



## Nanocomposite Coatings in Corrosion Protection Applications: (An Overview)

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### ABSTRACT

Corrosion is one of the biggest problems which affects the economy of the country, which occurs as a result of the interaction of the metal with its surroundings. One of the easiest ways to prevent corrosion is coatings of the metals with paint, plastic or wood. Several types of coatings have been adopted by corrosion scientists in the prevention of corrosion that are mainly based on electrochemical principles. Fortunately, based on cost and effectiveness, four types of coatings are variably employed by the metal and metallurgy industries. One among the cheapest and effective way to prevent corrosion is to use barrier coatings like plastic, powder and paint. Hence, nanocomposite coatings by electrochemical deposition offers an excellent, scratch and corrosion resistance on the metal surface. These coatings may be used to restoration of the components instead of interchanging them, resulting in reduced maintenance costs and disturbance. Significant improvements in the corrosion protection of steel have been reported by using metal-metal matrix, metal-metal oxide matrix, metal-polymer matrix, and ceramic-metal matrix nanocomposite. This review presents an overview of works related to nanocomposite coatings and to re-evaluate the literature for the future research in the field that still lacks validation.

**Keywords:** Corrosion protection, Coatings, Nanocomposites, Electrochemical deposition.

### INTRODUCTION

Corrosion is the process of deterioration or destruction of metals or materials when it comes in contact with the corrosive medium like acids,

alkalis and compressed gases. Generally, there are two strategies adopted to prevent/control corrosion. Corrosion prevention compounds are the substances added directly into the corrosive medium to suppress the corrosion happening in the



metals. For the past two decades various substances like organic compounds containing heteroatoms, inorganic compounds, polymeric compounds, natural polysaccharides, natural product extracts were attempted to inhibit the corrosion process. These corrosion prevention compounds suppresses corrosion in a significant way but it is temporary and post-production treatment which is not effective over many high-performance coating systems. Hence corrosion prevention and control is needed to design any system of metals to reduce corrosion, repairs and its maintenance especially for the exceptional lifetime of the materials. The process of application of nanocomposites as nanocoatings onto the metal surface is an often-effective way of protecting the substrate from the corrosion.

### Nanocomposites

Nanocomposites are the heterogeneous multiphase solid material where one of the phases has nanoscale structures like nanorods, nanospheres, nanotubes, or nanoflower<sup>1</sup>. It is prepared by incorporating one matrix into other by various methods like in-situ polymerization, melt mixing, solution mixing, precipitation, sol-gel process and electrospinning. When two different materials with different constituents are assorted up, it results in a new material with its own characteristic significant properties which are superior to the individual materials<sup>1-3</sup>. Hence nanocomposites are found to possess excellent unique characteristics like stiffness and strength, low coefficient of expansion, simple repair of damaged structures, and resistance against fatigue, wear resistance and corrosion prevention.

### Nanocomposite coatings

Nanocomposite coatings are new generation coatings designed to offer smart and inexpensive functional surface coatings with superior properties for corrosion resistance, antimicrobial, antifogging, and adhesive applications<sup>4</sup>. On comparing with conventional coatings, nanocomposite coatings are always superior because of its enhanced morphology with nanoscale phase separated domains<sup>5</sup>. In general there are 4 main groups of nanocomposite coating as follows;

- (i) Organic/inorganic nanocomposite coatings (O/I nanocomposite coatings).

- (ii) Organic/organic nanocomposite coatings (O/O nanocomposite coatings).
- (iii) Inorganic/organic nanocomposite coatings (I/O nanocomposite coatings).
- (iv) Inorganic/inorganic nanocomposite coatings (I/I nanocomposite coatings).

### Organic Matrix

In the case of organic matrix, mostly polymers like epoxy resin<sup>6</sup>, polyurethane<sup>7</sup>, polyamide<sup>8</sup>, polyacrylate<sup>9</sup>, PEG<sup>10</sup>, PVDF<sup>11</sup>, PVA<sup>12</sup>, polyester<sup>13</sup>, polycarbonate<sup>14</sup> etc are variably employed. Organic matrix containing natural polymers like starch, gluten, chitosan (CS), and vegetable oils also been reported<sup>15</sup>. Pine needles, a natural fibers were also used in the making of nanocomposite coats<sup>16</sup>.

