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# Studies on electrodeposition and characterization of PTFE polymer inclusion in Ni-W-BN nanocomposite coatings for industrial Applications

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## Abstract

Ni-W-BN-PTFE nanocomposite coating having excellent corrosion and friction resistance alongside hardness and smooth surface was developed. This was achieved by introducing polytetafluoroethylene (PTFE) polymer in the optimized Ni-W-BN nanocomposite coating deposited on a mild steel substrate by direct current (DC) and pulse current (PC) methods. The deposition was characterized by using field-emission Scanning Electron Microscopy (FE-SEM), Energy Dispersive X-ray Analysis (EDAX) and X-ray Diffractrometry (XRD). Microhardness and friction resistance of the coatings were measured by using the Vicker's micro hardness tester and Scratch tester TR-101-M4. The contact angle (CA) of a water droplet on the surface of nanocomposite coating was measured by Optical Contact Goniometry (OCA 35). The corrosion behaviour was measured by using Tafel Polarization and Impedance methods in 3.5% NaCl solution. It was observed that, co-deposition of PTFE solid lubricant particles in the Ni-W-BN nanocomposite coating resulted in comparatively smooth surface, higher microhardness, less friction coefficient, excellent water repellency and enhanced corrosion resistance. PC method has shown enhanced performance than DC coating due to uniform and smaller grain deposits.

**Keywords**: Pulse deposition, nanocomposite, water repellency, corrosion resistance, impedance.

## 1 Introduction

Electrodeposition method is widely applied for the production of nanocomposite coatings. The amount of incorporating particles determines the properties of the coating which is influenced by deposition parameters such as concentration of the particles in the bath, current density, bath agitation and pH[1]. Ni-W nanostructured alloys are known to exhibit superior mechanical and chemical properties than Ni coatings[2]. Nickel boron nitride [Ni-BN] composites are gaining importance for potential engineering applications due to their high hardness and anti wear properties[3]. Tribological properties are successfully improved due to the incorporation of hexagonal boron nitride particles[4-5]. Whereas, co-deposition of PTFE was studied by Bercot et al[6]. Ni-PTFE composite coatings prepared by electrodeposition method have received much more attention recently for their good water repellency and solid lubrication due to their low surface free energy and friction coefficient[7]. Different types of metallic and polymeric coatings used in the automotive industry are widely applied to improve the tribological behaviour of steel based mechanical components. Mechanical components are frequently need good corrosion resistance, because often they come into contact with corrosive environments. Generally, pulse plating yields a finer grained deposit, as the current density is used in pulse plating can be significantly higher than that of direct current. This resulted in higher over potential and subsequently increasing the nucleation rate which leading to the formation of finer grains and smoother surfaces. It has been proved that, the application of pulse current in composite plating results in deposits with more particles embedded, uniformly distributed and better surface morphology than those obtained under direct current conditions[8]. Multicomponent EN-PTFE-SiC composite coatings have demonstrated a promising combination of mechanical and tribological properties as well as low surface energy[9]. Homogeneous distribution of respective second phase particles have lead to improve mechanical properties, tribological properties, corrosion resistance as well as anti-oxidation properties of the composite coatings[10-11]. Polymeric composites offer wide range of tunable physical properties and are frequently used in high performance applications[12]. Fluorine containing films have shown more attention because of their chemical inertness, anticorrosion, anti sticking and low dielectric constant which makes a promising deposition for various applications[13]. The corrosion resistance properties of Ni-P-PTFE coatings are superior to Ni-P coatings[14]. All of the above research findings suggest that, incorporation of two or more filler materials, each having a distinct functionality (one providing lower coefficient of friction and the other a corrosion resistance), can result in a composite coating with the potential of enhancing tribological performance. PTFE is a popular polymer solid lubricant because of its chemical inertness, relatively high melting point, low surface tension, and high thermal stability[15]. It's coefficient of friction is lower than that of almost any other polymers because of its very low surface energy and excellent non-stick properties. However, studies on polymer nano composite coatings have mostly based on PTFE with hard particle[16-18]. No literatures are available for PTFE based Ni-W-BN nanocomposite electrodeposition. There are several forms of boron nitride particles available. Hexagonal boron nitride particles are employed in this investigation as they have structure related to graphite and are most stable and soft form compared to cubic boron nitride particles. Therefore, in this work, friction and corrosion properties of the Ni-W-BN-PTFE nanocomposite coatings deposited by DC and PC methods on mild steel substrates were investigated.

## 2 Experimental Sections

Cold rolled mild steel plate of size 3×2.5×0.05 Cm cathodes were polished with fine abrasive paper, degreased with trichloroethylene, cathodically electro cleaned in alkaline solution for 2 min and anodically for 30 s. They were rinsed in running water, dipped for 10 s in 5% $H_2SO_4$ solutions. Electrolytic nickel plate of size 4×2.55×0.4 Cm was used as the anode for DC and PC electrodeposition using a Myriad Bipolar pulsed power supply. Table-1 summarizes the conditions of the electrodeposition procedure. After the deposition, all samples were cleaned with deionized water and dried under ambient conditions. PTFE particles of approximately 1µm size were used in this study. Prior to electrodeposition, PTFE polymer was ultrasonication for 1 hour. Cetyltrimethyl ammonium bromide (CTAB) surfactant was employed for particle dispersion to prevent agglomeration of second phase particles in the solution. Additionally, mechanical stirring (600 rpm) was used for thorough mixing of all the components and heated to plating temperature at 65 °C. We have kept the inert particles in contact with the bath solution for 24 hours and then followed the stirring. Certainly, the stirring has offered a uniform mass transfer and particle attachment to the cathode. By the use of magnetic stirrer, the suspended particles were thoroughly stirred in order to attain the uniform distribution of nanoparticles in the bath solution. The hardness of the electrodeposits was measured by using MHG Everyone Hardness Tester (Hong Kong) on the Vicker's scale. It had a diamond pyramid of a square base with an angle of 136 ° at the vertex between two opposite faces. The microhardness of the deposit in kgf mm$^{-2}$ was determined in each case by using the formula

$$Hv = 1854 \times \frac{L}{d} \qquad (1)$$

Where, *L* is the load applied in g and *d* the diagonal of the indention (µm). The load applied was 50 g. Scanning electron microscope (FE-SEM) (FEG-Quanta250, Czech Republic) was used to follow the surface morphology of the composite coatings. The crystalline structure of the plated substrate was identified by X-ray diffraction using Brooker D8 advance X-ray diffractometer operated with Cu K∞ radiation at a rating of 40 kV, 20 mA. The scan rate was 0.05 per step with the measuring time of 15 per step. The crystallite size of the metal composites was determined by using the Scherrer equation.

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (2)$$

Where, $D$ is the crystalline size, $\lambda$ is the incident radiation (1.5418 Å), $\beta$ is the corrected peak width at half-maximum intensity and $\theta$ the angular position. Thickness of the coating was measured from the cross-sectional FE-SEM images. Electrochemical polarization studies were carried out by using an electrochemical analyzer (EG&G – Auto Lab Analyzer Model: 6310) containing three electrode cell assembly. The exposed 1 $cm^2$ area of mild steel substrate was used as working electrode. A rectangular platinum foil and a saturated calomel electrode were used as auxiliary and reference electrodes respectively. The test solution was 3.5% NaCl kept at 30 °C. Electrochemical impedance measurements were carried out on the electrodeposits after they attained steady state potential. The impedance measurements were made in the frequency range of 10 K $cs^{-1}$ to 10 m $cs^{-1}$ with a sinusoidal perturbation of 10 mV[19]. Surface Roughness of the coatings was assessed by using Roughness Measuring station (Make: Mitutoyo, Model: Surftest SJ-310). This instrument was used to analyze the average roughness value (Ra) with measuring speed of 0.5 mm/s and the travelling distance of 5 mm. An average value of five readings is reported. Moreover, Scratch tester TR-101-M4 (Make-DUCOM) was used to determine the coefficient of friction for the coatings. All the samples were run against at 5N normal loads at 0.2 $ms^{-1}$speed. The measurement of water repellency of the Ni-W-BN-PTFE nanocomposite coating was evaluated by determining the static contact angle for water drops with the help of Optical Contact Goniometry (OCA 35).

