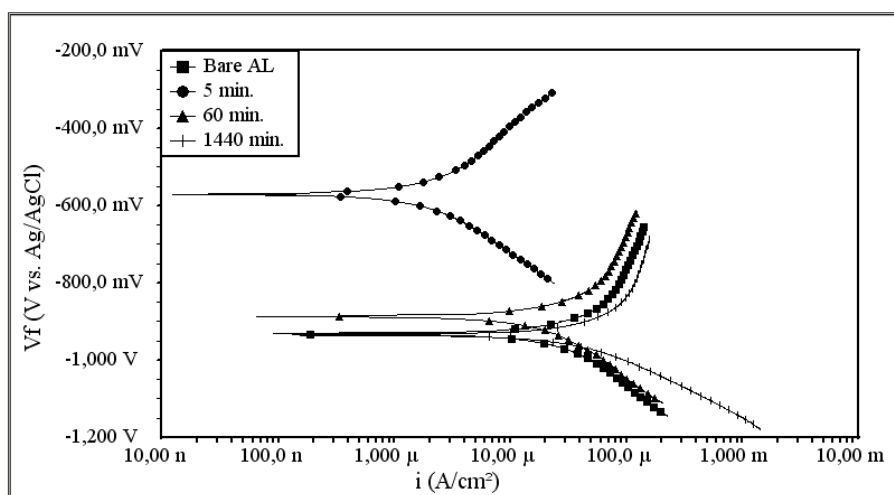


Figure 6.86: Polarization curves of DN1_1-2-3 coated Al left in 1 M H₂SO₄.

Table 6.21: Corrosion values of DN1_1-2-3 coated Al left in 1 M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	27,20	-570,0	3,058	1,886	11,69	97,1
60	276,0	-887,0	1,087	33,20*10 ³	118,4	71,5
1440	315,0	-934,0	841,0*10 ³	0,5757	135,4	67,4
Bare	969,0	-931,0	0.373	0,125	415,8	-

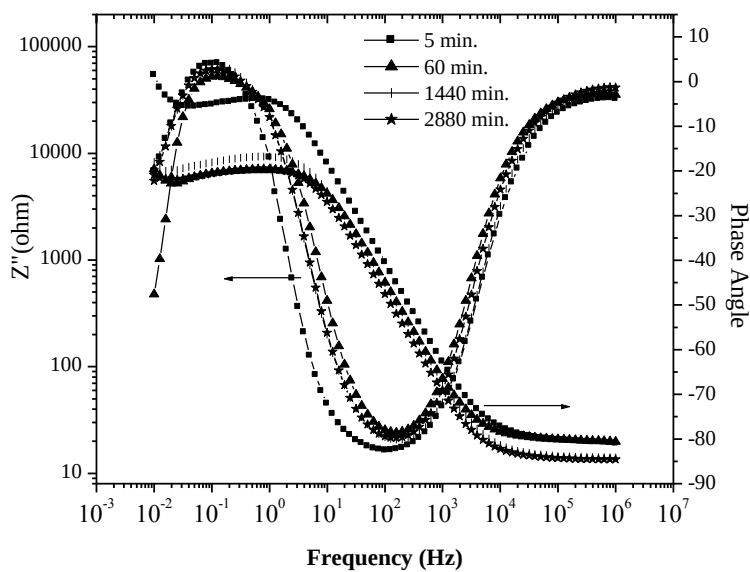


Figure 6.87: Bode diagrams of DN1_1-2-3 coated Al electrode.

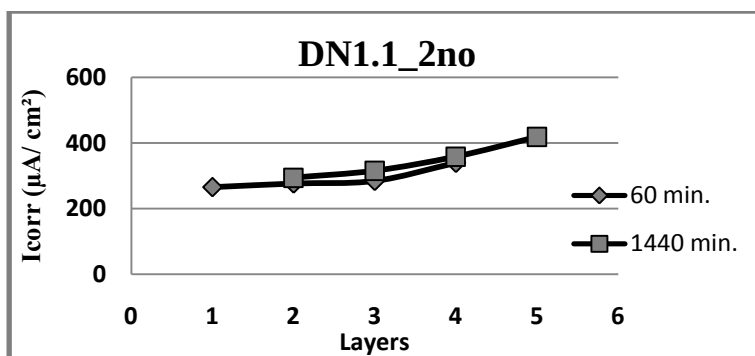


Figure 6.88: Changes of i_{corr} values for DN1_1-2 coated Al electrodes.

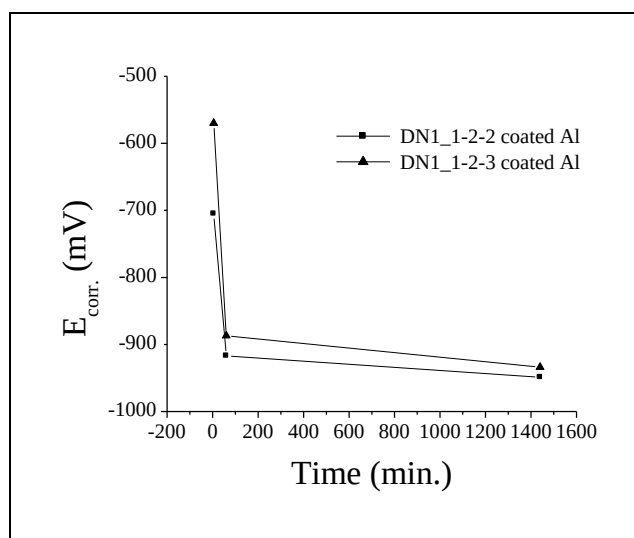


Figure 6.89: Time dependence of $E_{corr.}$ values for DN1_1-2-2, DN1_1-2-3 coatings.

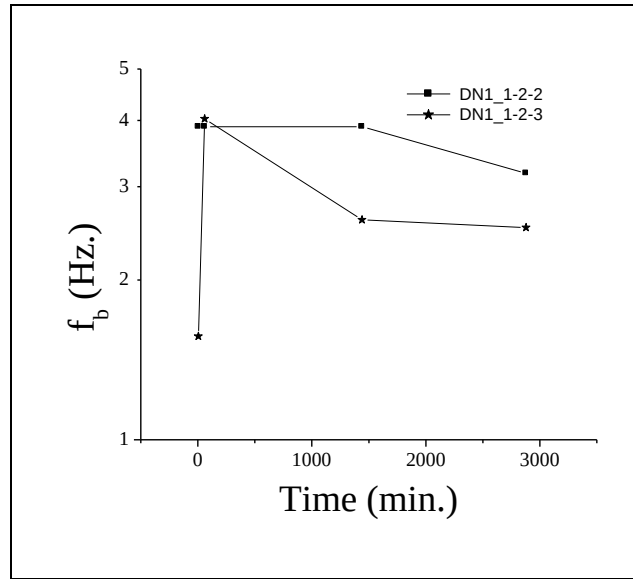


Figure 6.90 : Time dependence of f_b values for DN1_1-2-2, DN1_1-2-3 coatings.

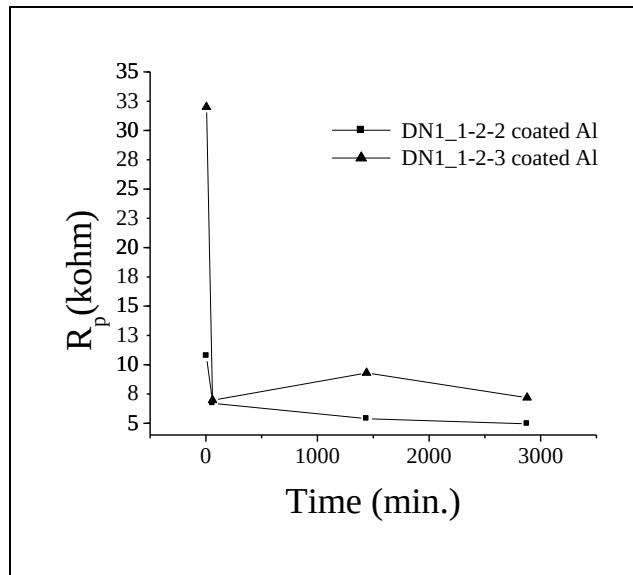


Figure 6.91: Time dependence of R_p values for DN1_1-2-2, DN1_1-2-3 coatings.

Polymer (DN1_1) concentration increased further (DN1_1-3) and coatings at different layer applied. Results obtained from polarization curves and EIS measurements summarized below Figure 6.92, Figure 6.94 and Figure 6.93, Figure 6.95 and Table 6.22, Table 6.23.

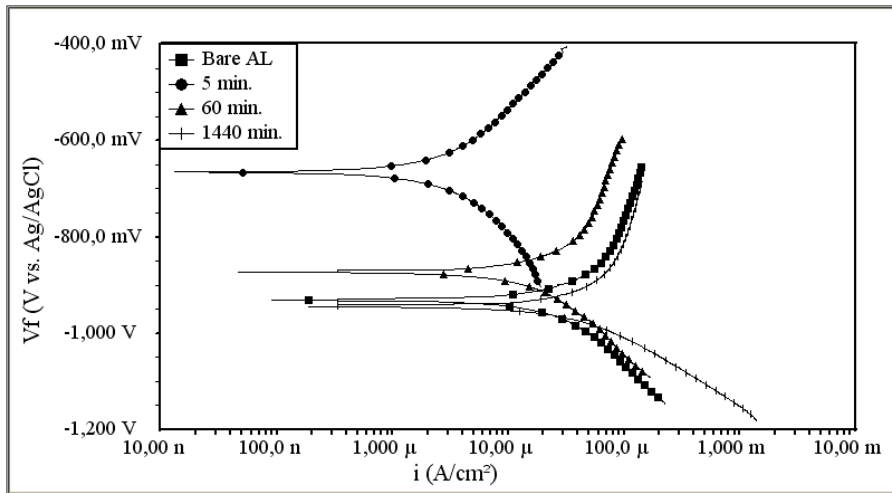


Figure 6.92: Polarization curves of DN1_1-3-2 coated Al left in 1 M H₂SO₄.

High changes in corrosion currents and high inhibition efficiencies suggest a protective coatings Table 6.22, Table 6.23. Although IE values decrease with exposure time they still high and indicating a stable coatings. Changes in i_{corr} values with time and layer number suggest that 2 layer coating for DN1_1-3 has minimum value and more favorable Figure 6.96.

Table 6.22: Corrosion values of DN1_1-3-2 coated Al left in 1M H₂SO₄.