### Inorganic matrix

In most of the extensive studies researchers used the inorganic matrix in the nanophase range and the nanoparticles like metal carbides (WC-Co)<sup>17</sup>, metal oxides (SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>)<sup>18</sup>, nitrites<sup>19</sup>, clay<sup>20</sup>, CNT<sup>21</sup> were used as inorganic nanofillers.

### Coating methodologies

The nanocomposite coatings could be done by several methods and they are chemical vapor deposition (CVD)<sup>22,23</sup>, powder metallurgy<sup>24</sup>, physical vapor deposition (PVD)<sup>25,26</sup>, thermal plasma spray<sup>27</sup>, sol-gel<sup>28,29</sup>, in-situ polymerization<sup>30</sup>, electroless deposition method<sup>31,32</sup>, electrodeposition<sup>33-35</sup>, solution dispersion<sup>36</sup>, spin coating methods<sup>37,38</sup>. Hence depending on the application, different polymeric, metallic, ceramic, clay or composite functional coating can be adopted by any one of the coating methodologies<sup>39</sup>.

This paper mainly focuses on the how wide variety of nanocomposite materials are applied as corrosion prevention compounds by coating methodologies.

### Nanocomposite coatings as corrosion prevention methods

Composites in which one phase is a metal and second phase would be an either polymer, metal, ceramic or another metal is said to be metal matrix composites.

Metal-metal matrix coatings (MMC) containing metals, influences the corrosion rate on various forms of corrosion like galvanic, pitting, stress corrosion, corrosion fatigue, and tribo corrosion<sup>40</sup>. The MMC coatings can be achieved by stir casting, powder metallurgy, CVD, and diffusion bonding.

Biljana Bobic and his team<sup>41</sup> investigated the corrosion behavior of aluminium MMCs reinforced with boron, SiC, Al<sub>2</sub>O<sub>3</sub>, graphite fibers or particles and mica particles. The incorporation of boron on aluminum was fabricated by diffusing the boron microfilaments with the aluminum foils. It was reported that boron/aluminium composites experienced significantly less corrosion rate than the unreinforced aluminium alloy. Also the corrosion rate of B/Al MMCs increases with increase in the concentration of Boron microfilaments. Hence while diffusion bonding, imperfect bonding or extra microfilament affects the surface of the metal results in improper coating which affects the corrosion protection efficiency. In addition, most of the commercial work on industries involved in aluminum uses metal matrix composites as corrosion protection compounds in order to achieve higher corrosion resistance.

Metal matrix composite coatings of cupronickel embedded with nanoplatelets were employed to improve the corrosion resistance of stainless steel in sea water<sup>41</sup>. In this study, exfoliated montmorillonite (Mt) nanoplatelets were incorporated into Cu-Ni alloy on stainless steel by electrodeposition improved corrosion resistance as well mechanical properties. Addition of equal concentrations of Mt nano plates and Cu-Ni matrix produced the best inhibition efficiency and stabilized the corrosion potential for the duration of 30 days immersion in sea water. To determine the reduction potential cyclic voltammetry was done. As Mt nanoplatelets are non electroactive particles, they do not affect the electrode potentials but however, it helped to shift the onset of hydrogen evolution to the more positive potentials. Hence it was concluded that addition of Mt nanoplatelets in the electroplating solution decreases the corrosion rate to a higher extent. Also in the immersion study, authors found that OCP of pure Cu-Ni and various concentrations of Mt (0.15%) added Cu-Ni were shifted after three and seventeen days, respectively. Fig. 1 shows the OCP of Cu-Ni-0.15% Mt stayed stable over the

extended period of 30 days compared to the other coatings. The results of the study clearly revealed that Mt Nano platelets forms a barrier protection for Cu-Ni coated over the stainless steel and increased the corrosion resistance.

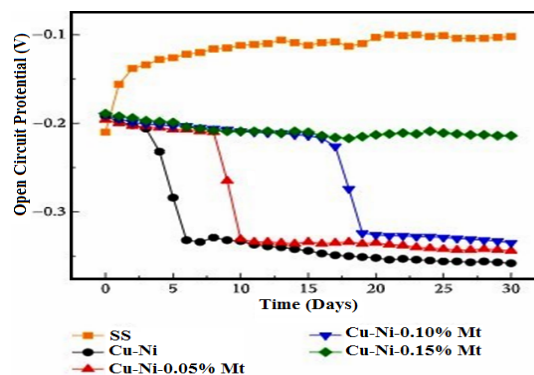


Fig. 1. Plot of immersion test for the Cu-Ni, Cu-Ni-Mt nanocomposites measured By OCP vs Time<sup>40</sup>