**Table 1**

| Plating bath | Composition | Plating conditions |
|---|---|---|
| Nickel Sulphate | 0.17 M | Pulse peak c.d 1.2 A/cm$^2$ |
| Sodium tungstate | 0.15 M | pH 8 Time 60 min |
| Tri Ammonium Citrate (TAC) | 0.30 M | Temperature 65 °C |
| Ammonium Chloride | 0.20 M | Constant Stirring |
| Dimethyl Sulphoxide | 0.06 M | **Pulse duty Cycle** |
| Cetyltrimethyl ammonium Bromide (CTAB) | 0.50 g/L | On time- 40ms<br>Off time- 60ms |
| BN (h) powder | 6.0 g/L | |
| PTFE | 5-15 g/L | |

## 3 Results and discussion

### 3.1. Effect of PTFE particle concentration in the Ni-W-BN nanocomposite deposition

The variation of PTFE particle concentrations in the optimized Ni-W-BN nanocomposite coating is shown in Fig.1. As the PTFE particle concentration in the bath increases from 5 to 15 g/L in the fixed current density of 1.2 Adm$^{-2}$ at 65 °C, the amount of particles co-deposited were also increased. Actually, increasing the concentration of PTFE particle in the solution has produced a higher particle density (particles per liter) and created more opportunities for particle adsorption onto the electrode[20]. The cationic surfactant (CTAB) and mechanical stirring were found to be effective in suspending the PTFE particles in the plating solution. For a given cationic surfactant concentration, the coating rate was increased with increasing PTFE concentration in solution until reaching a maximum value at approximately 15 g/L. It can be explained by the two- step adsorption model which has been suggested by Gugliemi[21]. The cationic surfactant has offered adhesion force between PTFE nanoparticles and the cathode results in increase of co-deposited PTFE inert particles. Besides, cationic surfactant has also developed a net positive charge on its surface, so increasing their affinity towards the cathode and hence increases the stability of particle suspension and prevents agglomeration. Like this, it is understood that, cationic surfactant enhances the incorporation of particles in the metal matrix. Zeta potential of the nanoparticles would be increased by the addition of cationic surfactant CTAB. The positive Zeta potential values gave extra adhesion force between the inert particles and the cathode. Increasing the amount of concentration of PTFE (5 g/L to 15 g/L) nanoparticles in the bath has enhanced the adsorption rate of PTFE on the cathode surface. Further increase in the concentration of (above 15 g/L) PTFE particles in the electrolytic bath did not show any progress of adsorption on the cathode surface. Above 15 g/L of PTFE particles, the bath solution was getting saturated and agglomeration of particles took place. Hence, 15 g/L of PTFE particles was taken as an optimum concentration in the electrolytic bath. PC deposition had more particle incorporation than DC plating due to the higher nucleation rate in the PC deposition.

### 3.2. Effect of current density on coating thickness

The effect of current density on the Ni-W-BN-PTFE nanocomposite coating thickness was illustrated in Fig. 2. The coating thickness was increased with increasing the current density up to 1.2 A/dm$^2$ and then decreased gradually. This may be due to the fact that, the current density increases beyond 1.2 A/cm$^2$ results in more rapid deposition of nanocomposite coating and smaller amount of particles are incorporated in the coating. The increment of current density beyond 1.2 A/cm$^2$, the deposited particles has got agglomerated, that causes a decrease of coating thickness and increase of surface roughness. Coating thickness was slightly higher in PC deposition than DC due to smallest amount of $H_2$ evolution reaction, homogeneous distribution of particles and more particle incorporation have been observed in pulse deposition. In order to create a better understanding of the effect of current density on the electrodeposition of Ni-W-BN-PTFE nanocomposite coating, the thickness of the coating was determined by a cross-sectional SEM image. Fig.3 (a&b) display the typical images from cross-sectional FE-SEM view of a coating obtained at a current density of 1.2 Acm$^2$ in Ni-W-BN-PTFE (DC & PC) nanocomposite coatings. The thickness of the coating was 27 µm and 36 µm for DC and PC respectively.

### 3.3. XRD measurement

XRD patterns of Ni-W-BN and Ni-W-BN-PTFE (DC&PC) nanocomposite coatings are shown in Fig 4 (a-c). The crystalline size of nanocomposite coating was calculated from the Debye-Scherrer's equation. Ni-W alloy matrix has face centered crystalline structure. The peaks at 44° and 65° are confirmed from Standard XRD reports for Ni–W (JCPDS 65-4828). The grain sizes of the electrodeposited Ni-W-BN and Ni-W-BN-PTFE (DC&PC) nanocomposite coating were found to be 26 nm, 20 nm and 14 nm respectively. After the incorporation of PTFE particles in the Ni-W-BN nanocomposite coating, the grain size was reduced. It was due to the grain refinement of PTFE particles and changes in the microstructure of the composite coating. Moreover, addition of cationic surfactant (CTAB) is one of the most important organic molecules, and it has been widely used as the stabilizer and structure-directing agent to control nucleation, growth and alignment of crystals. Pulse current deposits have smaller grain size than the direct current electrodeposits. The decrease in grain size is due to evenly distributed PTFE particles and it produces crack free deposits. Fig.4 (a-c) show the peak appeared at an angle of 26.8° (JCPDS 85-1068) has confirmed the incorporation of BN particles. When compared to Fig 4a very less intensity of BN peaks are seen in Fig. (4b & 4c) due to the inclusion of PTFE particles reduced the peak intensity of BN particles. According to (JCPDS 47-2217), Figs. (4b & 4c) have showed the peak for PTFE appeared at an angle of 18° in the Ni-W-BN-PTFE nanocomposite coating[22]. The crystalline structure of the Ni-W-BN is not affected due to the maintenance of the homogeneity bath. PTFE particles are completely mixed with the bath solution.

### 3.4. SEM with EDAX study

The SEM morphologies of the electrodeposited Ni-W-BN and Ni-W-BN-PTFE (DC&PC) nanocomposite coatings are shown in Fig. 5 (a-c). As shown in Fig. 5, Ni-W-BN nano composite coating has seen in long needle shaped deposits. By introducing PTFE polymer into the deposits, the surface morphology was covered with distorted spherical shaped particles. The Co-deposited PTFE nano- particulates are much uniformly distributed in the Ni-W-BN-PTFE nanocomposite coating. The deposits obtained from PC method have shown bright, smooth and smaller grains compared to the deposits obtained from DC method. Moreover, the size mentioned from XRD studies was same as the size obtained from the FE-SEM results (Fig. 6a). Agglomerated Ni-W-BN-PTFE nanocomposite coating was shown in Fig. 6(b). EDAX analysis has confirmed the successful electrodeposition of PTFE on the Ni-W-BN nanocomposite coating. The elements Ni, W, B, N and C, F can be precisely detected as shown in Fig. 7. The EDAX analysis gives the % of elements present in the Ni–W–BN-PTFE nanocomposite coatings. When compared to DC deposition more particles are embedded in PC deposition. Because, during DC there is one diffusion layer, but for PC two diffusion layers formed due to the pulse. In addition, longer $T_{off}$ promotes the transfer of more particles near the cathode and consequently a higher number of particles are incorporated. During ON time (40 ms pulse), nucleation and growth of the metal nanoparticles have taken place. But the OFF time (60 ms pulse) (zero current or close to equilibrium potential) has allowed to compensating the depletion of metal ions around the electrode and prevents the overlapping of diffusion Zones. Hence, particle incorporation is higher in PC method than the DC method. During Ni-W alloy deposition

$NiWO_4$ is formed, which react with citrate to form $[(WO_4)\ (Cit)\ (H)_x]^{x-5}$ complex. After that, metallic tungsten is formed from tungstate complex[19]. The electrochemical reduction of $WO_4^{2-}$ ion occurs as,

$$WO_4^{2-} + 8H^+ + 6e^- \longrightarrow W + 4H_2O \qquad (3)$$

The composite electrodeposition mechanism was proposed by Guglielmi's model. According to this model, composite electrodeposition procedure proceeds by two steps. The first step is the loose adsorption of particles adhered on the cathode surface by Van der Waals forces with a high degree of surface coverage which can be presented by Langmuir adsorption isotherm. In the second step, particles are strongly adsorbed on the surface by Columbic forces under the effect of applied electric field and incorporated into the growing metal matrix.