Time (minute)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV)	B_a (V/decade)	B_c (V/decade)	CR (mpy)	IE %
5	34,70	-665,0	3,371	1,518	14,91	96,4
60	227,0	-873,0	1,022	$40,21 \cdot 10^3$	97,41	76,5
1440	206,0	-944,0	675,2	0,3924	88,52	78,7
Bare	969,0	-931,0	0.373	0,125	415,8	-

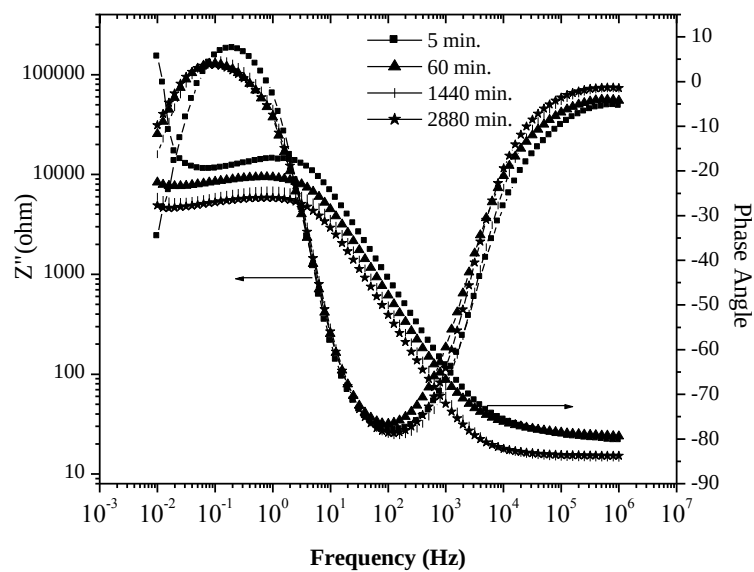


Figure 6.93: Bode diagrams of DN1_1-3-2 coated Al electrode.

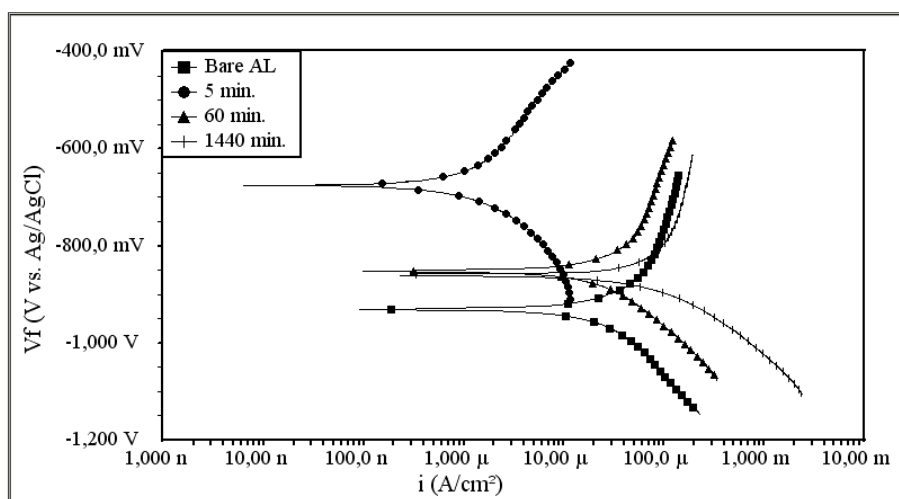


Figure 6.94: Polarization curves of DN1_1-3-3 coated Al left in 1M H₂SO₄.

Table 6.23: Corrosion values of DN1_1-3-3 coated Al left in 1M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE%
5	7,680	-675,0	81,94*10 ⁹	0,4755	3,299	99,2
60	217,0	-852,0	443,3*10 ¹²	0,6975	93,37	77,6
1440	198,0	-861,0	1,000*10 ¹⁵	0,2091	85,20	79,5
Bare	969,0	-931,0	0.373	0,125	415,8	-

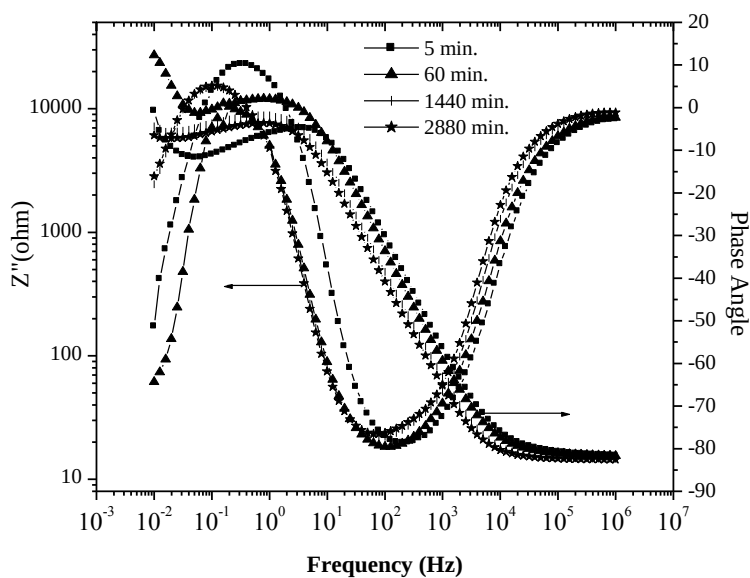


Figure 6.95: Bode diagrams of DN1_1-3-3 coated Al electrode.

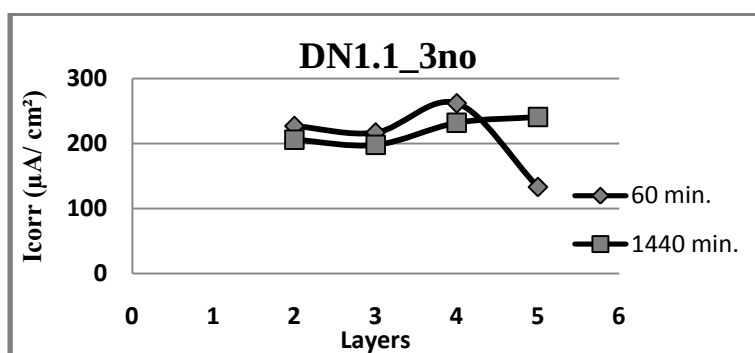


Figure 6.96: Changes of i_{corr} values for DN1_1-3 coated Al electrodes.

Changes in corrosion potentials (E_{corr}), breakpoint frequencies (f_b) and polarization resistance (R_p) with exposure time support the conclusion that DN1_1-3 coatings also effective and stable Figure 6.97, Figure 6.98, Figure 6.99.

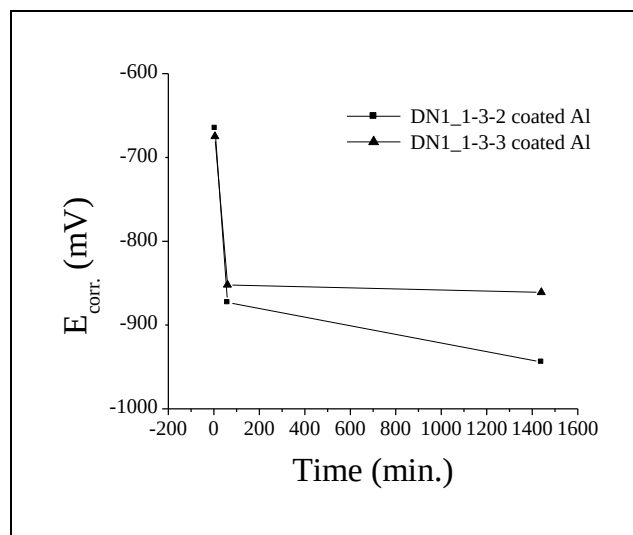


Figure 6.97: Time dependence of E_{corr} values for DN1_1-3-2, DN1_1-3-3 coatings.

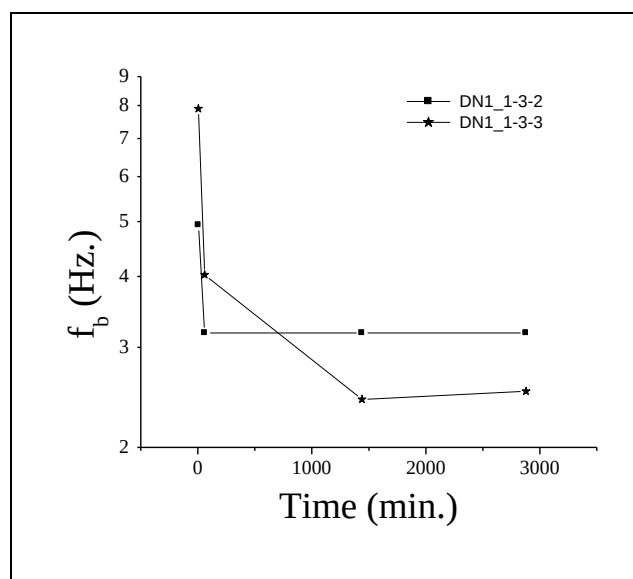


Figure 6.98 : Time dependence of f_b values for DN1_1-3-2, DN1_1-3-3 coatings.

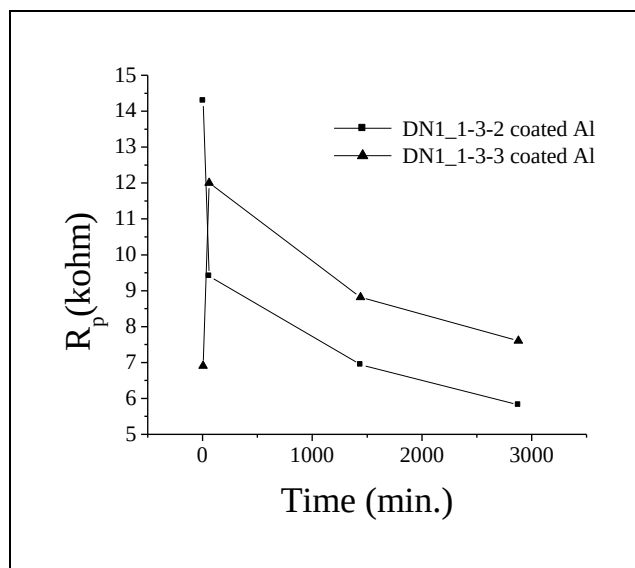


Figure 6.99: Time dependence of R_p values for DN1_1-3-2, DN1_1-3-3 coatings.

Nyquist diagrams of DN1_1 coated aluminum electrodes obtained from different solutions DN1_1-1, DN1_1-2, DN1_1-3 Table 5.1 were compared each other for different exposure time Fig 6.100, Fig 6.101. For one hour DN1_1-1, DN1_1-3, coating shows similar behavior and the semicircle has the higher diameter (higher R_p values) than DN1_1-2. After 48 hour the decrease in R_p values for DN1_1 is smaller than DN1_1-3. Delamination due to water uptake is become pronounced after a certain thickness and it explains why the protection efficiency of thinner coating is higher than the thicker ones.

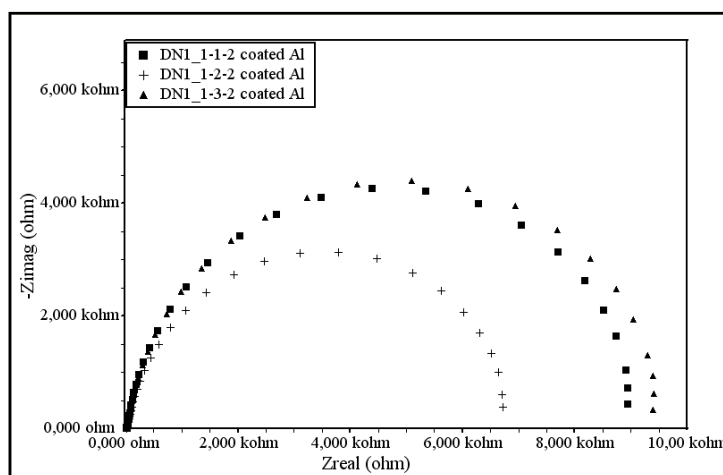


Figure 6.100: Nyquist diagrams of values for DN1_1-1-2, DN1_1-2-2, DN1_1-3-2 coated Al electrodes (1 hour).