Graphene metal matrix composite coatings are extensively applied in numerous areas such as automobile industries, ship building industries, metallurgical industries etc. because these composites provide greater properties such as smooth surface, improved corrosion performance and better solderability<sup>42</sup>. Graphene based ZnNi nanocomposite coatings were performed through electrodeposition method and its corrosion behavior was studied<sup>43</sup>. It was reported that the coatings results in excellent corrosion resistance and higher oxidation resistance. Also it with increase in deposition frequency, the number of nanoparticles absorbed from the coating layer to substrate increases. And this enhances the coating performance and thus decreasing the metal-solution diffusion.

Polyaniline is one of the most excellent conjugated polymer, showed excellent corrosion inhibition properties when reinforced with carbon nanotubes, montmorillonite, graphite and some inorganic nanoparticles<sup>44</sup>. The corrosion protection efficiency of PANI-Nano diamond coatings was explored using electrochemical studies in 3.5% NaCl solution on mild steel<sup>45</sup>. The nanocomposite coatings were done by spray method and it was found that the corrosion protection efficiency was sustained with 90% even upto 3 days.

Several researchers used nano clay coatings to protect mild steel from corrosion as they are impermeable to water and corrosive ions. But

these clays when modified with nanofiller/matrix it shows excellent enhanced anti-corrosion behavior. The nanoclay structure modified with polyester amide hyperbranched polymer showed decreased water permeation and enhanced corrosion protection<sup>45</sup>. The polyesteramide adsorbed onto the nanoclay structures and made it to hydrophobic in nature on the metal surface, thus showed excellent corrosion inhibition property than the pure clay.

Radhakrishnan *et al.*,<sup>46</sup> investigated the corrosion inhibition properties of Polyvinyl butyrl/PANI-TiO<sub>2</sub> nanocomposite coatings on steel plates in saline solution. The PANI-TiO<sub>2</sub> was prepared using in-situ polymerization. It was reported that pure PVB coated plate got degraded and rusted completely, while PVB/PANI-TiO<sub>2</sub> coated steel plates were maintained its structure. Only after 30 h of exposure in saline solution, the corrosion rate started increasing which shows the nanocomposite coatings were sustained even under drastic conditions and this was mainly attributed to large nanoparticle surface area and increased diffusion barrier.

Titanium nanotubes reinforced with epoxy matrix loaded with dodecylamine (DOC) were synthesized and tested for its anti-corrosion behavior on carbon steel by electrochemical impedance spectroscopy<sup>47</sup>. The nanocomposite coated samples were dipped in 3.5% NaCl at pH 2 and 5 for 12 days of immersion. It was found that, for the first four days of immersion, the charge transfer resistance values obtained were higher which shows the nanocomposite coatings on the metal able to protect it against the corrosive behavior. After four days of immersion, it started losing its ability which decreased the R<sub>ct</sub> value. Interestingly, in later days it was found that there was again increase in R<sub>ct</sub> values attributed to the release of DOC nanoparticles which was again forming a protective film, hence inhibiting the corrosion process.

Many researchers widely employed nickel as metal matrix for preparing nanocomposite coatings on various metallic surfaces due to its high corrosion resistance and its micro hardness. Incorporation of graphene particles into nickel matrix provide excellent structural and chemical properties<sup>42</sup>. Electro-codeposition is the commonly used method for the coatings of Ni-G on the metallic surfaces because of its low processing cost,

extraordinary deposition rates with homogeneity<sup>48</sup>. Corrosion resistance of electro-codeposited Ni-G coated plates in 0.5 M NaCl was investigated by voltammetry method<sup>49</sup>. Authors reported that Ni-G coated plates were pronounced significantly with lower corrosion rates than the pure Ni coated plates. They concluded with the statement that the mixing of organic compounds resulted in compressive stress in the layers of coating, which also induces the anti-corrosion behavior.

Yabuki *et al.*,<sup>50</sup> investigated the corrosion protection of aluminium 5083 alloy with vinylester polymer-TiO<sub>2</sub> coatings. They stated that the coated nanocomposite on the alloys acted as a best protective layer. Even in the case of film damage, one of the chemical precursors of vinylester, Bisphenol A was released and acted as barrier coating in the cracks and thus prevents the alloy for dissolution. A schematic representation of Vinylester polymer-TiO<sub>2</sub> is shown in Figure 2.

