Journal of Sustainability Science and Management Special Issue No. 3 2017: Improving the Health of Setiu Wetlands Ecosystems and Productivity of Crustacean Resources for Livelihood Enhancement: 1-6

ISSN: 1823-8556

CYTOXICITY OF TiO_2 NANOPARTICLES AND EFFECT OF INCORPORATION OF NANOTiO_2-PEDOT:PSS COMPOSITE IN PVAc COATING ON ANTICORROSIVE PERFORMANCE

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Abstract: Titanium dioxide, TiO_2 has commonly been used as additives in anticorrosion coating. However, coating production involving nano-sized metal oxide has been a concern since it can potentially be transmitted into the human body through inhalation or contact with skin. Therefore, the cytotoxicity of the TiO_2 nanoparticles was studied via assay of fibroblast cells viability. The anticorrosive performance of nanotitanium dioxide-poly (3, 4-ethylenedioxythiophene) polystyrene sulfonate (nanoTiO_2-PEDOT:PSS) composite as additives in PVAc matrix was also studied via potentiodynamic polarization (PP) by varying the weight percentage (wt.%) of additives from 1-5 wt.%. From this work, after 24 and 48 hours of exposure, TiO_2 induced only 40% cell death (40% inhibition), indicating low cytotoxicity. For anticorrosive performance, 2 wt.% of nanoTiO_2-PEDOT:PSS composite content displayed the best corrosion protection as I_{corr} , E_{corr} and corrosion rate is the lowest with 0.067 μA/cm^2;0.0751 V; and 0.0008 mm/yr; respectively. Thus, TiO_2 is safe to human cell and its incorporation with PEDOT:PSS is able to protect metals from corrosion.

Keywords: Anticorrosion coating, PEDOT:PSS, potentiodynamic, PVAc, TiO_2 nanoparticles.

Introduction

The ubiquitous use of nanoparticles in various industries these recent years raises great concerns over the adverse effects it poses to human health and the environment, since industrial workers are at risk of exposure to TiO_2 nanoparticles through inhalation or skin contact (Yah *et al.,* 2012). Besides, there is also the possibility that it might leach into the environment, causing damage to the ecosystem.

PVAc as a polymer is relatively inferior in terms of mechanical strength and water resistance. However, several studies have shown that this polymer latex can be enhanced with the addition of nanoparticles (NP). Wen *et al.* (2008) reported that the properties of PVAc can be stabilized with the addition of silicon oxide (SiO_2) nanoparticles, with which it formed long, stable raspberry-like composite spheres. This improved the stability of PVAc and enhanced its water resistant properties. The addition of TiO_2 nanoparticles in the PVAc based formulation will thus form coating films with good mechanical and corrosion protection properties. Patil *et al.* (2006) reported that a PVAc coating with ZnO nanoparticles-polyaniline (PANI) composite lasted longer in saline waters compared to a sole coating of PVAc, showing that the mechanical properties of PVAc can be enhanced with the incorporation of nanoparticles and its composite derivatives. The development of anticorrosion coatings has brought to light the use of nanoparticles-conducting polymer composite as effective anticorrosive additives (Armelin *et al.,*

2009). Apart from PANI, this is a widely used conducting polymer, PEDOT:PSS has shown good anticorrosion properties (Hou *et al.*, 2013). Even so, it is rarely used in coatings, and more often applied in solar cells and electronic devices (Inzelt, 2011).

Thus, this study combined TiO_2 nanoparticles with PEDOT:PSS as composite to further explore its potential in anticorrosion coatings. The cytotoxicity of the TiO_2 nanoparticles was studied in order to establish a coating that is not only feasible, but also environmental friendly. The effect of addition of nanoTiO_2-PEDOT:PSS composite in PVAc based coatings on the corrosion protection performance was also analyzed to ensure the sustainability of metal structures.

Materials and Methods

Materials

Stainless steel grade 316L was obtained from CG Tradeware. The alloy composition is laid out in Table 1.

Table 1: Chemical composition (%) of stainless steel 316L (SS 316L).