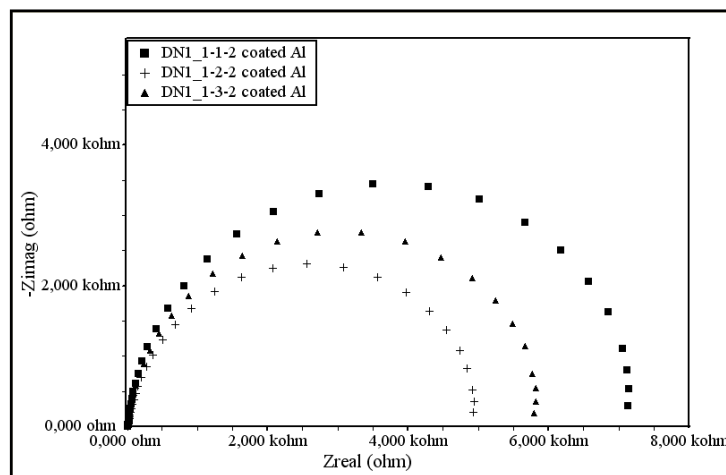


Figure 6.101: Nyquist diagrams of values for DN1_1-1-2, DN1_1-2-2, DN1_1-3-2 coated Al electrodes (48 hour).

6.4 PCz and PPy Homopolymers Coatings

PCz coated potentiostatically at 2V constant potential. PCz coated Al electrode was investigated by polarization curves and EIS measurements Figure 6.102, Figure 6.104 at different exposure time.

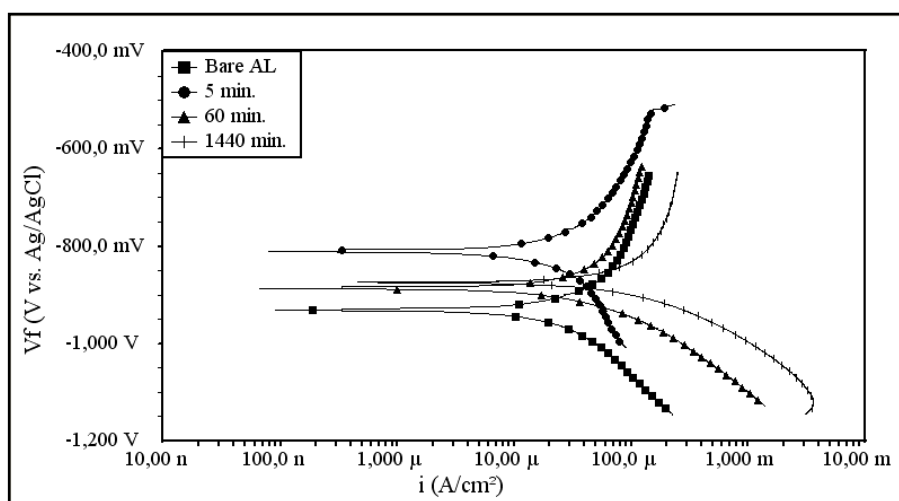


Figure 6.102: Polarization curves of PCz coated Al left in 1M H₂SO₄.

Results obtained from polarization curves (Table 6.24) suggest protection. The currents and IE% values of PCz coated Al electrodes are lower than DN1_1 coatings which is a copolymer of carbazole and silicone tegomer. Mechanical properties of conducting polymers are weak and damage of coating might easily occur. They have porous structure that allows electrolyte to penetrate into them. Lower efficiencies of PCz coated electrodes than copolymer (DN1_1) coated ones suggest that protection efficiency of carbazole containing polymers can be improved by silicone tegomer.

Table 6.24: Corrosion values of PCz coated Al left in 1M H₂SO₄.

Time (minute)	I_{corr} (μA/ cm²)	E_{corr} (mV)	B_a (V/decade)	B_c (V/decade)	CR (mpy)	IE %
5	240,0	-810,0	0,9441	304,1*10 ³	103,0	75,2
60	105,0	-886,0	5,905	0,2076	44,92	89,2
1440	259,0	-874,0	1,000*10 ¹⁵	0,1821	111,2	73,2
Bare	969,0	-931,0	0.373	0,125	415,8	-

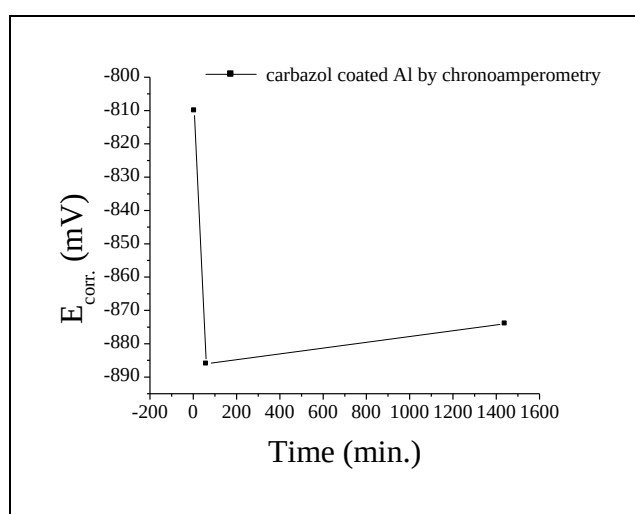


Figure 6.103: Time dependence of E_{corr} values for PCz coating.

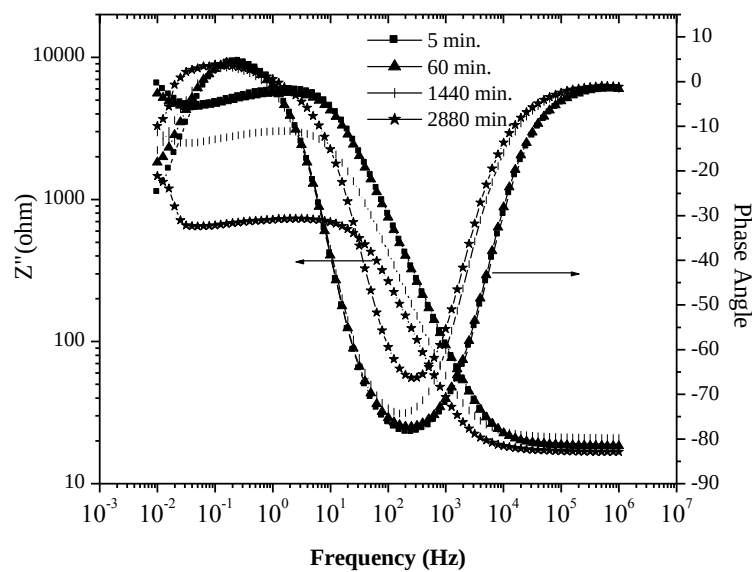


Figure 6.104: Bode diagrams of PCz coated Al electrode.

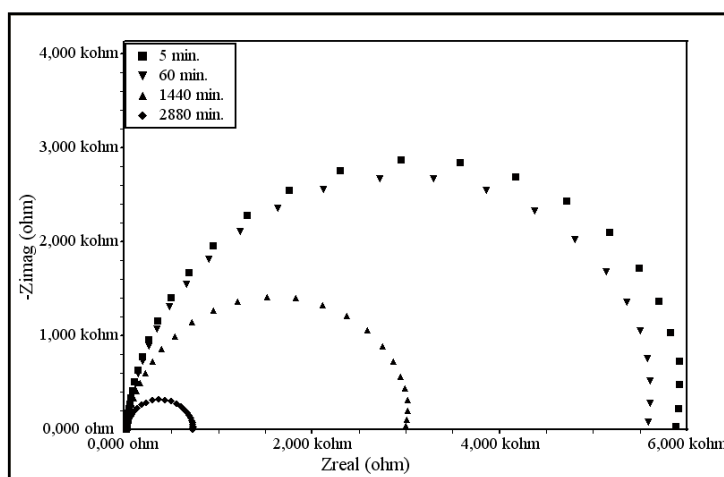


Figure 6.105: Nyquist diagrams of values for PCz coated Al electrode.

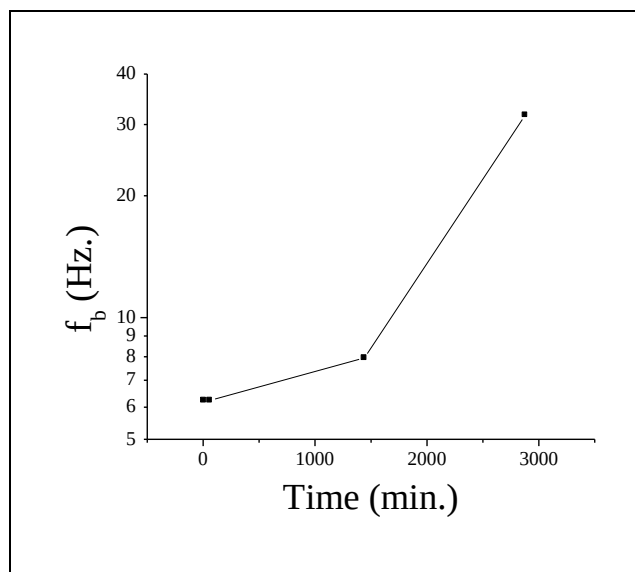


Figure 6.106 : Time dependence of f_b values for PCz coating.

Although the changes in f_b and R_p values of PCz coated Al electrode are low, they are a little higher than DN1_1 and these results support the conclusion above.

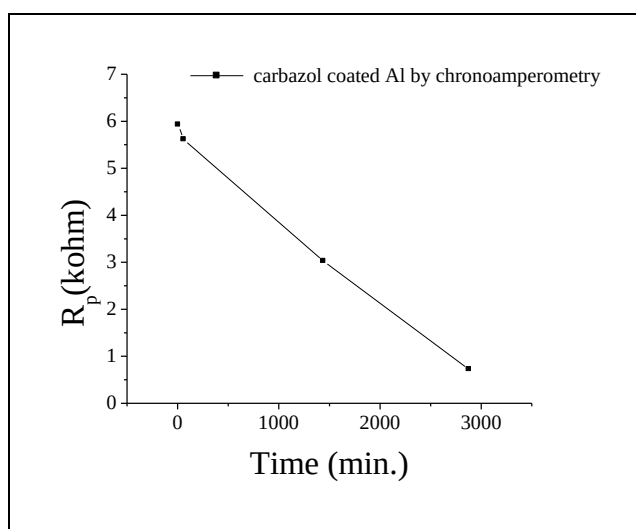


Figure 6.107: Time dependence of R_p values for PCz coating.

Similarly Al electrode coated with PPy at a constant potential of 2.3 V and tested with polarization and EIS measurements. Results obtained from polarization measurements (Figure 6.108, Figure 6.109 and Table 6.25) higher IE values than PCz homopolymer (Table 6.24) Ppy homopolymer coating have similar protection efficiency to silicon tegomer containing copolymers (DN4 and DN6).