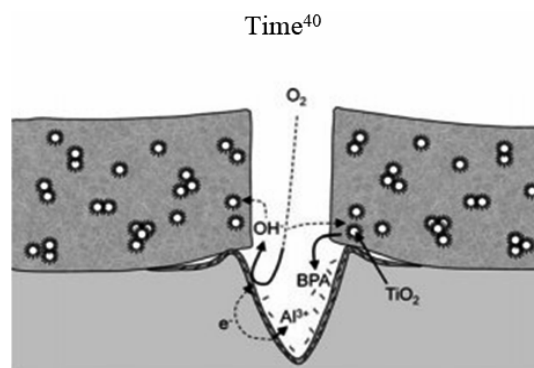


Fig. 2. Schematic representation of self-healing effect of Vinylester-TiO<sub>2</sub> nanocomposite coatings<sup>50</sup>

Poly (methacrylic acid)/silver nanoparticles composite (PMAA/AgNPs) were prepared by in-situ polymerization and employed as corrosion inhibitor in H<sub>2</sub>SO<sub>4</sub> medium on aluminium<sup>51</sup>. The potentiodynamic studies revealed that the presence of inhibitor has slight influence on the cathodic and anodic reactions. It behaved like mixed-type inhibitor. The impedance studies also revealed that the increase in capacitive loop was a function of concentration of the composite which forms protective layer on the aluminium surface.

Few researchers reported polymer/silica nanocomposite coatings for the corrosion resistance of aluminium alloy. Silica nanoparticles were incorporated into acrylic based polymer using

in-situ hydrolysis and coated over the surface of aluminium. It was reported that corrosion resistance was increased due to silica nanoparticles and exceptional anti-corrosion protection was achieved<sup>52</sup>.

The corrosion-resistance hydrophobic coatings of polystyrene-graphene oxide nanocomposites on copper substrate was investigated.<sup>53</sup> The coatings were done by electrophoretic deposition. The authors reported that polystyrene-graphene oxide nanocomposites coatings can be utilized to achieve an efficient high performance anti-corrosion nanocomposite. Poly(vinylidene fluoride) (PVDF) and carbon black nanocomposite was fabricated and tested for its anti-corrosive behavior in 0.5 M H<sub>2</sub>SO<sub>4</sub> on mild steel by electrochemical measurements<sup>54</sup>. They reported that the composite exhibits corrosion resistance upto 5% wt nanofiller concentration.

## CONCLUSION

With a rapid development in the field of nanotechnology, today nanocomposite coatings become excellent, cheaper, smart and more efficient. The nanocomposite coatings are expected to provide wide varied applications in various fields specifically in anticorrosion barrier coatings, self-repair coatings, self-scratch repair coatings.

We have reviewed the recent developments in corrosion protection of metals by nanocomposite coatings. Nanocomposite coatings paves a way for the corrosion prevention with higher efficiency. Even though the other corrosion prevention methods offers an excellent inhibiting property but it is limited to time, temperature and other factors. But the film of nanocomposite coated metals when undergoes damages due to severe corrosive environment, the nanofillers/nanomatrix present in the nanocomposite releases active materials and thus heals the damaged surface and mitigates the corrosion process. As the present world depends mainly on sustainable energy, the smart or easy-to-clean coatings provided by nanocomposites will be a long lasting and highly efficient Future works in nanocomposite coatings will focus on the development of high-yield fabrication with eco-friendly composites.

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## Conflict of interest

The author declare that we have no conflict of interest.