## 3.5. Tribological study

### 3.5.1. The effect of Hardness

The microhardness profile of the Ni-W-BN and Ni-W-BN-PTFE coating is depicted in Fig. 8. The microhardness values were measured for varying concentration of PTFE in the optimized Ni-W-BN nanocomposite bath. The microhardness value of the Ni-W-BN coating is ~ 566 HV. After the inclusion of PTFE particles, the microhardness value has increased gradually. Ni-W alloy matrix can provide effective protection for the two solid lubricants BN&PTFE which is helpful to improve the coatings durability in harsh environments[23]. An increase of microhardness values is due to the dispersion-strengthening and grain refining of the composite particles[24]. This strengthening effect was owing to homogeneous distribution of nanoparticles in the nanocomposite coatings[25]. Instead, the synergistic effect between PTFE polymer and Ni-W-BN nanocomposite has enhanced the microhardness value. The microhardness value is mainly depends on the co-deposited filler particles. If the co-deposited particles are hard material like SiC, $Al_2O_3$ etc. the microhardness values increased rapidly. But, if the selection of filler particles is soft materials like h-BN, PTFE and $MoS_2$ moderate microhardness values achieved. PC deposition of PTFE particles into the Ni-W-BN nanocomposite coating has significantly increased the microhardness values than DC deposition due to the fine grain size and compact nature of the coating. During PC deposition, the higher pulse frequency could make a higher over potential, providing additional energy for the adsorption of inert particles such as PTFE polymer. Increase in microhardness value is also due to the dispersion strengthening effect of second phase particles in the composite coatings which blocking the dislocation motion. Besides, Pulse current coating had a finer grain size, which reduced the porosity and improved the compact structure. Ni-W alloy has fine grained fcc crystalline structure. The particles are largely closer together and arranged in order. This has made the uniform and pores free deposition, which enhances the microhardness. In addition, the presence of multicomponent in the Ni-W-BN-PTFE nanocomposite coating is responsible for the improved microhardness.

### 3.5.2. Effect of surface Roughness

Surface roughness measurements on the electrodeposited coatings are repeated three times at various locations and recorded the average values. Fig. 9 shows the typical roughness profile of the (a) Ni-W-BN (b) Ni-W-BN-PTFE nanocomposite coatings. As shown in Fig. 9 the average surface roughness (Ra) value of Ni-W-BN nanocomposite coating was 0.41 μm. After the inclusion of PTFE (optimized concentration 15 g/L) particles in the Ni-W-BN nanocomposite coating, the average surface roughness (Ra) value was reduced to 0.26 μm. It is observed that, the surface roughness values decreased with the addition of PTFE particles in the coatings. Thus, the two solid lubricant fillers have played a vital role to reduce the surface roughness. The decrease in roughness is probably due to the dense coating and self lubricating property of the PTFE particles. PC coating has lower surface roughness values than the DC coatings due to uniform and compact surface. Pulse deposited coatings are accomplished with greater cathodic current densities than the DC coatings. It is recognized that, lower over potential coating generates deposition with larger surface irregularities on the surface of the cathode; while higher over potential deposits generate coatings with smooth surfaces. Hence, the average surface roughness value of pulse current deposition for Ni-W-BN-PTFE nanocomposite coating was reduced.

### 3.5.3. Effect of Coefficient of friction

Fig. 10 illustrates the effect of various content of PTFE particles incorporation into the Ni-W-BN nano composite coatings on coefficient of friction. Averages of five readings were noted. The friction coefficient value of Ni-W-BN nanocomposite coating was found to be 0.28. In order to further decrease the friction coefficient value by adding PTFE as the second solid lubricant filler. Inclusion of more solid lubricant was promising effect of decreasing friction coefficient[26]. Increasing the amount of PTFE in the deposit has led to decrease the coefficient of friction. PTFE is a typical solid lubricant and when applied to a metal surface, it imparts non-stick properties and lowers its coefficient of friction. The average coefficient of friction for Ni-W-BN-PTFE nano composite coating was the lowest in the range of 0.15 indicating excellent friction reduction performance. The decreasing value of the coefficient of friction of the coating is due to the inclusion of two solid lubricant particles such as BN and PTFE. One of the most effective properties of organic coatings is the good adhesion to the substrate. This property of adhesion strength is great importance to the reduction of friction coefficient. Besides, rough surfaces usually have lower wear resistance and higher friction coefficients than smooth surfaces. PTFE incorporated in the optimized Ni-W-BN nanocomposite coating has reduced the surface roughness values of the coating. Hence, PTFE was an efficient organic filler to reduce the friction. Some interaction between the Ni-W-BN nanocomposite coating and the solid lubricant PTFE polymer inclusion has reduced the friction coefficient. Based on these results, lower coefficient of friction in association with the use of Ni-W-BN-PTFE nanocomposite coating was attained. As we discussed before, using PC deposition the surface uniformity increases and hence, reduces the coefficient of friction significantly than the DC deposition. This is consistent with the microhardness results as shown in Fig.8.

## 3.6. Electrochemical characterizations

### 3.6.1. Potentiodynamic polarization study

The detailed corrosion potentials and corrosion current densities of the samples have obtained in 3.5% NaCl solution by electrochemical methods. Fig.11 signifies the polarization curves obtained for various DC deposits by potentiodynamic polarization method. The corrosion resistance parameters such as corrosion potential ($E_{\mathrm{corr}}$) and corrosion current ($I_{\mathrm{corr}}$) values are listed in Table 2. Inclusion of PTFE particles in the optimized Ni-W-BN nanocomposite coatings have shifted the corrosion potential values positively from −0.561 V to −0.417 V and the corrosion current density values significantly decreased from 4.3 μA/cm$^2$ to 2.4 μA/cm$^2$ [27]. This positive shift in the corrosion potential was proved the well passivation property of PTFE polymer. The potential shifting towards more positive side indicates the creation of more protective passivation layer on the surface of the cathode representing more corrosion resistant. The largest potential shift is seen in the 15 g/L of PTFE particle inclusion at optimized Ni-W-BN nanocomposite coating. The positive shift of corrosion potential designates the more protection of mild steel substrate against corrosion by the self lubricating nature of the polymer. These statements, evidence the noble character of PTFE polymer. When PTFE was added as a fourth component in the Ni-W-BN nanocomposite system a protective oxide layer was formed on the surface of the cathode. PTFE particles have also minimized the defects which act as active sites for corrosion. On the other hand, the uniformly distributed PTFE particles in the deposit have behaved as a passive layer between corrosive media and deposit surface. Fig.5 shows that, there may be pore free composite surface. Therefore, it can be accomplished that, the presence of PTFE increases the corrosion resistance property of the nano composite coatings. PTFE also performs as an efficient barrier against corrosive ions and this self lubricating polymer was acted as a binder between the substrate and the nanoparticles. The addition of PTFE particles in PC deposits has lower corrosion current than the deposits obtained from DC method (Fig. 12 and Table 3) because; the PC method has provided smaller crystallites and grain boundaries. Deposits with smaller grain size have higher density of nucleation sites for passive film, which leads to higher fraction of passive layer and thus a lower passive current density[28]. Hence, smaller grain coatings have offered enhanced corrosion resistance[29].

**Table 2**

| **PTFE concentration (g/L)** | **$E_{corr}$ Vs SCE (mV)** | **$I_{corr}$ (µA cm$^{-2}$)** |
|---|---|---|
| 0 | -561 | 4.30 |
| 5 | -502 | 3.66 |
| 10 | -459 | 2.81 |
| 15 | -417 | 2.47 |

**Table 3**

| **PTFE concentration (g/L)** | **$E_{corr}$ Vs SCE (mV)** | **$I_{corr}$ (µA cm$^{-2}$)** |
|---|---|---|
| 0 | -548 | 2.54 |
| 5 | -507 | 1.71 |
| 10 | -438 | 0.97 |
| 15 | -386 | 0.75 |

### 3.6.2. Electrochemical impedance study (EIS)

Fig.13 and Table 4 represent the Nyquist plots for Ni-W-BN and the addition of various amounts of PTFE particles obtained by DC method. Charge transfer resistance ($R_{ct}$) values have increased and double layer capacitance ($C_{dl}$) values decreased with the inclusion of PTFE particles in the deposit. This indicates that, it is influenced by the state of the electrode / solution interface and the real contact area between the electrode and solution[27]. Lower $C_{dl}$ values resulted from a reduction in the dielectric constant and/or raise the thickness of the electrical double layer. Moreover, the double layer capacitance value is related to the porosity of the coating. A smaller value of double layer capacitance was confirmed the less porous in nature and decrease in porosity enhances the anticorrosion property of the deposits. After the inclusion of PTFE polymer in the Ni-W-BN nanocomposite coating, the thickness of the coating was also increases. The increment of the coating thickness has prevented the expansion of corrosion cavity and increases the anticorrosion properties of the coating. The Nyquist plots obtained for Ni-W-BN deposits and the addition of various amounts of PTFE particles prepared by using the PC method are shown in Fig.14 (a) and Table 5. The proposed equivalent circuit for examine the impedance spectra is shown in Fig.14 (b). As it was noted in the previous sections, smaller grain size has a higher fraction of passive layer and low corrosion rate due to the high density of nucleation sites for passive film. Hence, PC coating was more corrosion resistant than the electrodeposited DC coating[30]. All the Ni-W-BN-PTFE nano composite coatings have shown higher charge transfer resistance and lower double layer capacitance values than Ni-W-BN nano composite coating. The incorporation of PTFE has lower chemical activity and will help to reduce the pore size in the nanocomposite coating and prevent the corrosive pits from growing up. These data clearly indicated that, the presence of chemically inert nature of PTFE nanoparticles has not affected by corrosive environment. On the other hand, the hydrophobic character of the PTFE particles hinders the anodic reaction and decreases the corrosion rate. In other words, Ni-W-BN-PTFE nanocomposite coatings have lower chemical activity and better chemical stability than the Ni-W-BN deposits. The nanocomposite coatings employed in this current study contains four different particles and its combined properties are efficient for the protection of mild steel surface against corrosion.