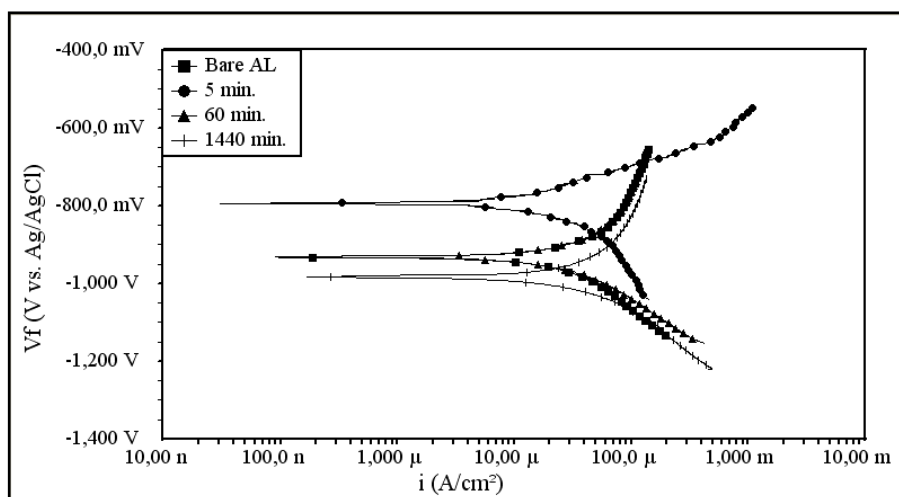


Figure 6.108: Polarization curves of PPy coated Al left in 1M H₂SO₄.

Table 6.25: Corrosion values of PPy coated Al left in 1M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	21,70	-793,0	0,1344	0,2433	9,295	97,7
60	236,0	-932,0	101,0*10 ⁶	0,6764	101,5	75,6
1440	193,0	-982,0	231,4*10 ⁶	0,4752	82,89	80,1
Bare	969,0	-931,0	0.373	0,125	415,8	-

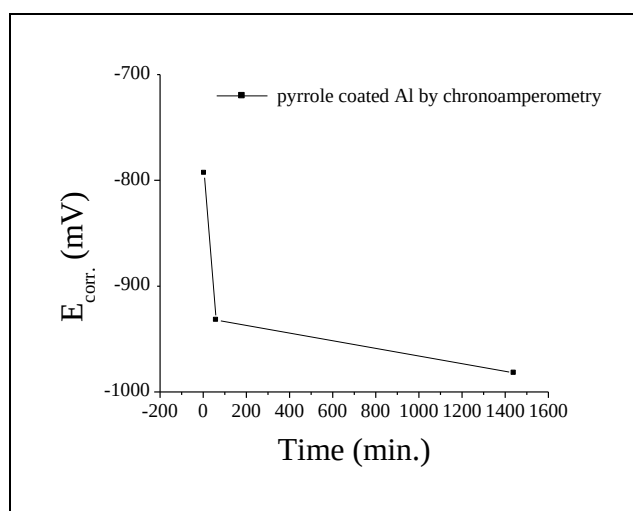


Figure 6.109: Time dependence of E_{corr.} for PPy coating.

f_b and R_p values obtained from Bode and Nyquist diagrams (Figure 6.110, Figure 6.111) of PPy coated Al electrode also suggest formation of unstable and not strongly adherent coating layers on the substrate Figure 6.112 and Figure 6.113.

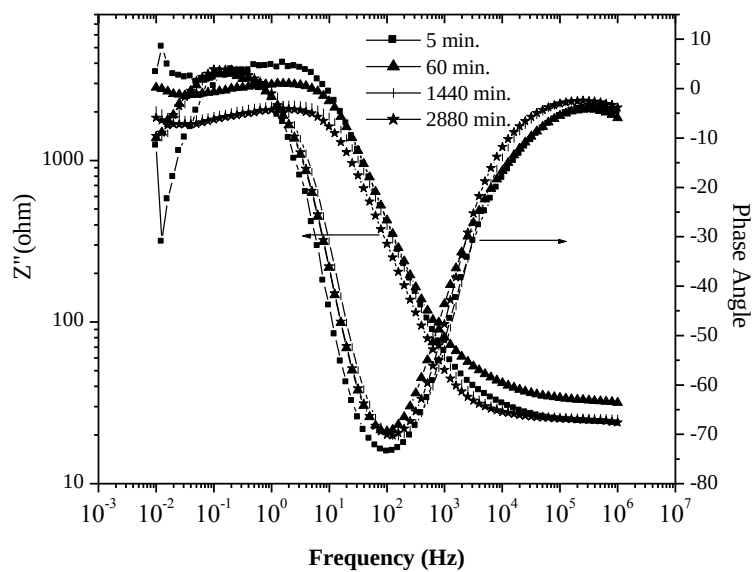


Figure 6.110: Bode diagram PPy coated Al electrode.

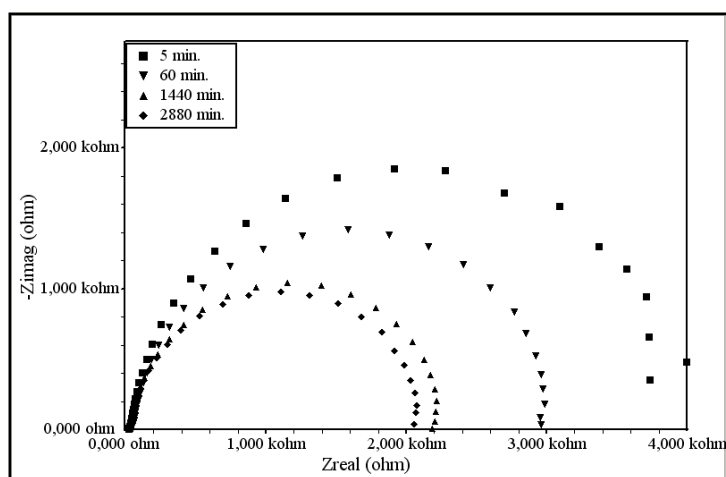


Figure 6.111: Nyquist diagrams of values for PPy coated Al electrode.

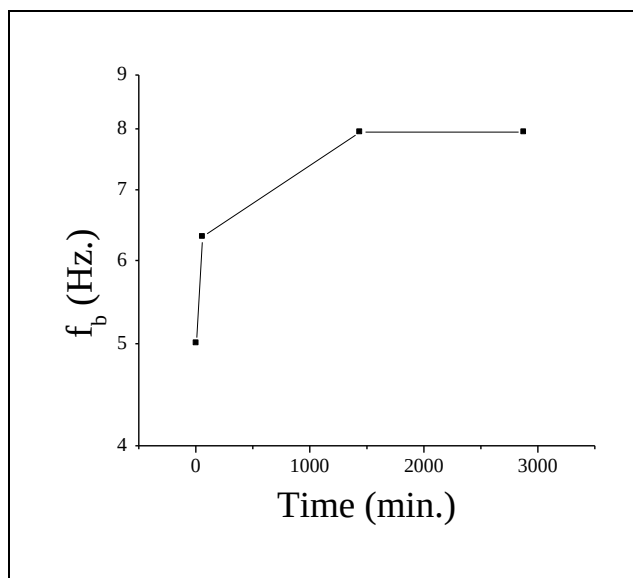


Figure 6.112 : Time dependence of f_b values for PPy coating.

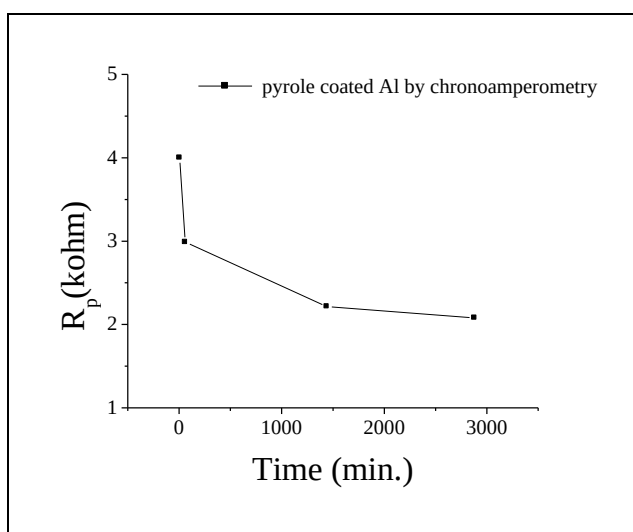


Figure 6.113: Time dependence of R_p for PPy coating.

6.5 PCz and PPy Modified CF Coatings

In this part of study small amount of conducting polymers PCz and PPy used as modifiers for organic coating. Cyclohegzanon formaldehyde resin was modified by the addition PCz at two percent i.e. 8.0 and 10.0 % w/w and PPy added at 10.0%

Polarization curves and results obtained for these measurements for PCz modified (8%) CF coated Al are given in Figure 6.114 and Tablo 6.26.

E_{corr} values of coated electrode shift in anodic direction indicating an anodic protection. Corrosion currents of coated electrodes significantly decreased as compared to bare electrodes and very high inhibition efficiencies were obtained Table 6.26.

Although efficiencies of PCz and DN1_1 coated decreased by exposure time, for PCz modified (8%) CF coated Al there is very little loss in efficiencies.

PCz(0,13g)+CF

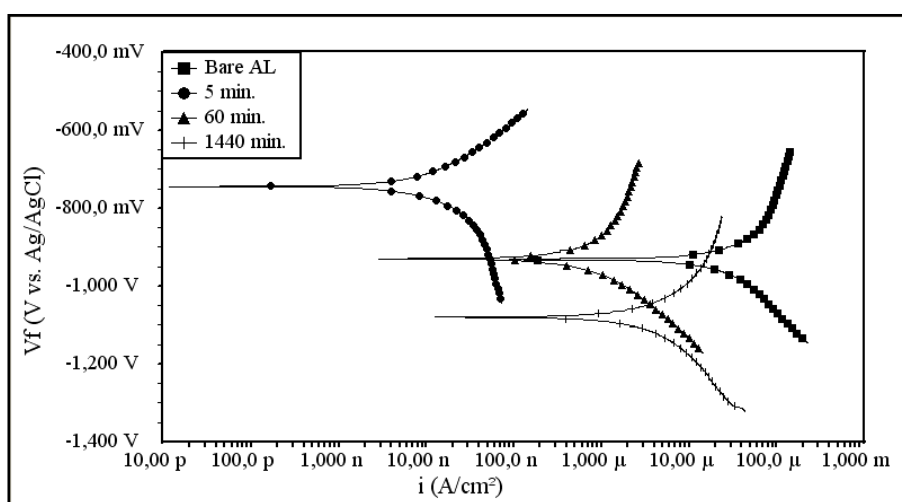


Figure 6.114: Polarization curves of PCz modified (8%) CF coated Al left in 1M H_2SO_4 .

Table 6.26: Corrosion values of PCz modified (8%) CF coated Al left in 1M H_2SO_4 .