Element	Stainless Steel 316L (%)
C	0.03max.
Mn	2.00max.
P	0.045max.
S	0.03max.
Si	0.75max.
Cr	16.00-18.00
Ni	10.00-14.00
Mo	2.00-3.00
N	0.10max.
Fe	Balance

The materials used in coating preparation, PEDOT: PSS (2.8 wt.% dispersion in H_2O), TiO_2 nanoparticles (<25 nm), dimethyl sulfoxide (DMSO), and PVAc were acquired from Sigma Aldrich. For cytotoxicity analysis, the fibroblast cells and AlamarBlue™ were acquired from ATCC while 96 well plates were from Nunc.

Cytotoxity assay of TiO_2 nanoparticles using AlamarBlue™

Cytotoxicity assay was done to determine the cell growth or cell viability after treatment with different concentrations of TiO_2 nanoparticles sample (0, 15.63, 31.3, 62.5, 125 and 250 µg/mL). The control sample is the untreated cells, with concentration 0 µg/mL TiO_2 nanoparticles. For this study, the cytotoxicity assay was performed using AlamarBlue™ reagent. After each treatment, 10 µL of AlamarBlue™ was added directly to cells in a 96 well plate, then incubated 1 to 4 h at 37 °C according to the method established by (Al-Nasiry *et al.,* 2007). After incubation, the plates were measured at a wavelength of 570 nm for excitation and 585 nm for emission using fluorescence microplate reader (Thermoscientific, USA). The percentages of cell viability were analyzed according to Hamid *et al.* (2004) as in Equation 1;

$$\textit{Percentage of cell viability (\%)} = \frac{\textit{(Absorbance of treated cells)}}{\textit{(Absorbance of untreated cells)}} \times 100\%$$

Equation 1

Coating formulation

The matrix, PVAc was dissolved in DMSO at ratio of 1:7 with constant stirring for 6 hours. Meanwhile, the nanocomposite was prepared by mixing TiO_2 and PEDOT: PSS at a ratio of 1:49 and stirred using a magnetic stirrer for an hour. Then, the nanocomposite was added into the matrix at varying weight percentage, from 1 wt.% to 5 wt.%. The whole mixture was further stirred for 4 hours at 1200 rpm followed by sonication for 30 minutes to ensure a uniform distribution of TiO_2 NP. The coatings are designated as PVAC1, PVAC2, PVAC3, PVAC4 and PVAC5, where PVAC indicates the matrix, while the numbers 1-5 indicate the weight percentage of the nanocomposite dispersed in the coating.

Application method

The substrates were cut into 25 mm x 25 mm x 1.5 mm and were cleaned according to ASTM G1-2004. The substrates were coated by dip coating technique and then dried in an air circulating oven at 110 °C for 24 hours.

Evaluation of anticorrosive properties

The corrosion protection of the coated substrates was studied using potentiodynamic polarization (PP). The electrochemical behavior test was conducted using a three-electrode cell; the working electrode is the coated substrates with an exposed area of 1 cm^2, the reference electrode was a saturated Ag/AgCl electrode, and the counter electrode was glassy carbon electrode. The test was performed in 3.5% NaCl solution at a frequency range of 10 kHz to 0.1 Hz at room temperature, and analyzed using NOVA software. The anodic and cathodic curves of the generated Tafel plot were extrapolated, and the intersection point of these curves show the corrosion current density, I_{corr}, corrosion potential, $E_{corr,}$ and corrosion rate values. These parameters are measured to represent the anticorrosion properties of the coating.

Results and Discussion

Percentage of cell viability after treatment with TiO_2 nanoparticles

Figure 1 shows the comparison of cell viability percentage after 24 and 48 hours treatment with different concentrations of TiO_2nanoparticles (0, 15.63, 31.3, 62.5, 125 and 250 µg/mL), where the sample with concentration of 0 µg/mL TiO_2 nanoparticlesis the control sample.

The result shows that after 24 hours incubation, TiO_2 nanoparticles induced the highest cell death (20% inhibition) at concentration 62.5 µg/mL. The 48 hours treatment showed a similar trend to 24 hours, with the highest cell death (40% inhibition) also observed at TiO_2 nanoparticles concentration of 62.5 µg/mL.