**Table 4**

| PTFE concentration (g/L) | $R_{ct}$ ($\Omega cm^2$) | $C_{dl}$ ($\mu F cm^{-2}$) |
|---|---|---|
| 0 | 616 | 51.70 |
| 5 | 1025 | 31.24 |
| 10 | 1122 | 28.27 |
| 15 | 1314 | 24.33 |

**Table 5**

| PTFE concentration (g/L) | $R_{ct}$ ($\Omega cm^2$) | $C_{dl}$ ($\mu F cm^{-2}$) |
|---|---|---|
| 0 | 1116 | 28.53 |
| 5 | 1250 | 25.23 |
| 10 | 1450 | 21.51 |
| 15 | 1643 | 19.23 |

### 3.7. Contact angle measurements

To understand the water-repellency of Ni-W-BN nanocomposite coating and addition of various concentrations of PTFE particles obtained by PC deposition was done by the contact angle determination for water droplet. Contact angle measurement is a simple quantitative method to analyze the wettability/hydrophobic nature of the solid surface. Surfaces with contact angle larger than 90° are said to be as hydrophobic. The volume of the water droplet was 8 µL on both Ni-W-BN and Ni-W-BN-PTFE nanocomposite coatings are shown in Fig. 15. It was found that, the water repellency/hydrophobic was developed noticeably. The weight percentage of PTFE concentration increases the hydrophobic nature also increases. This hydrophobic behaviour was helpful for water removal and makes it difficult for water adhering. The surface irregularities were also reduced. It was due to well dispersed PTFE particles in the bath by ultrasonication and constant stirring. Hence, the weight percentage of PTFE increases the water contact angle also increases. The contact angle for the Ni-W-BN nanocomposite coating (A) was about 115°, while that for the PTFE (15 g/L) polymer inclusion of Ni-W-BN-PTFE nanocomposite coating (B) was about 136°, has shown a better water-repellency/hydrophobic nature. This means that, incorporation of the self lubricating PTFE polymer has improved the water repellency property of Ni-W-BN-PTFE nanocomposite coating. The water repellency behaviour of the PTFE polymer was clearly indicating the hydrophobic nature of the Ni-W-BN-PTFE nanocomposite coating. This hydrophobic behaviour was helpful for water removal and makes it difficult for water adhering which improved the corrosion resistance property of the nanocomposite coating

## 4 Conclusions

Electrodeposition of Ni-W-BN-PTFE nanocomposite coatings by direct and pulse current methods on the mild steel substrate was successfully employed from Watts' type Nickel bath. The cationic surfactant CTAB was used to suspend the PTFE particles well in bath solution. The inclusion of PTFE particles in the optimized concentration of Ni-W-BN nanocomposite coatings have significantly improved the microhardness, thickness, corrosion resistance, excellent friction reduction and decrease the surface roughness of the nanocomposite coatings. Chemically inert and hydrophobic nature of PTFE particles has decreased the corrosion rate. The solid lubricating nature of the PTFE particle has greatly influenced the friction reduction and surface roughness.

A contact angle measurement of Ni–W-BN-PTFE nanocomposite coating has shown a hydrophobic behaviour with CA values of about 136°. PC deposition of Ni-W-BN-PTFE nanocomposite coating has exhibited better performance than the deposits obtained from the direct current nanocomposite coating due to the uniform, crack free deposits and also smaller crystalline size.

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**Table captions**

Table 1: Plating bath Composition and conditions

Table 2: Parameters derived from potentiodynamic polarization curves for Ni–W-BN and Ni–W-BN –PTFE nanocomposite coatings Prepared by DC Method

Table 3: Parameters derived from potentiodynamic polarization curves for Ni–W-BN and Ni–W-BN –PTFE nanocomposite coatings Prepared by PC Method

Table 4: Parameters derived from electrochemical impedance spectrum of Ni–W-BN and Ni–W-BN –PTFE nanocomposite coatings prepared by DC Method.

Table 5: Parameters derived from electrochemical impedance spectrum of Ni–W-BN and Ni–W–BN –PTFE nanocomposite coatings Prepared by PC Method

**Figure captions**

Fig.1. Effect of amount of PTFE in the bath (grams per litre) on the weight percentage of PTFE in the nanocomposite coatings.

Fig.2. Effect of current density on coating thickness

Fig.3. Cross sectional FE-SEM images of (a) Ni–W–BN –PTFE (DC) (b) Ni–W–BN –PTFE (PC) nano composite coatings.

Fig.4. XRD Patterns for (a) Ni–W– BN (b) Ni–W–BN –PTFE (DC) nano composite and (c) Ni–W–BN –PTFE (PC) nano composite coatings.

Fig.5. FE-SEM images of (a) Ni-W-BN (h) (b) Ni-W-BN -PTFE (DC) nanocomposite (c) Ni-W-BN -PTFE (PC) nanocomposite coatings.

Fig.6 (A). Crystal size of(a) Ni-W-BN (h) (b) Ni-W-BN -PTFE (DC) nanocomposite (c) Ni-W-BN -PTFE (PC) nanocomposite coatings.6(B) Agglomerated FE-SEM images of Ni-W-BN-PTFE nanocomposite coating

Fig.7. EDAX spectrum of (a) Ni-W-BN (h) (b) Ni-W-BN -PTFE (DC) nanocomposite (c) Ni-W-BN -PTFE (PC) nanocomposite coatings.

Fig.8. Effect of the amount of co-deposited PTFE on the microhardness of Ni-W-BN-PTFE nanocomposite coatings

Fig.9. Surface roughness profile of (a) Ni-W-BN (h) (b) Ni-W-BN-PTFE nanocomposite coatings.

Fig.10. Plot of Ni-W-BN and various concentration of PTFE inclusion on Ni-W-BN-PTFE nanocomposite coatings versus Friction Coefficient.

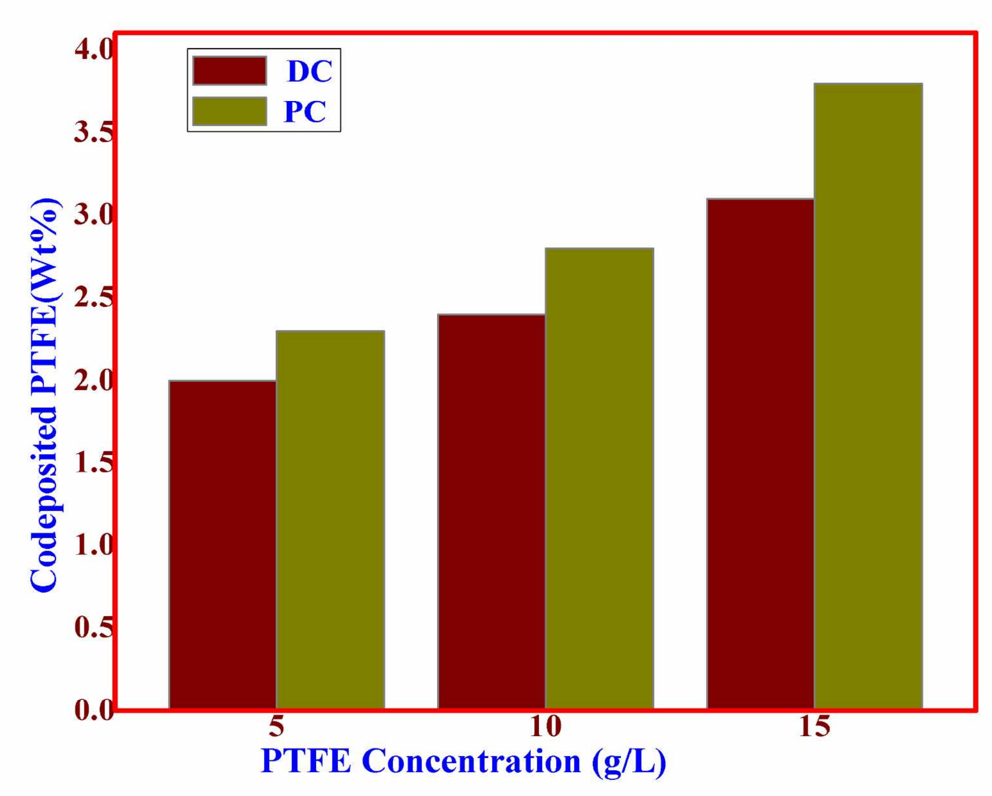
Fig.11. Potentiodynamic polarization curves for Ni–W –BN deposit and various amounts of PTFE incorporated into Ni–W-BN (h) nanocomposite by DC Method.