Time (minute)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV)	B_a (V/decade)	B_c (V/decade)	CR (mpy)	IE %
5	0,06050	-740,0	0,5469	1,395	0,02597	99,9
60	2,990	-929,0	$1,000 \cdot 10^{15}$	0,3402	1,285	99,7
1440	24,90	-1080	1,185	1,020	10,67	97,4
Bare	969,0	-931,0	0,373	0,125	415,8	-

E_{corr} values of PCz modified (8%) CF coated Al shift in cathodic direction with time. PCz amount increased from 8% to 10% and Al electrode coated with this coating mixture. Results for PCz modified (10%) CF coated Al are given in Figure 6.115, Figure 6.116, Figure 6.117, Figure 6.118, Figure 6.119 and Table 6.27.

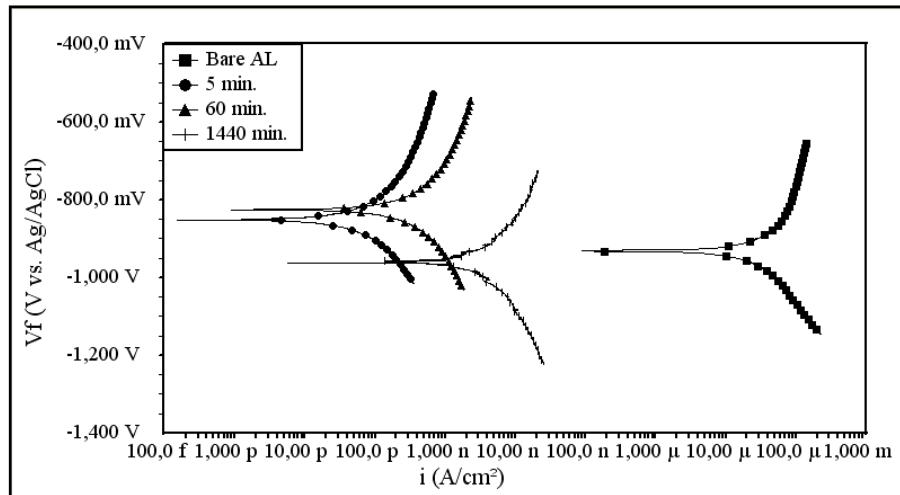


Figure 6.115: Polarization curves of PCz modified (10%) CF coated Al left in 1M H₂SO₄.

As it can be seen from polarization measurements and the I_{corr} values obtained from these curves 200 times lower currents were observed for fresh coating Table 6.26 and Table 6.27. These results show that CF modified by the further addition of low concentration of PCz, i.e. typically 2%, have been shown to impart better corrosion resistance than lower PCz (8%) containing ones. Very high inhibition efficiencies obtained after 1440 minute exposure time

Table 6.27: Corrosion values of PCz modified (10%) CF coated Al left in 1M H₂SO₄.

Time (minute)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV)	B_a (V/decade)	B_c (V/decade)	CR (mpy)	IE %
5	0,000318	-852,0	0,7768	0,7513	0,000136	99,9
60	0,002760	-825,0	1,655	1,446	0,001187	99,9
1440	11,30	-960,0	0,6055	0,6671	0,004865	99,8
Bare	969,0	-931,0	0.373	0,125	415,8	-

Corrosion potentials of PCz modified (10%) CF coating shift in anodic direction at first and then start to decrease again Fig 6.115.

F_b and R_p values of coated electrodes calculated from Bode and Nyquist diagrams (Figure 6.116 and Figure 6.117. Changes f_b values with exposure time are very low (Figure 6.118), R_p (Figure 6.119) values of coated electrodes decreased from 100 kohm to 20 kohm after 2880 minutes left in corrosion medium. This change is due to water uptake of coating as expected.

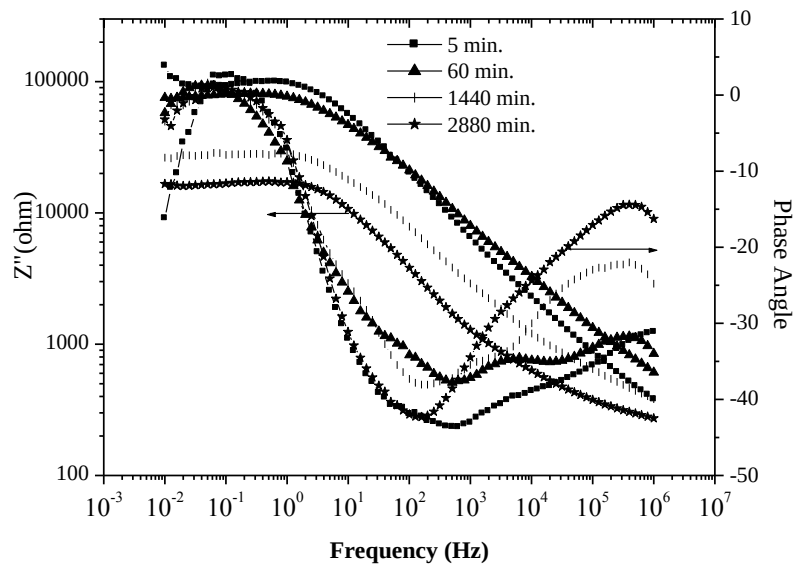


Figure 6.116: Bode diagrams of PCz modified (10%) CF coated Al electrode.

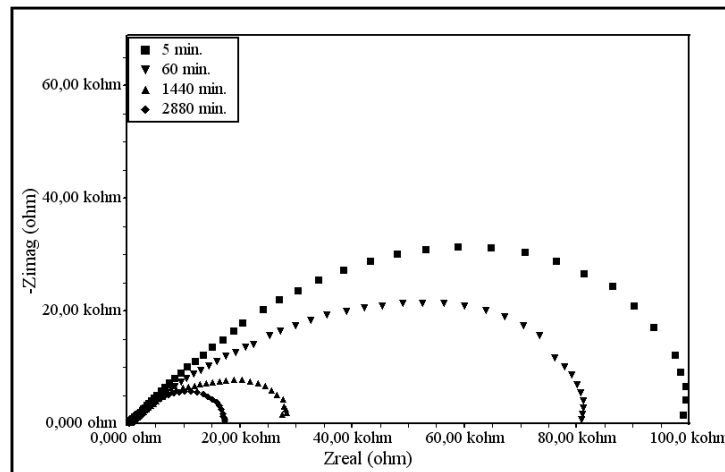


Figure 6.117: Nyquist diagrams of values for PCz modified (10%) CF coated Al electrode.

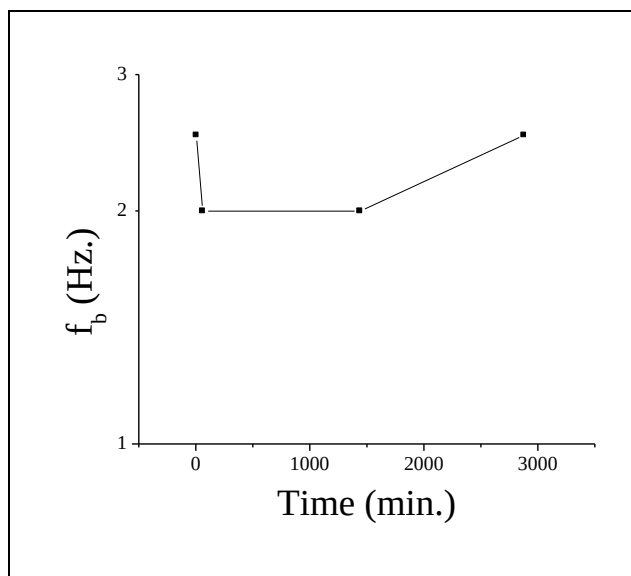


Figure 6.118 : Time dependence of f_b values for PCz modified (10%) CF coating.

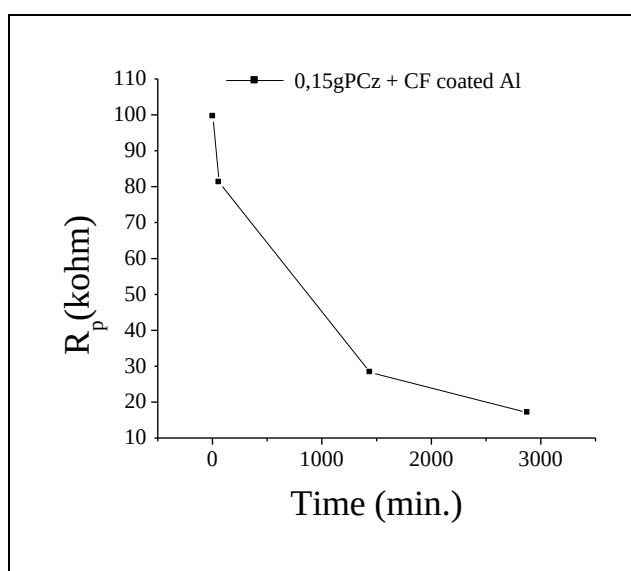


Figure 6.119: Time dependence of R_p values for PCz modified (10%) CF coating.

Similarly to PCz, PPy also dispersed in CF resin and Al electrodes were also coated with this PPy (10%) modified CF resin. Coated electrode tested by polarization and EIS measurements. Polarization curves and values calculated from these curves show that PPy (10%) modified CF resin coating exhibit excellent protection for Al electrode Figure 6.115 and Table 6.27.

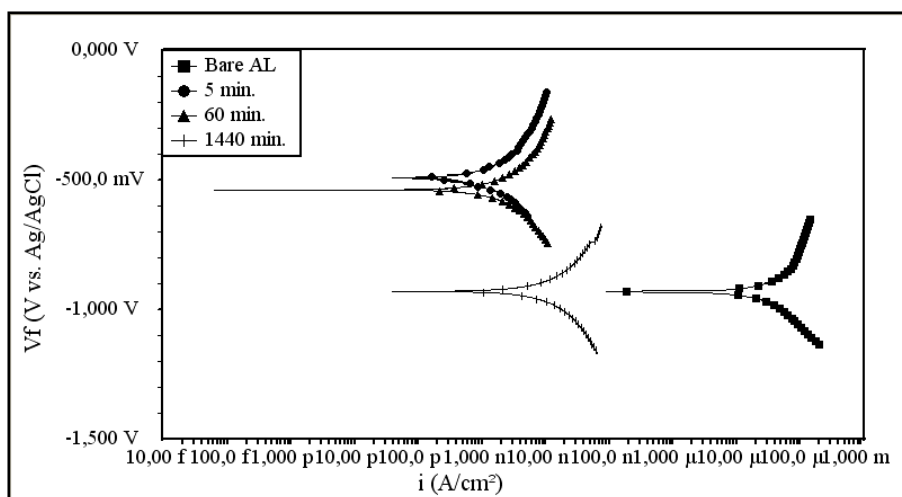


Figure 6.120: Polarization curves of PPy+CF coated Al left in 1M H₂SO₄.

Table 6.28: Corrosion values of PPy+CF coated Al left in 1M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	0,003850	-494,0	0,6588	0,4710	0,001653	99,9
60	0,01180	-538,0	1,337	1,030	0,005064	99,9
1440	0,04420	-930,0	0,7779	0,8390	0,01897	99,9
Bare	969,0	-931,0	0.373	0,125	415,8	-

E_{corr} values coated electrodes shift in anodic direction by coating and decrease with time Table 6.28 and Figure 6.126.