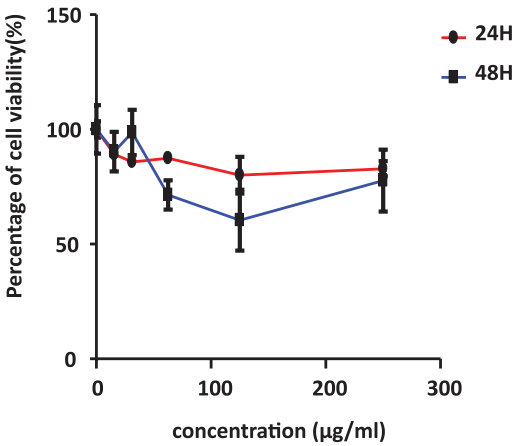

Figure 1: Comparison between percentage of cell viability after 24 and 48 h treatment with different concentrations of TiO_2 nanoparticles

A particular substance is said to be toxic only if it induced cell death of more than 50% inhibition (IC50) (Dechsakulthom *et al.,* 2007). Hence, the acquired results suggest that TiO_2 nanoparticles do not have a toxicity effect on fibroblast cells at concentration of ≤250 µg/mL. The low toxicity effect of TiO_2 nanoparticles may due to its insolubility (Pujalté *et al.* 2011). The effects of nanoparticles solubility was determined in a study by Brunner *et al.* (2006) who demonstrated that insoluble nanoparticles such as TiO_2 and CeO_2 may promote lower toxicity effect than soluble NPs such as ZnO and Fe_2O_3. Furthermore, as discussed by Fabian *et al.* (2008), even though TiO_2 nanoparticles was found to accumulate in the internal organs, the presence of the nanoparticles in the body does not adversely affect health or cause inflammatory response.

This is due to the formation of a passivation film of Cr_2O_3 on the surface of the film, which increases its surface protential (Ramya *et al.,* 2010). Nevertheless, the I_{corr} and corrosion rate values of PVAC1 are better than the bare SS316L, which proves that the presence of PVAc coating on the stainless steel impart higher corrosion protection to the

Evaluation of corrosion resistant properties

The parameters generated from Tafel plotsare shown in Table 2 whereas the Tafel plots are presented in Figure 2.

Table 2: I_{corr}, E_{corr}, and corrosion rate values of formulated coatings.

Samples	Corrosion current, I_{corr} (μA/cm^2)	Corrosion potential, E_{corr} (V)	Corrosion rate (mm/yr)
Blank (SS 316L)	60.60	-0.2603	0.6440
PVAC1	1.120	-0.2945	0.0128
PVAC2	0.067	0.0751	0.0008
PVAC3	0.332	-0.0627	0.0039
PVAC4	0.701	-0.0029	0.0081
PVAC5	0.584	0.0291	0.0068

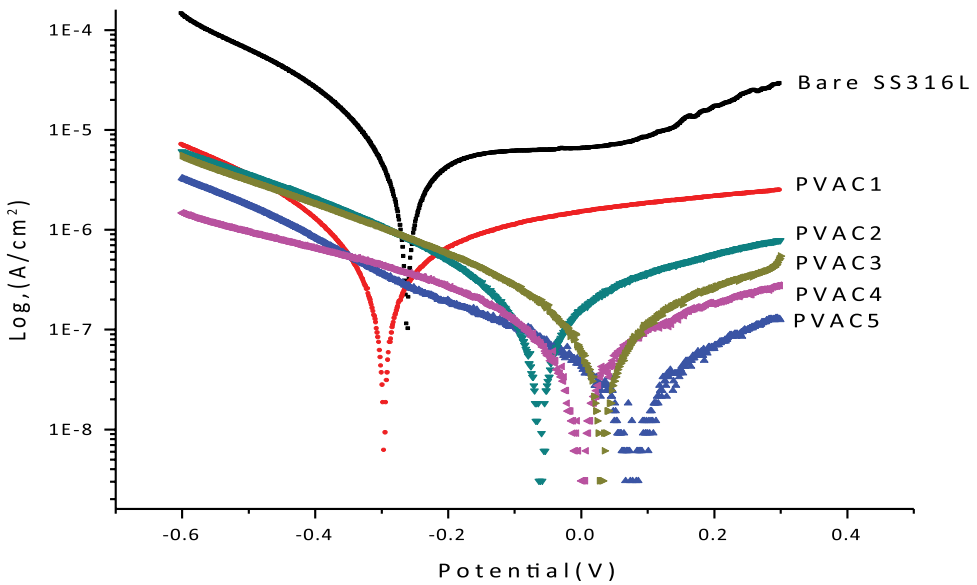

Figure 2: Tafel plots of bare and coated SS 316L.