Fig.12. Potentiodynamic polarization curves for Ni–W-BN (h) deposit and various amounts of PTFE incorporated into Ni–W-BN (h) nanocomposite by PC Method.

Fig.13. Nyquist plots (Z''vs Z') obtained for Ni–W-BN (h) deposit and various amounts of PTFE incorporated into Ni–W-BN (h) nanocomposite by DC Method.

Fig.14 (a). Nyquist plots (Z''vs Z') obtained for Ni–W-BN (h) deposit and various amounts of PTFE incorporated into Ni–W-BN (h) nanocomposite by PC Method.14(b). Equivalent electrical circuit.

Fig.15. Contact angle measurements of a water droplet (8 μL) on the (a) Ni-W-BN (b) Ni-W-BN-PTFE (5g/L) (c) Ni-W-BN-PTFE (10g/L) (d) Ni-W-BN-PTFE (15g/L) nanocomposite coatings.



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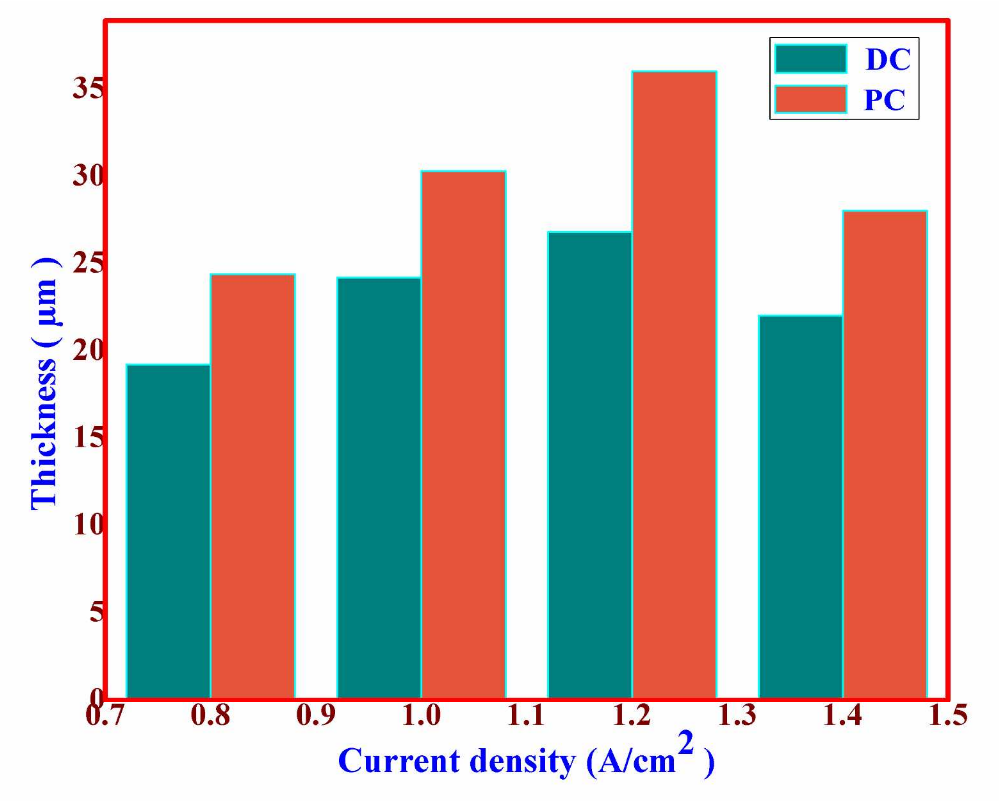

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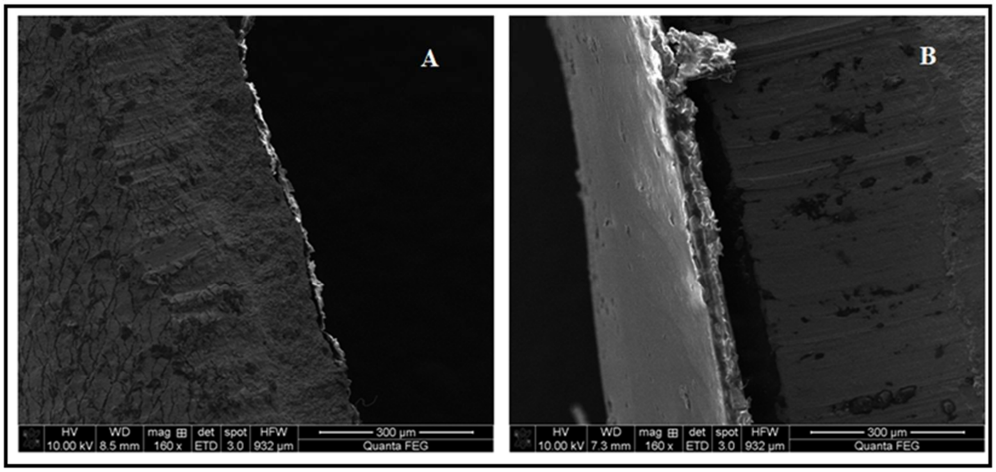

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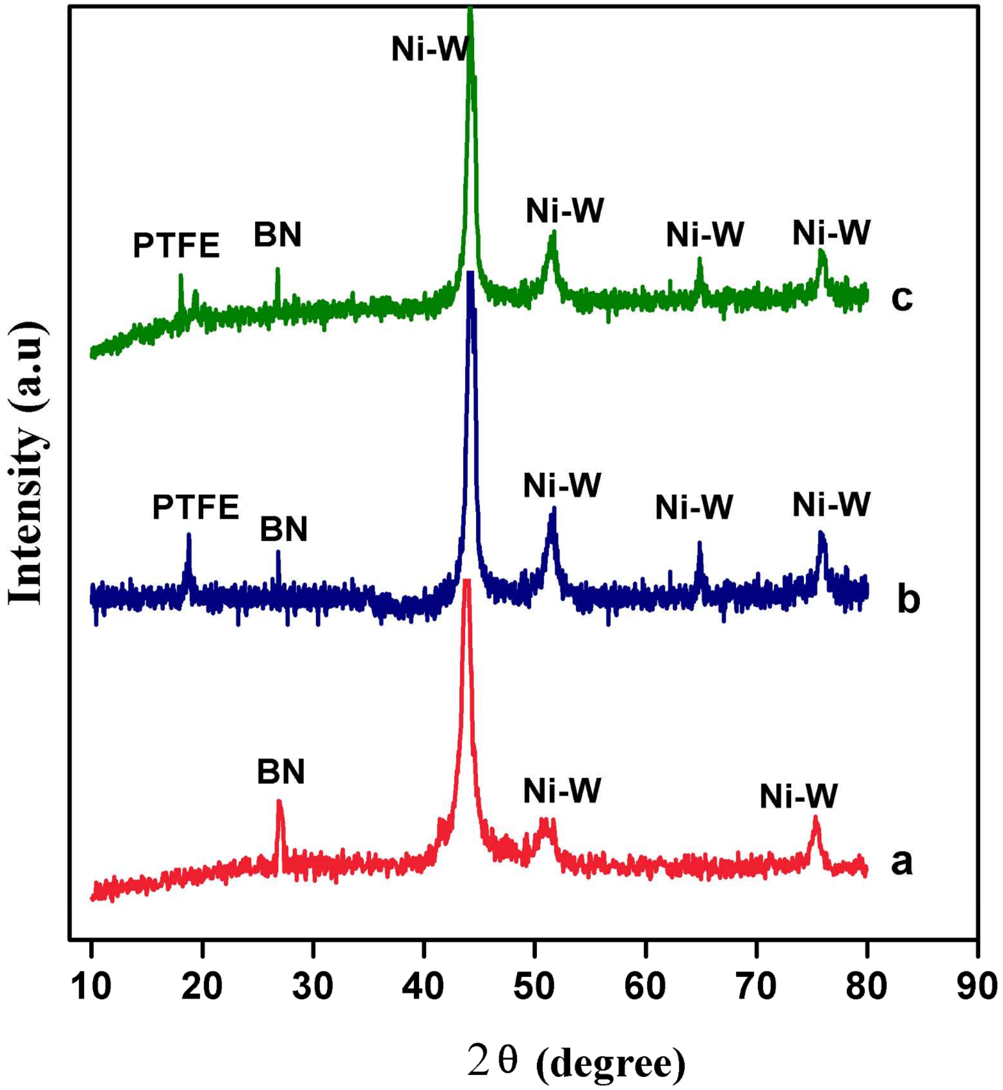