## REFERENCES

- Phuong Nguyen-Tri.; Tuan Anh Nguyen.; Pascal Carriere.; Cuong Ngo Xuan. *Int J Corros.*, **2018**, *2018*, 1-20.
- Xiaofeng Liu.; Markus Antonietti. *Carbon.*, **2014**, *69*, 460-466.
- Weon Ho Shin.; Hyung Mo Jeong.; Byung Gon Kim.; Jeung Ku Kang.; Jang Wook Choi., *Nano Lett.*, **2012**, *12*(5), 2283 -2288.
- Handbook of Nanoceramic and Nano composite Coatings and Materials, Nedal Y. Abu-Thabit and Abdel Salam Hamdy Makhlof., **2015**, 515-549.
- Wang, C.; Xiao, Y.; Xing, H.; Xu, S.; Zhang, *J. Mater Chem A.*, **2015**, *3*, 6742-6746.
- Yeh, J.; Huang, H.; Chen, C., Su, W.; Yu, C. *Surf Coat Technol.*, **2006**, *200*, 2753-2763.
- Sung, LP.; Comer, J. *J Coat Technol Res.*, **2008**, *5*, 419-430.
- Behler, KD.; Stravato, A.; Mochalin, V.; Korneva, G.; Yushin, G.; Gogotsi, Y. *ACS Nano.*, **2009**, *3*, 363-369.
- Pourhashem, S.; Vaezi, MR.; Rashidi, A.; Bagherzadeh, A. *Corros Sci.*, **2017**, *115*, 78-92.
- Wang, W.Y.; Shi, J.Y.; Wang, J.L.; Yan-Ling Li.; Ning-Ning Gao.; Zheng-Xin Liu.; and Wei-Tao Lian. *RSC Advances.*, **2015**, *103*, 84746.
- Toor, A.; So, H.; Pisano, AP. *ACS Appl Mater and Inter.*, **2017**, *97*, 6369-6375.
- Habouti, S.; Kunstmann-Olsen, C.; Hoyland, JD.; Rubahn, HG., Es-Souni. *Appl Phys A: Mater Sci & Process.*, **2014**, *115*, 645-649.
- Golgoon, A.; Aliofkhaezraei, M.; Toorani, M.; Moradi, M.; Rouhaghdam, AS. *Procedia Mater Sci.*, **2015**, *11*, 536-541.
- Pradhan, B.; Setyowati, K.; Liu, H.; Waldeck, D.; *Chen, J. Nano Letters.*, **2008**, *1142*, 8-13.
- Handbook of Composites from Renewable Materials, Prasanta Baishya and Moon Mandal., **2017**, 433-459.