F_b and R_p values obtained from Bode (Figure 6.121) and Nyquist (Figure 6.122) diagrams respectively, were plotted against time Figure 6.123 and Figure 6.124. Changes in f_b values are very small and R_p values changed from 50 kohm to 5 kohm after 2880 minutes due to water absorption of coatings.

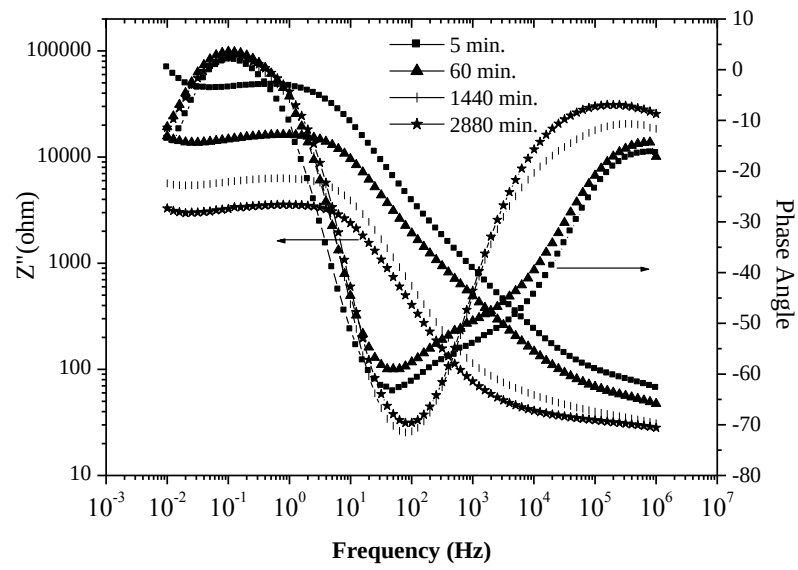


Figure 6.121: Bode diagram PPy + CF coated Al electrode.

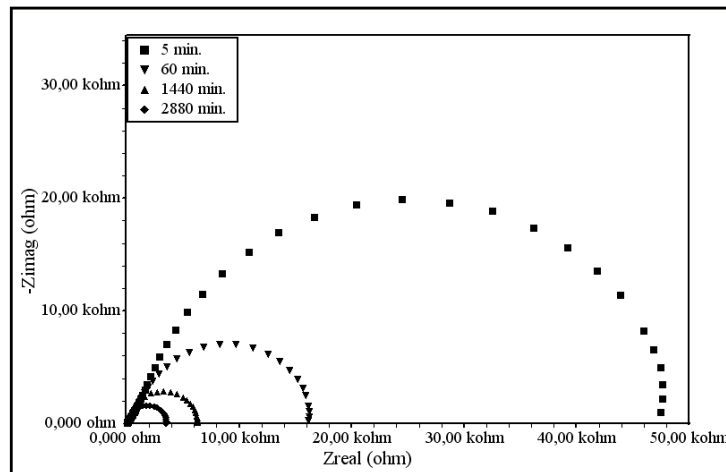


Figure 6.122: Nyquist diagrams of values for CF+PPy coated Al electrode.

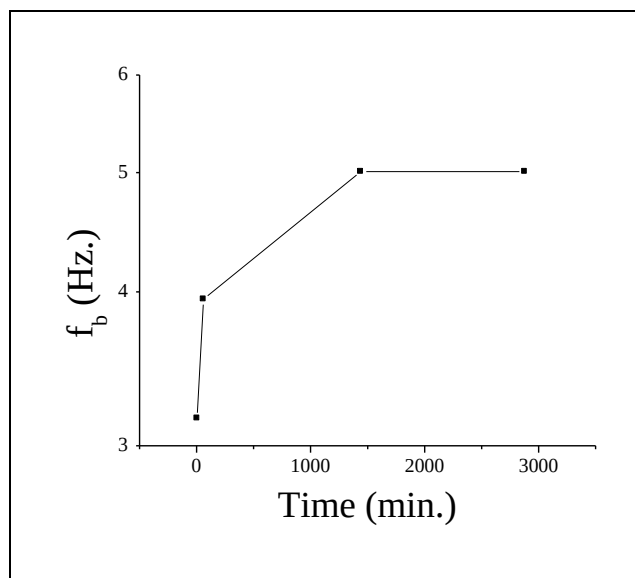


Figure 6.123 : Time dependence of f_b values for CF+PPy coating.

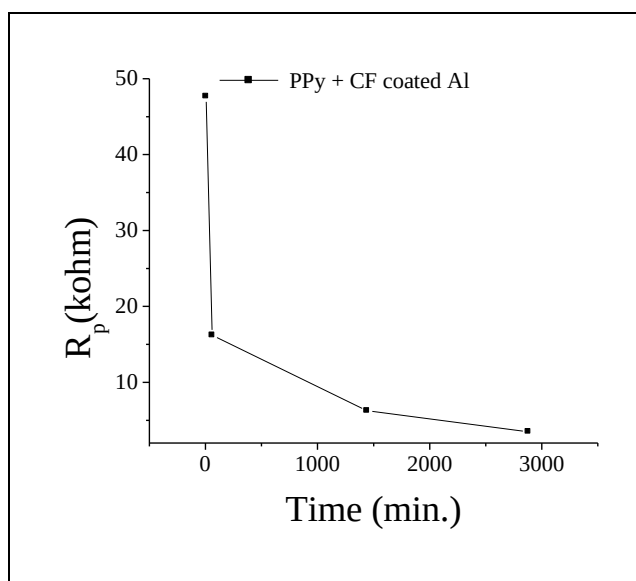


Figure 6.124: Time dependence of R_p for CF+PPy coating.

The protection against corrosion imparted by CF resin modified by the addition of PCz and PPY (10% w/w) has been compared with unmodified CF resin.

6.6 CF Coating

Similarly it is coated and tested by polarization measurements Figure 6.125. Corrosion potential shifted about 600 mv in anodic direction and corrosion current decreased significantly as compare to bare Al electrode Table 6.29.

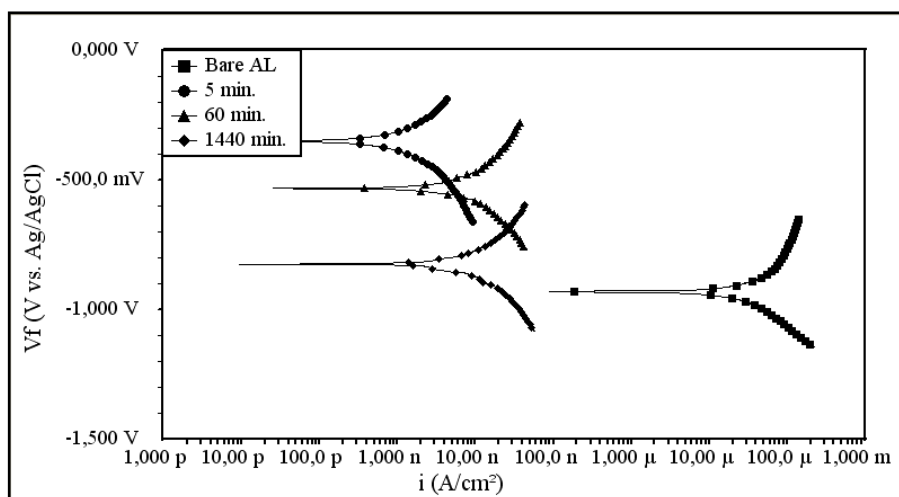


Figure 6.125: Polarization curves of CF coated Al left in 1M H₂SO₄.

Table 6.29: Corrosion values of CF coated Al left in 1M H₂SO₄.

Time (minute)	I _{corr} (μA/ cm ²)	E _{corr} (mV)	B _a (V/decade)	B _c (V/decade)	CR (mpy)	IE %
5	0,02350	-350,0	5,674	3,073	0,01010	99,9
60	0,1300	-529,0	13,37	2,113	0,05570	99,9
1440	0,03330	-825,0	0,8744	0,7224	0,01430	99,9
Bare	969,0	-931,0	0.373	0,125	415,8	-

Corrosion potential of CF coated Al electrode decrease with time as can be seen from Figure 6.126. Although the changes of E_{corr} values for CF coated Al are similar to PCz modified CF coated Al, PPy modified CF resin coating seems more stable since the changes in E_{corr} are very small than the others Figure 6.126.

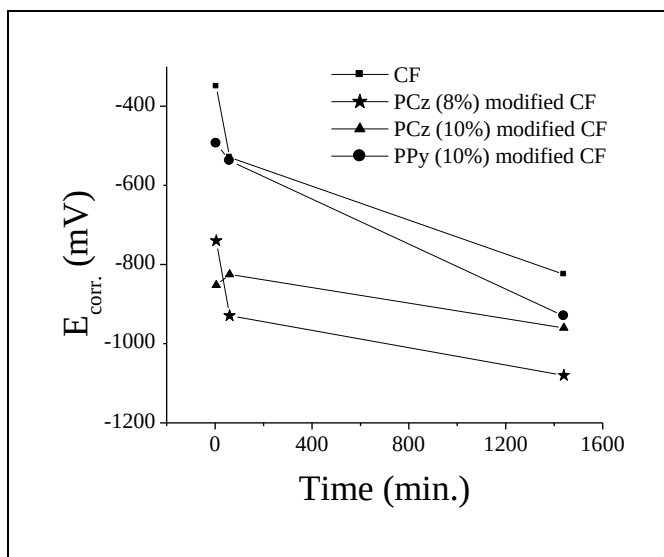


Figure 6.126: Time dependence of E_{corr} values for unmodified CF, PCz and PPy modified CF coated Al.

When changes in corrosion currents with time compared with modified and unmodified CF resin coated Al electrodes PPy modified (10%) CF coating seems more favorable than the others Figure 6.127.

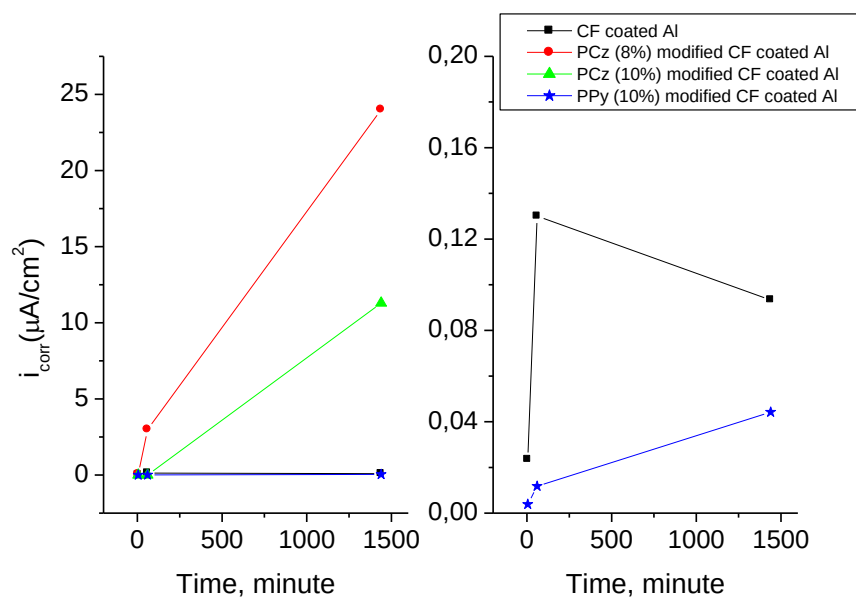


Figure 6.127: Changes of i_{corr} values for unmodified CF, PCz and PPy modified CF coated Al.