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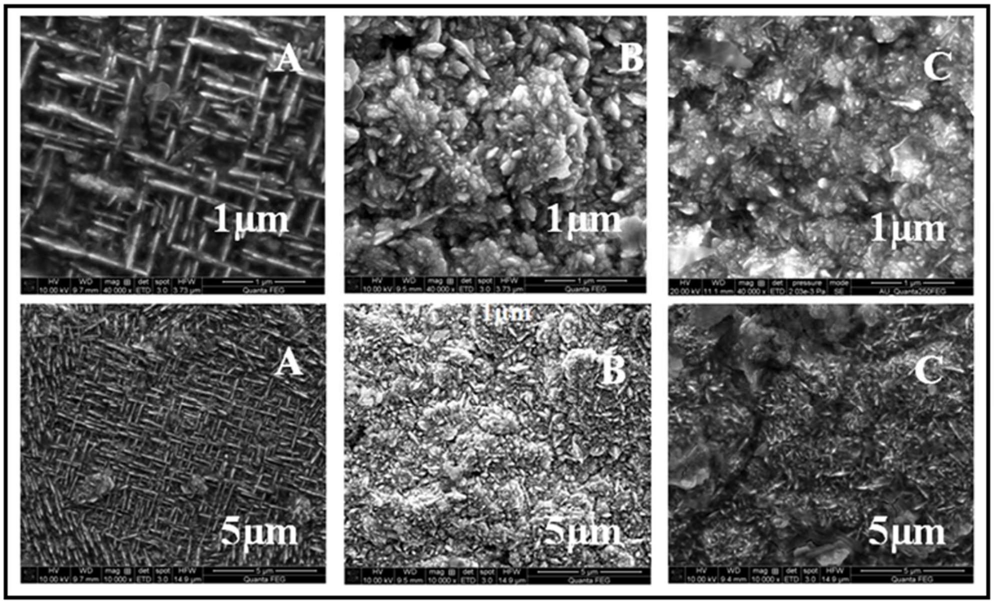

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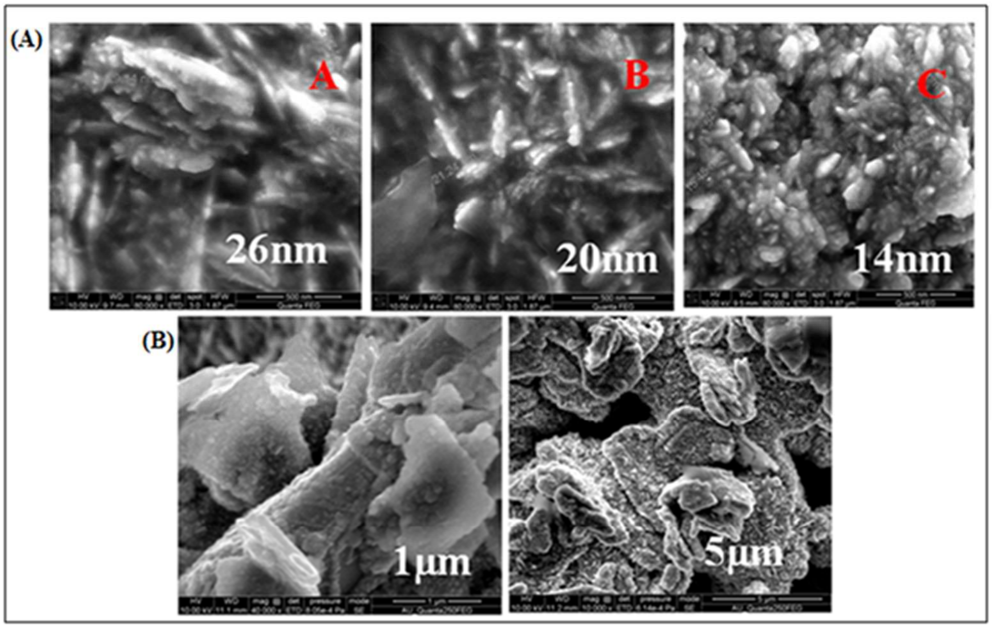

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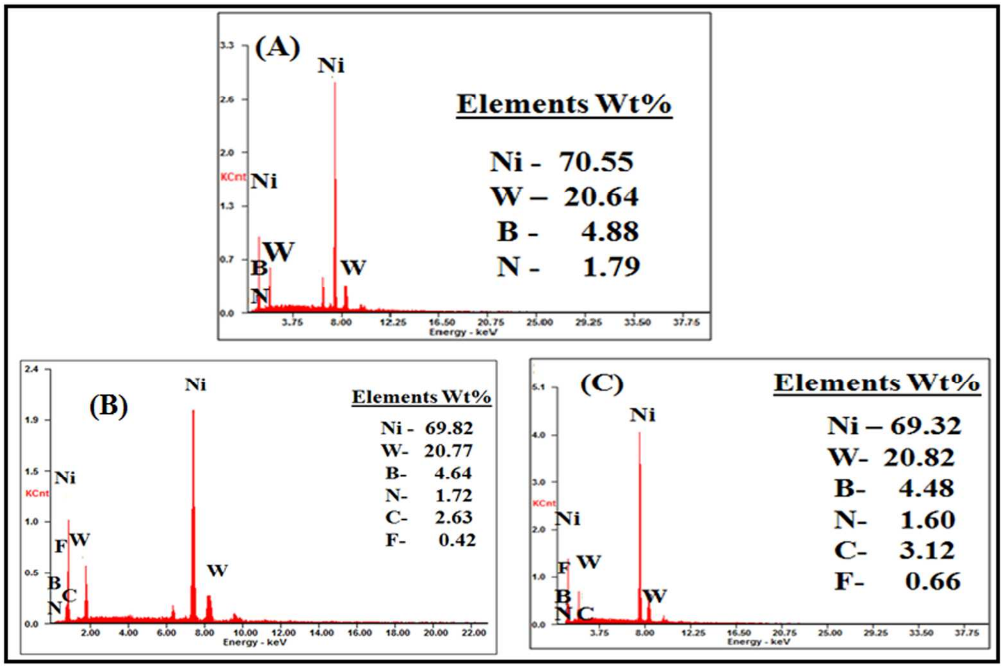

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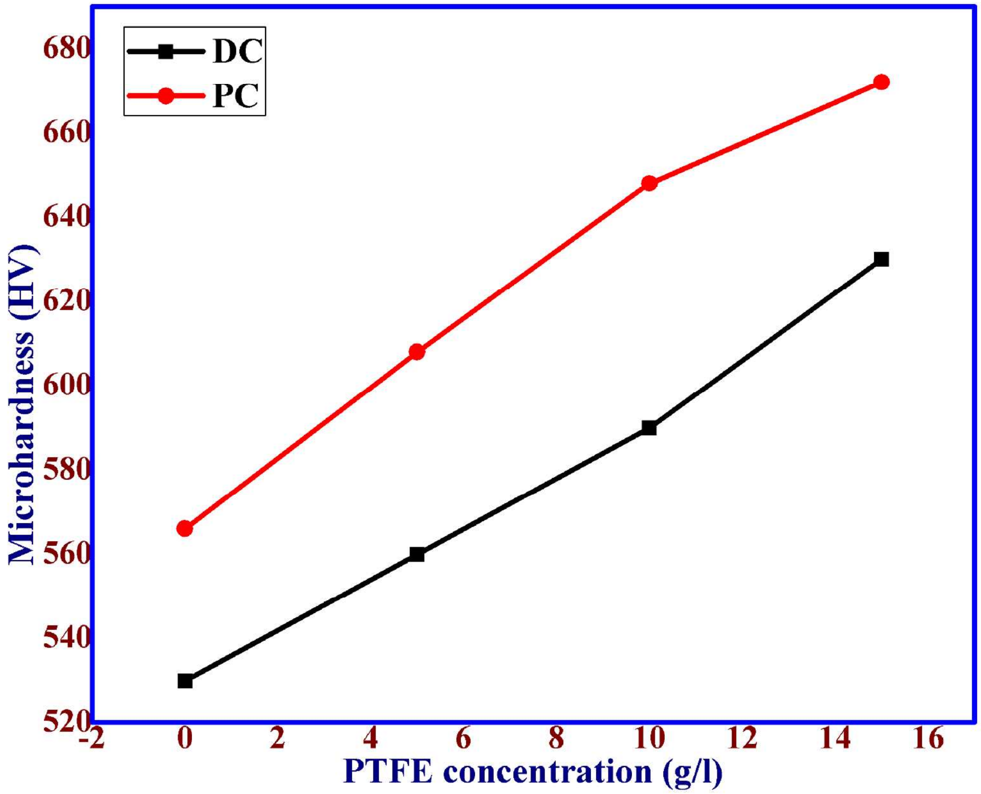