16. Singha, AS.; Thakur, VK. *J. Reinf. Plast Compos.*, **2010**, *29*, 700-709.
17. Li, C.J.; Yang, G.J.; Gao, P.H.; Ma, J.; Wang, Y.Y.; Li, C.X. *J Therm Spray Technol.*, **2007**, *16*, 100-107.
18. Shi, X.; Nguyen, T.A.; Suo, Z.; Liu, Y.; Avci, R. *Surf Coat Technol.*, **2009**, *204*, 237-245.
19. Luo, X.T.; Li, C.J. *Materials and Design.*, **2015**, *60*, 249.
20. Golgoon, A.; Aliofkhaezei, M.; Toorani, M.; Moradi, M.; and Rouhaghdam, A.S. *Procedia Materials Science.*, **2015**, *11*, 536-541.
21. Cho, S.; Takagi, K.; Kwon, H.; Seo D.; Ogawa, K.; Kikuchi, K.; Kawasaki, A. *Surf Coat Technol.*, **2012**, *206*, 3488-3494.
22. Hou, X.; Choy, K.L.; Brun, N.; Serin, V. *Journal of Nanomaterials.*, **2013**, *2013*, 1-8.
23. Alexandrov, S.E.; Kirill, S.; Tyurikov, Kirilenko, D.A.; Redkov, A.V.; Andrey A. Lipovskii. *Adv. Mater. Inter.*, **2017**, *4*, 170.
24. Sergeev, V.; Psakhi, S.; Chubik, P.; A.; Solntsev, V.; Khristenko, YU. *Vacuum.*, **2017**, *143*, 454-457.
25. Ma, Q.; Li, L.; Xu, Y.; Ma, X.; Xu, Y.; Liu, H. *Int J Refract Metals and Hard Mater.*, **2016**, *59*, 114-120.
26. Kumar, C.H.; Nair, P.K.; Ramamoorthy, B. *Int J Adv Manuf Technol.*, **2008**, *38*, 622-629.
27. Ali, O.; Ahmed, R.; Faisal N.H. *Tribo Lett.*, **2017**, *65*, 1-27.
28. Amiri, S.; Rahimi, A. *Iran Polym J.*, **2016**, *25*, 559-577.
29. Handbook of Sol-gel Science and Technology, M. Guglielmi, A. Martucci, Sol-gel Nanocomposites, Springer, Cham., **2016**.
30. In book: Industrial Applications for Intelligent Polymers and Coatings, Mehdi Honarvar Nazari, *Xianming Shi.*, **2016**, 373-398.
31. Bu, A.; Wang, J.; Zhang, J.; Jie Bai.; Quansheng Liu.; Guojun Ji. *J Sol-Gel Sci Technol.*, **2017**, *81*, 633-638.
32. Sharma, A.; Singh, A.K. *J Mater Engg Perform.*, **2013**, *22*, 176-183.
33. Toledano, R.; Mandler, D. *Chem Mater.*, **2010**, *22*, 3943-3951.
34. Zhitomirsky, I. *J Mater Sci.*, **2006**, *41*, 8186-8195.
35. Arunsunai Kumar, K.; Paruthimal Kalaigan, G.; Muralidharan, V.S. *Ceramics International.*, **2013**, *39*, 2827-2834.
36. Introzzi, L.; Blomfeldt, T.O.J.; Trabattoni, S.; Tavazzi, S.; Santo, N.; Schiraldi, A.; Piergiovanni, L.; and Farris, S. *Langmuir.*, **2012**, *28*, 11206-11214.
37. Marialaura Clausi, M.; Gabriella Santonicola.; Susanna Laurenzi. *Composites Part A: App Sci Manufact.*, **2016**, *88*, 86-97.
38. Sim, L.C.; Voo Tin Vui Richard.; Mariatti Jaafar. *Journal of Plastic Film and Sheeting.*, **2011**, *27*, 331-348.
39. Hari kumar, S.; Karthikeyan, S. *Int J Corros Scale Inhib.*, **2020**, *19*, 830-841.
40. Biljana Bobic.; Slobodan Mitrovic.; Miroslav Babic.; Ilija Bobic. *Tribol in Industry.*, **2010**, *32*, 3-11.
41. Thurber, C.R.; Ahmad, Y.H.; Calhoun, M.C.; Al-Shenawa, Nandika, A.; Souza, Adel, D.; Mohamed, M.A.; Teresa, D. *Int J Corros.*, **2018**, *2018*, 1-11 (2018).
42. Ahmed Khalid Hussain.; Uday, M.; Basheer Al NAIB. *J Metals Mater Minerals.*, **2019**, *29*, 1-9.
43. Rahmani, H.; Aliofkhaezei, M.; Karimzadeh, A. *Surf Rev Lett.*, **2017**, *24*, 1750.
44. Hu, Z.A.; Xie, Y.L.; Wang, YX.; Mo, LP.; Yang, Y.Y.; Zhang, ZY. *Mater Chem Phys.*, **2009**, *114*, 990-995.
45. Sari, M.G.; Ramezanzadeh, B.; Shahbazi, M.; Pakdel, A.S. *Corros Sci.*, **2015**, *92*, 162-172.
46. Radhakrishnan, S.; Siju, C.R.; Mahanta, D.; Patil, S.; Madras, G. *Electrochim Acta.*, **2009**, *54*, 1249-1254.
47. Muddasir Nawaz.; Noor Yusuf.; Sehrish Habib.; Rana Abdul Shakoor.; Fareeha Ubaid.; Zubair Ahmad.; Ramazan Kahraman.; Said Mansour.; and Wei Gao. *Polymers.*, **2019**, *11*, 852-872.
48. Kerr, C.; Barker, D.; Walsh, F.; *Archer, J. Transactions of the IMF.*, **2000**, *78*, 171-190.
49. Szeptycka, B.; Gajewska-Midzialek, A.; Babul, T. *J Mater Engg Perform.*, **2016**, *25*, 3134-3138.
50. Yabuki, A.; Okumura, K. *Corros Sci.*, **2012**, *59*, 258-262.
51. Solomon, M.M.; Umoren, S.A. *J Adh Sci Technol.*, **2015**, *29*, 2311-2333.
52. Khelifa, F.; Druart, M.E.; Habibi, Y.; Freddy Benard.; Philippe Leclere.; Marjorie Olivier.; Philippe Dubois. *Prog Org Coat.*, **2013**, *76*, 900-911.
53. Singh, B.P.; Jena, B.K.; Bhattacharjee, S.; Laxmidhar Besra. *Surface Coat Technol.*, **2013**, *232*, 475-481.
54. Antunes, R.A.; De Oliveira, G.; Ett, G. *Int J Hydrogen Ener.*, **2011**, *36*, 7162-7173.