6.7 ATR- FTIR Spectra of Materials

ATR- FTIR spectra of DN_1, copolymer, were taken as powder and as a film after coated on electrode from their solution. Its spectrum compared with PCz homopolymers obtained chemical polymerization by using ceric ammonium nitrate as an initiator. Results were given in Figure 6.128. The peak at 1365 cm⁻¹, for PCz homopolymer corresponds to N-O stretching of the nitro group. Presence of the peak at 800-860 cm⁻¹ in FTIR spectra of PCz homopolymer and DN_1 copolymer is evidence for the presence of trisubstituted benzene rings. Absorption bands in the range of 750-720 cm⁻¹ representing the presence of -C-H out of plane deformation of carbazole ring. A noticeable feature in the spectra of copolymer and PCZ homopolymer is absorption band around 790 cm⁻¹, which indicates polymerization through the α -position[47].

The peaks in the range of 1600-1450 cm⁻¹, 1260-1200 cm⁻¹, corresponds to aromatic ring and aromatic amin, - respectively.

The bands appearing around 3400, 3050-2960, 1080-1020, and 800 cm⁻¹ were due to -O-H, -C-H, -Si-O, and Si-CH₃ groups of tegomer blocks, respectively [42].

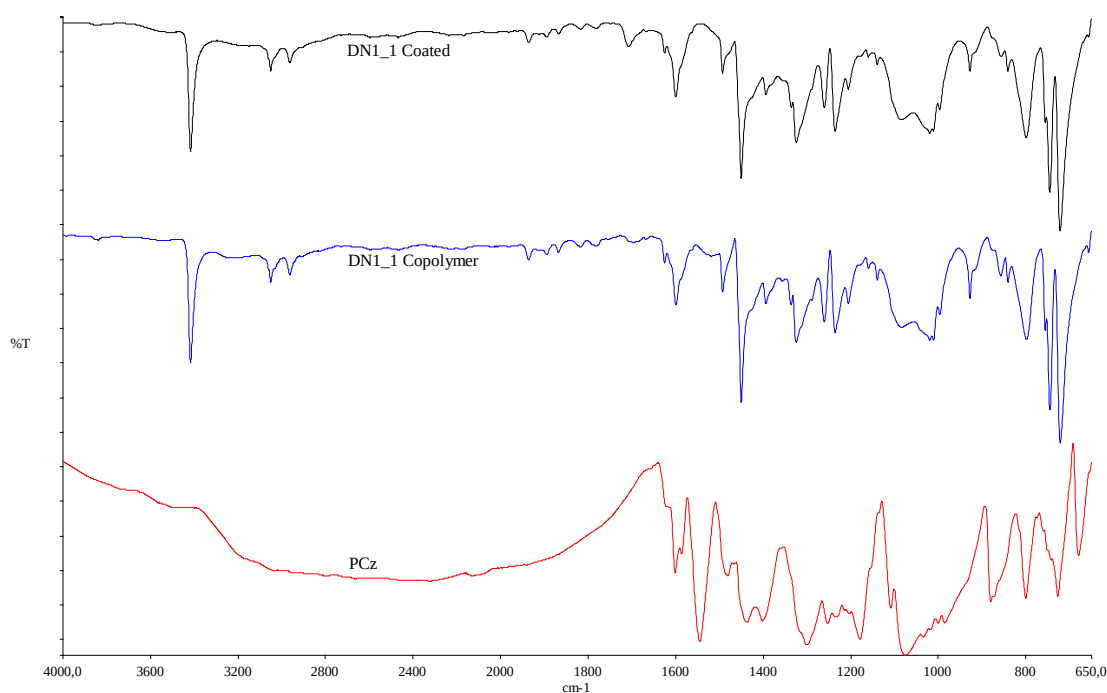


Figure 6.128: FT-IR spectra of DN1_1 coating, DN1_1 copolymer, PCz homopolymer obtained with CAN and cerium(IV)oxide (CeO₂).

FTIR spectra of chemically prepared PPy–silicone tegomer copolymers (DN4 and DN6) are shown in Figures 6.129 and Figure 6.130 comparatively with PPy homopolymer. Several research groups [48-49] have made the assignments of vibration modes of PPy. The band at 1630-1500 and 1087 cm⁻¹ in the spectrum of PPy corresponds to the –C=C stretching vibrations in pyrrole ring and –C-H vibration of trisubstituted pyrrole ring respectively. A red shift to 1650 cm⁻¹ of this band has been observed in DN4 and DN6 copolymers. It is known that the skeletal vibrations, involving the delocalized π -electrons, are affected by doping of the polymer [50]. The band of C–H out-of-plane deformation vibrations of the ring has a maximum at 1000 cm⁻¹ for PPy.

The bands at 1400 cm⁻¹ in the spectra correspond to C–N stretching vibration in the ring. The peak at 1384 cm⁻¹ was due to a NO₃⁻ ligand incorporated into the polymer. This peak was always observed as a sharp band in the spectrum of the copolymers, and it was observed at 1275 cm⁻¹ for PPy. The bands appearing around 3400, 3250, 1040-1080, and 800 cm⁻¹ were due to –O-H, –C-H, –Si-O, and Si-CH₃ groups of tegomer blocks, respectively [42].

One can see that in the spectra of DN4 and DN6 as powder and as casting film on electrodes, all bands are superimposed suggesting there is almost no difference when we coated these copolymers on electrode surface. The region of C–H and N–H in plane deformation vibrations from 1170 to 1150 cm⁻¹ is probably influenced for DN4 sample. The maximum is situated at about 1140 cm⁻¹ in PPy and at 1100 cm⁻¹ in copolymers.

The hydroxyl groups introduced in the tegomer affected by nucleophilic attack of solvent during the preparation and by this attack would finally produce carbonyl groups by keto-enol tautomerism hydroxyl units formed [51]. A band at 1710 cm⁻¹ in the spectrum of DN4 (Figure 6.129) corresponds to the presence of carbonyl group.

The difference in the spectra of PPy and copolymers was also found in the region from 1200 to 1100 cm⁻¹ that corresponds to the breathing vibration of the pyrrole ring.

The peaks at 796 cm⁻¹ (C–H out of plane ring deformation) are situated at the same position in the spectra of both copolymers.

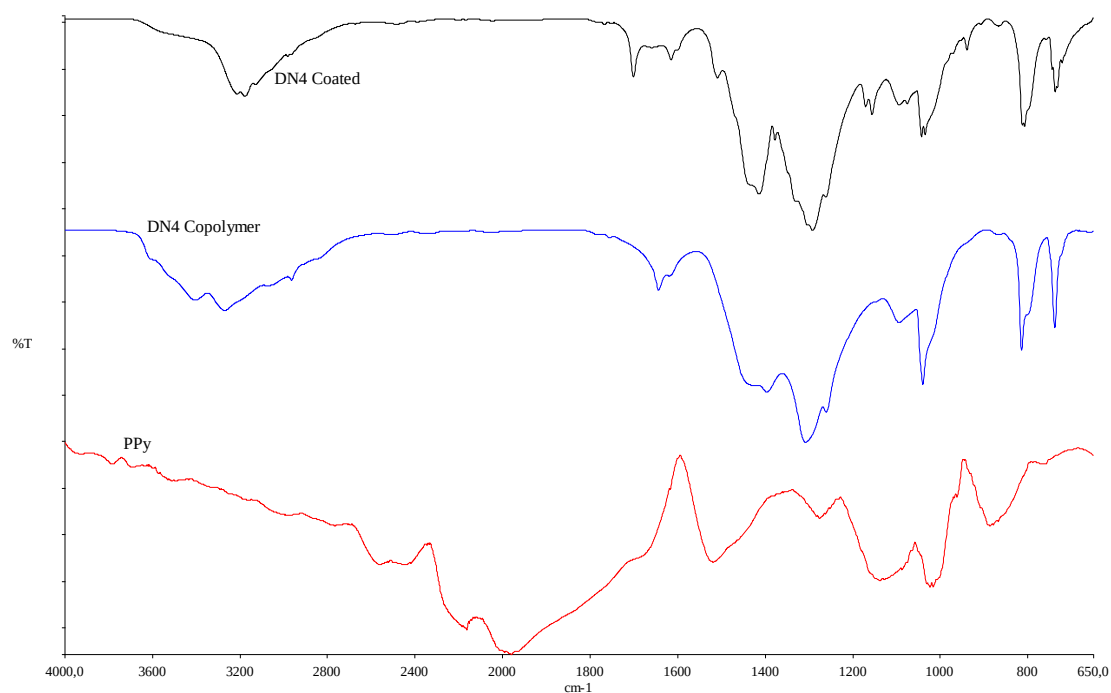


Figure 6.129: FT-IR spectra of DN4 coating, DN4 copolymer, PPy homopolymer obtained with CAN and cerium(IV)oxide (CeO₂).

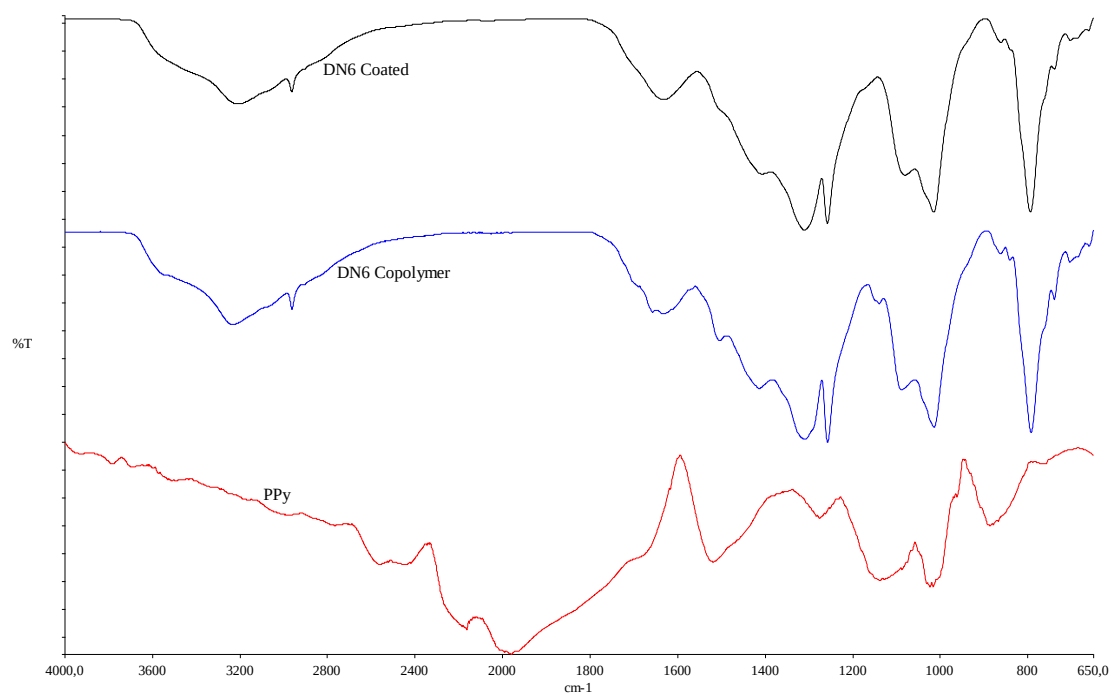


Figure 6.130: FT-IR spectra of DN6 coating, DN6 copolymer, PPy homopolymer obtained with CAN and cerium(IV)oxide (CeO₂).