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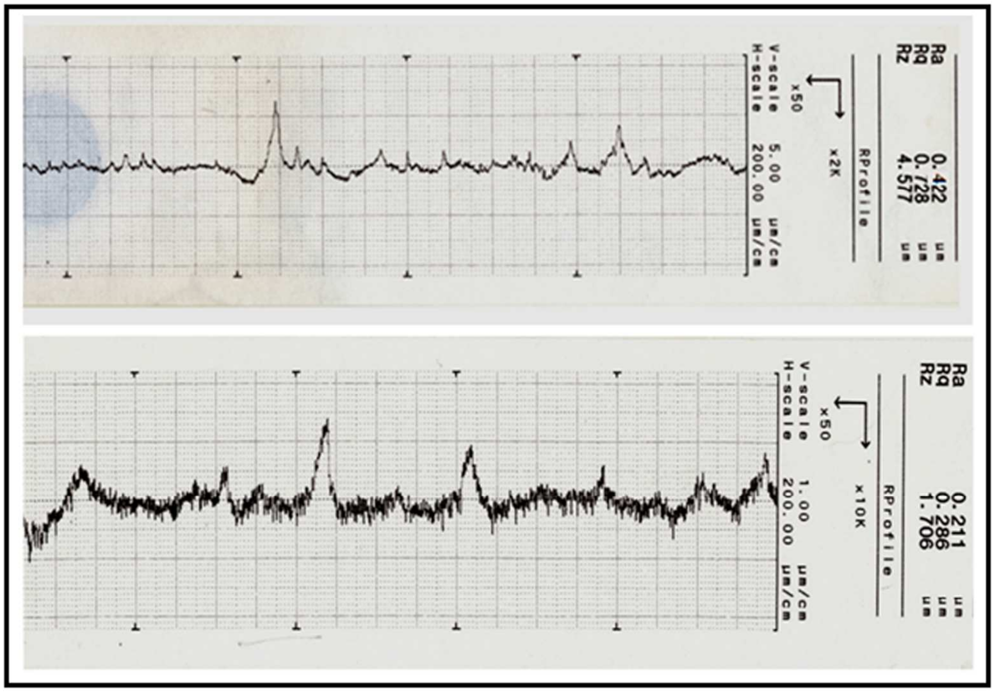

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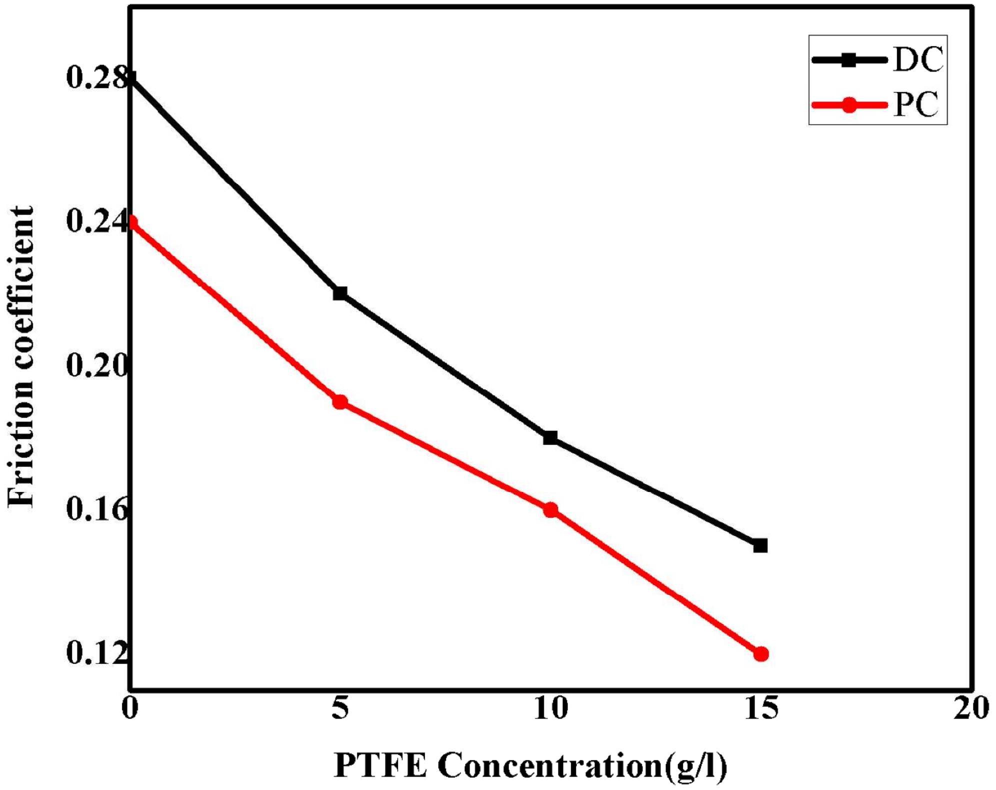

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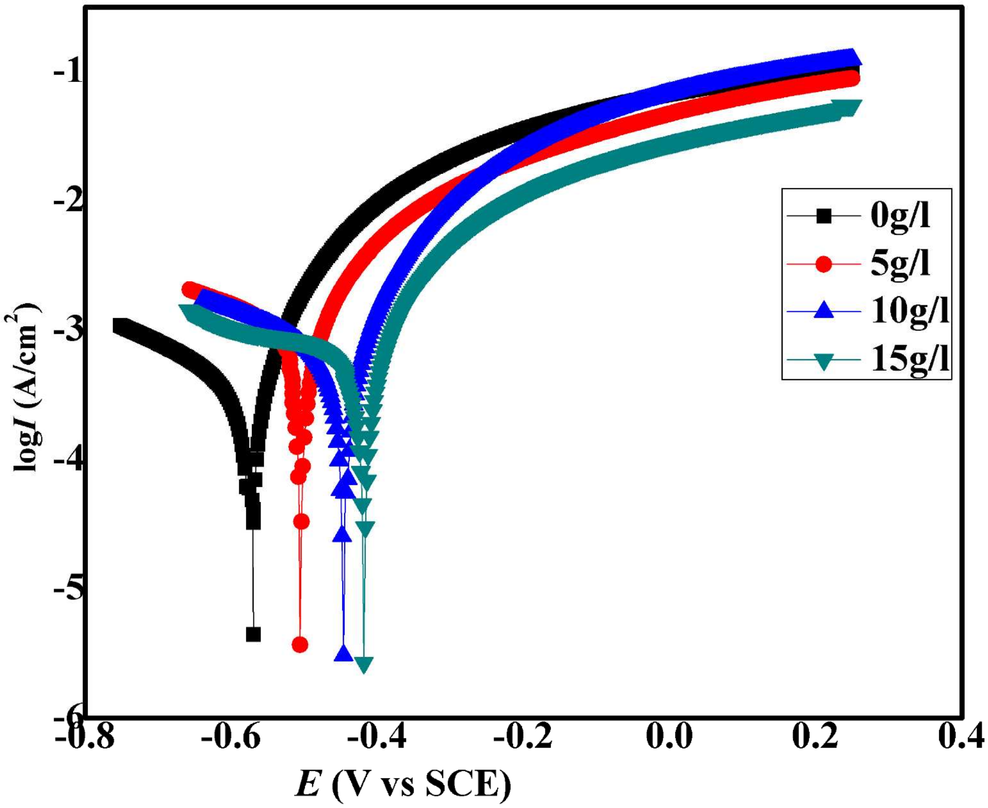