6.8 Scanning Electron Microscopy Analysis of Materials

The morphologies of coated polymeric films prepared by casting from their solutions were studied by SEM.

Figure 6.131 shows the SEM images of DN4, DN6 and DN1_1, films, which reflect the fully coverage of the electrode surface. Each coating seems has different morphology which effect the corrosion efficiency of coating. Although DN6 has more smooth structure, DN4 show a structure which resemble fringes. On the other hand DN1_1 show heterogenous structrure with different regions resembles root and mud.

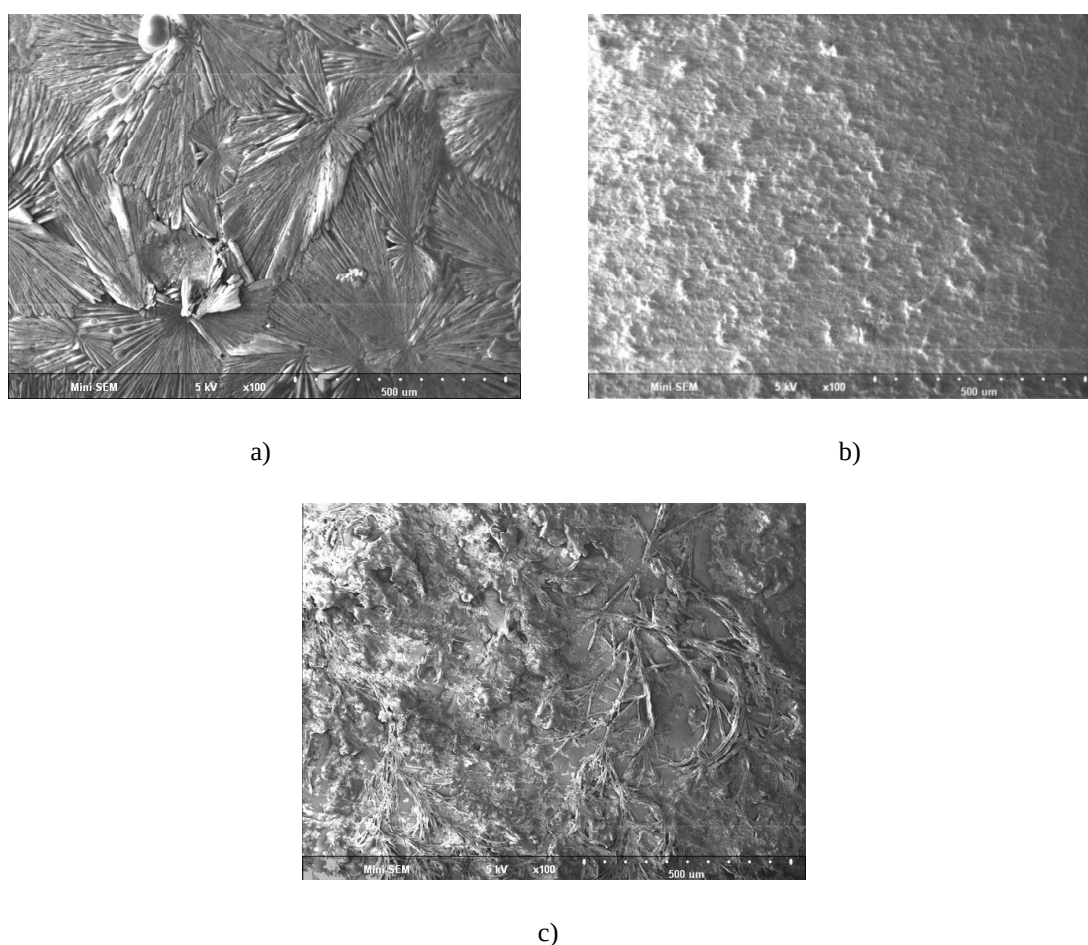


Figure 6.131: SEM images of a) DN4 [PPy_b_(DH.PDMS)] (mag. x100), b) DN6 [PPy_b_(DH.PDMS)] (mag. X100), and c) DN1_1 [PCz_b_(DH.PDMS)] (mag. x100).

When we compare corrosion currents of DN4 and DN6 coatings it can be seen that for longer exposure time DN4 is more efficient than DN6. This result can be explained with the morphology of the surface. Water uptake of DN6 can be expected to be higher than DN4 due to more porous structure. For longer exposure time, in the

case of DN6 delamination might be more which decrease the effectiveness of coating. Similar corrosion behaviour to DN6 was observed for DN1_1 which indicate a possibility of water uptake of relative high porous structure.

When the SEM images of unmodified CF coating compared with PCz and PPy modified CF coating it can be easily seen it has more smooth structure. Inclusion of PCz and PPy gives some roughness to structure Figure 6.132.

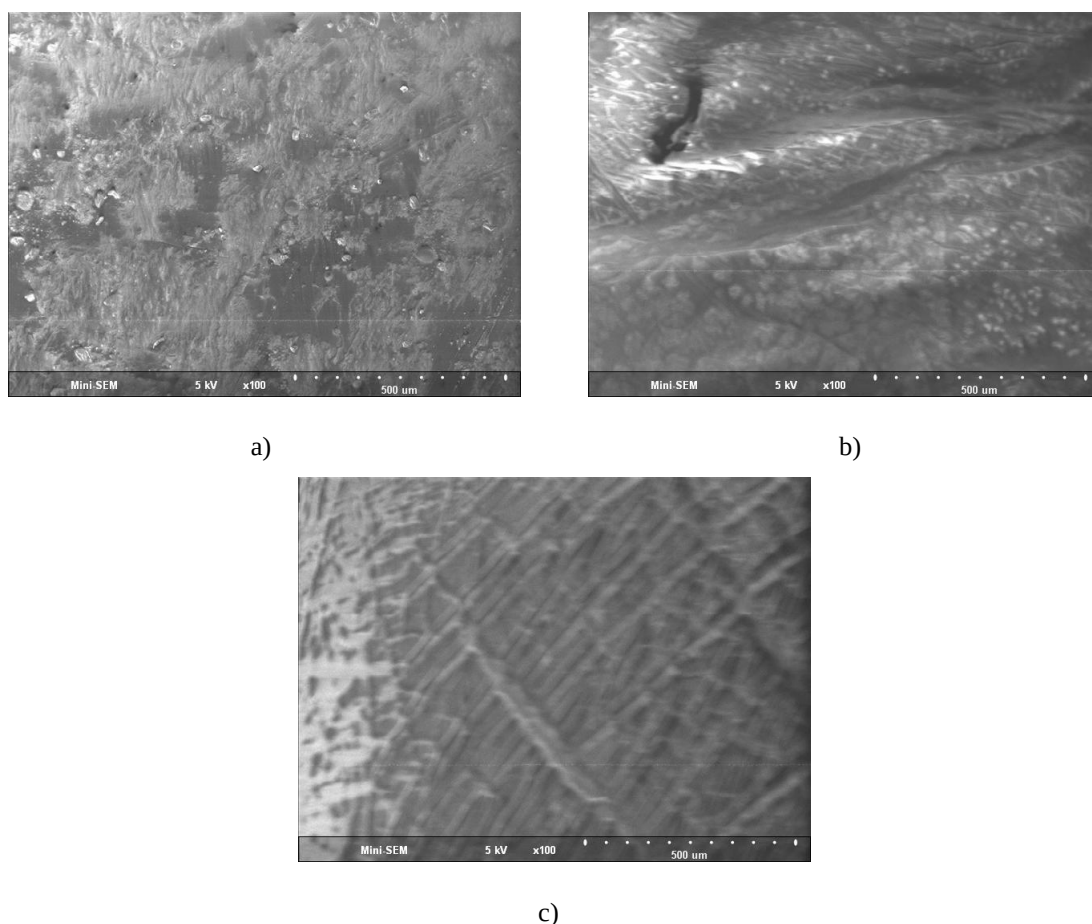


Figure 6.132: SEM images of a) PPy modified CF (mag. X100), b) PCz modified CF (mag. x100), and c) CF (mag. x100).

7. CONCLUSION

Corrosion performance of two block copolymers of Py with PDMS (DN4 and DN6), and copolymer of Cz with PDMS (DN1_1) were investigated comparatively with homopolymers of Ppy and PCz.

The only difference in DN4 and DN6 is initiator (ceric ammonium sulphate) concentration used in synthesis and it is lower in the case of DN6 which might result a higher molecules weight copolymer.

Five different solution that have different amount of DN4 copolymer and three different solutions of DN6 were prepared by using acetone and DMF mixture. Copolymers were coated from these solution by adding dropwise. The electrodes let to dry. The effect of layer number and thickness were tested by adding further solution to the electrode surface. After each addition the solvent evaporated from electrode surface. By this procedure electrode were coated with different layer and thickness. Corrosion efficiency of all coating were investigated by polarization and impedance measurements.

All results suggest that thick coatings show high protection on the surface for fresh coatings. However thinner coatings have better efficiency by increasing exposure time. The corrosion potentials of thick coatings shift to more cathodic region than the thinner coatings by the time. It seems water absorption of thinner coatings is less than thicker one and this makes coating more stable.

By increasing the layers or concentration of coating solution protection efficiency decreases due to delamination and desquamation of coating. It can be concluded that the thinner coatings are more favorable for longer time.

The best performance for DN4 were obtained for DN4-1-4 which means a coating obtained from the most diluted solution with four layers. For DN6 copolymer the best one is DN6-1-2. For longer exposure time DN4 which has lower molecular weight seems more efficient than DN6.

DN4 and DN6 have good protection than the homopolymer of polypyrrole because of the adhesion which is achieved by using the silicone tegomer (PDMS).

DN1.1-1-2 seems the optimum condition for DN1_1, block copolymers of the PCz with PDMS, coating to protect aluminum from acidic corrosion. When we compare DN1_1 and polycarbazole coating which was coated electrochemically by using constant potential, DN1_1 coating has excellent protection than the homopolymer of polycarbazole because of well adhesion.

Although homopolymer coatings of polycarbazole and polypyrrole seems have protection, they could delemenate easily from the substrate surface.

In order to improve the performance of homopolymers they were used together with cyclohexanone-formaldehyde resin (CF). They dispersed homogeneously in the resin and coated on Al electrode surface. Their performance were compared with unmodified CF.

PPy and PCz modified CF coatings durable material in the acidic medium and they have excellent adhesion and protection for aluminium. Their efficiency is much better than the DN4, DN6 and DN1_1 coatings.

Generaly it can be concluded that corrosion protection of PPy and PCz homopolymer coatings can be improved either by copolymerization with silicon tegomer or with dispersing them in a well adherent resin such as CF.

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