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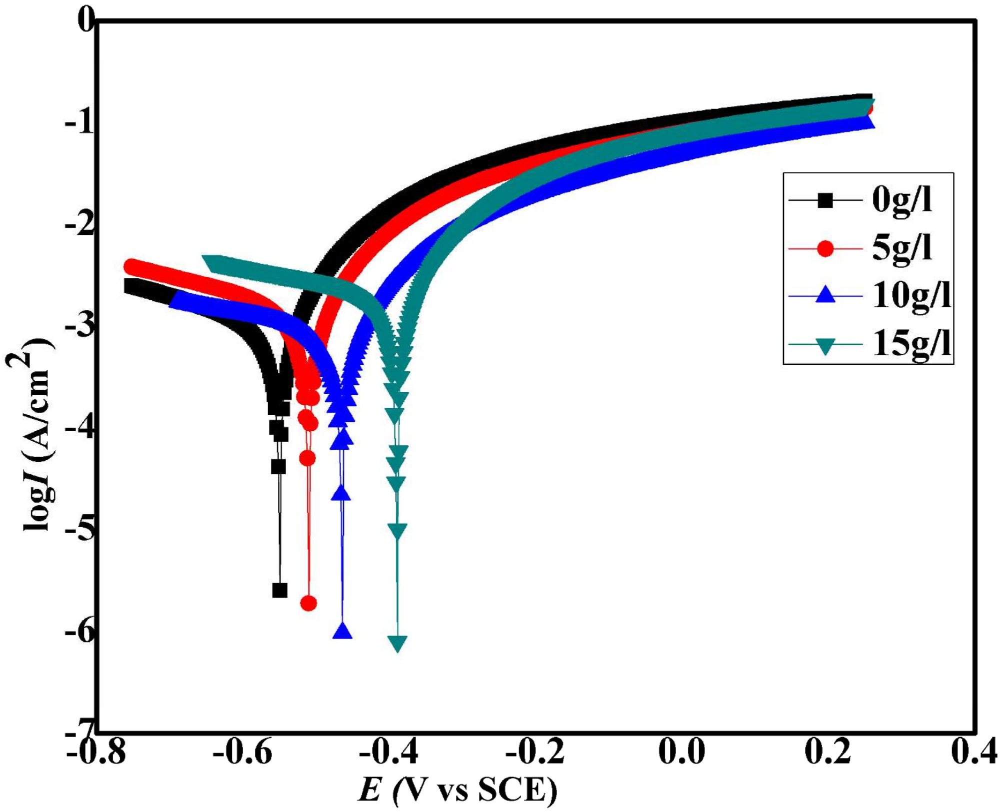

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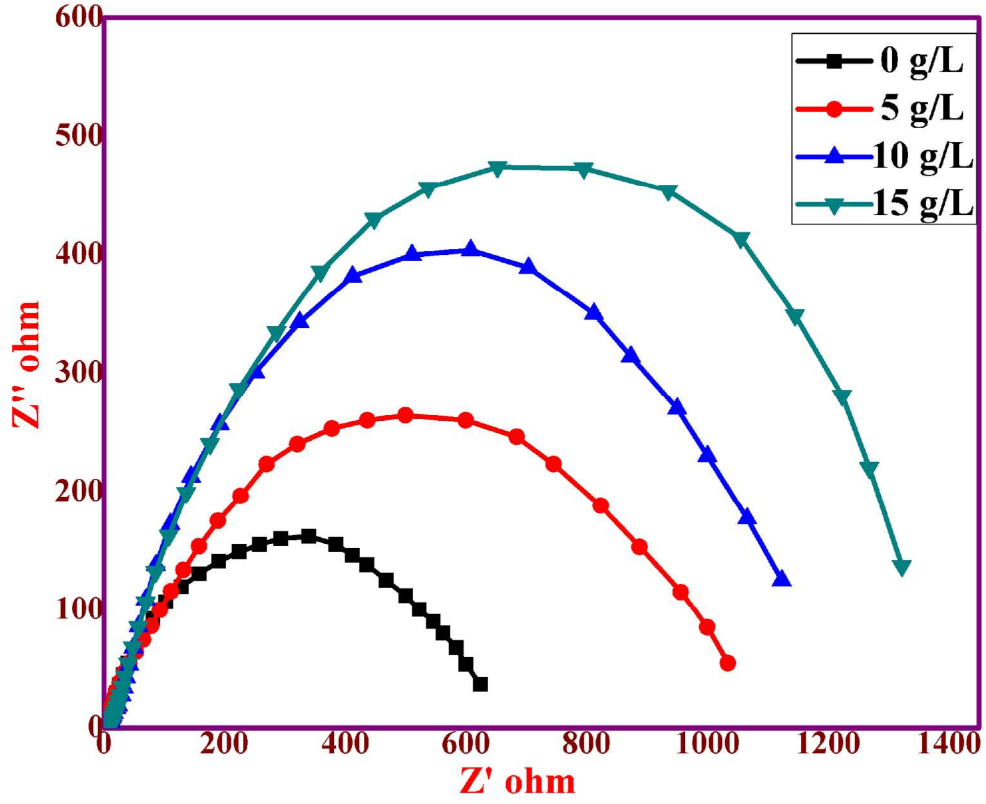

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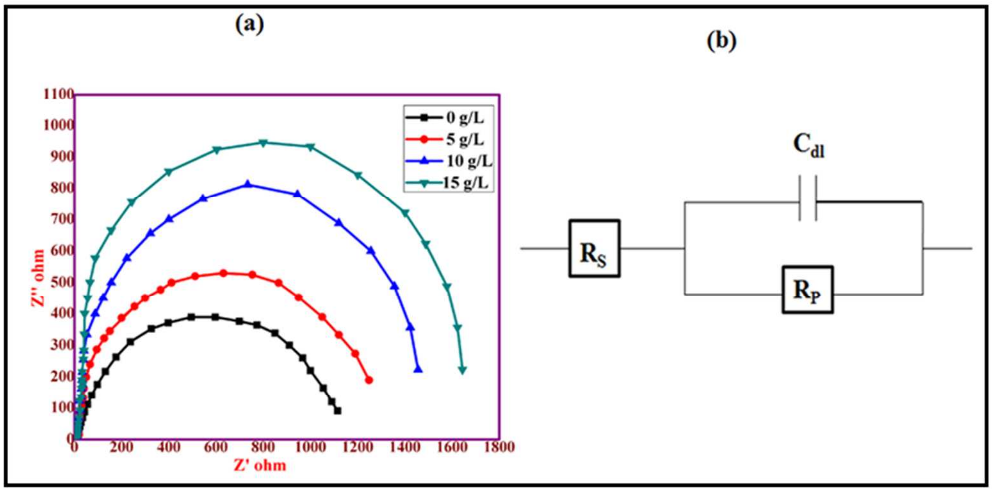

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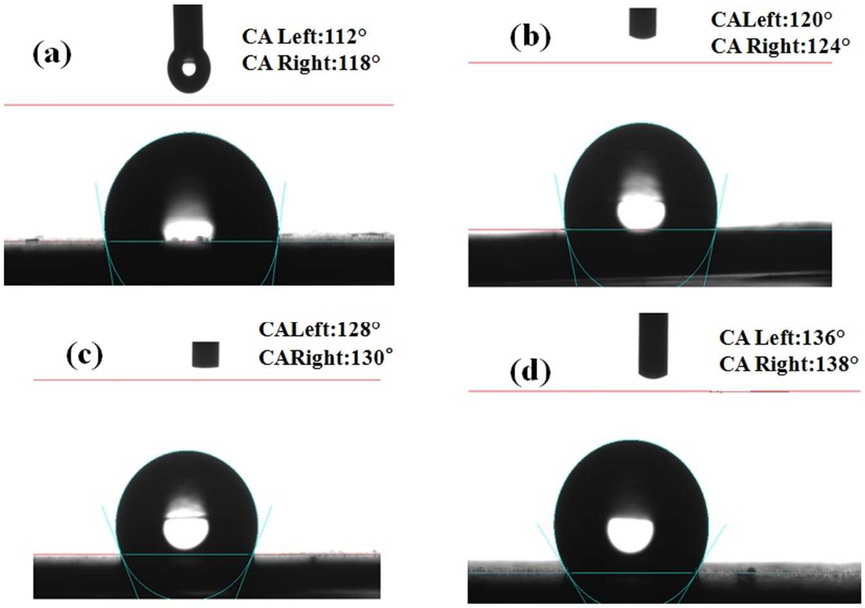

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