stainless steel. The results displayed in Table 2 shows that I_{corr} value of PVAC2 is the lowest, at 0.0672 μA/cm^2, which is two whole magnitudes lower than PVAC1 and a magnitude lower than the other coatings. The I_{corr} and corrosion rate values decrease greatly from PVAC1 to PVAC2, showing decrement in corrosion reaction, and start increasing slightly from PVAC3 upward. This suggests that the dispersion of nanoTiO_2-PEDOT:PSS composite in the coating provided efficient physical barrier against permeation of corrosive elements, hence the higher nanocomposite content gives better corrosion protection.

However, the anticorrosion performance starts decreasing as the nanocomposite content increases. This might be due to the weakening of bonds between the matrix polymers due to excessive additive content, causing easier penetration of the electrolyte into the coating, thus promoting

failure of the protective barrier formed by the coating (Castro *et al.,* 2005). The corrosion potential, E_{corr}, indicates electrochemical current activity. A shift of E_{corr} values towards the positive region shows a passivation reaction, which means that the surface of the steel is made less susceptible to corrosion (Ruhi *et al.,* 2015). From the Tafel plot in Figure 2, it is observed that PVAC2 is shifted towards the positive region the most. Hence, it is evident that PVAC2 coating provides the most anodic corrosion protection of the stainless steel. The synergistic effect of the nanoTiO_2-PEDOT:PSS composite also contributes to the corrosion protection by providing a potential barrier at the coating/stainless steel interface. This is explained by Radhakrishnan *et al.* (2009), where TiO_2 is *n*-type semiconductor, while conducting polymer is *p*-type, thus their interaction creates a potential barrier which limits corrosion current flow. Thus it can be said that 2 wt.% is the optimum amount of nanoTiO_2-PEDOT:PSS composite in this coating, where the additive amount is able to provide efficient physical and potential barrier, but not tamper with the mechanical properties of the coating.

Conclusion

In this study, a PVAc based anticorrosion coating was formulated by incorporating different weight percentages (wt.%) of nano-TiO_2-PEDOT:PSS composite into a PVAc matrix. Based on assessments of the data obtained, the coating containing 2 wt.% of nanocomposite displayed the best anticorrosion propertiesas I_{corr}, E_{corr} and corrosion rate values are the lowest at 0.067µA/cm^2; 0.0751 V; and 0.0008 mm/yr; respectively. This is due to the passivation of the steel surface and the potential barrier that resulted from the nanoTiO_2-PEDOT:PSS nanoparticles interaction. The cytotoxicity assessment of TiO_2 nanoparticles showed only 40% cell inhibition, indicating no toxic effect on fibroblast cells.

Acknowledgements

The authors would like to express the highest gratitude to the Ministry of Higher Education Malaysia for funding this research project under NRGS grant (Project No. NRGS/2015/53131/14).

References

Al-Nasiry, S., Geusens, N., Hanssens, M., Luyten, C., & Pijnenborg, R. (2007). The use of Alamar Blue assay for quantitative analysis of viability, migration and invasion of choriocarcinoma cells. *Human reproduction,* 22(5): 1304-1309.

Armelin, E., Meneguzzi, Á., Ferreira, C. A., & Alemán, C. (2009). Polyaniline, polypyrrole and poly (3,4-ethylenedioxythiophene) as additives of organic coatings to prevent corrosion. *Surface and Coatings Technology,* 203(24): 3763-3769.

Brunner, T. J., Wick, P., Manser, P., Spohn, P., Grass, R. N., Limbach, L. K., Bruinink, A., & Stark, W. J. (2006). In vitro cytotoxicity of oxide nanoparticles: comparison to asbestos, silica, and the effect of particle solubility. *Environmental Science and Technology,* 40(14): 4374-4381.

Castro, Y., Ferrari, B., Moreno, R., & Durán, A. (2005). Corrosion behaviour of silica hybrid coatings produced from basic catalysed particulate sols by dipping and EPD. *Surface and Coatings Technology,* 191(2): 228-235.

Dechsakulthorn, F., Hayes, A., Bakand, S., Joeng, L., & Winder, C. (2007). In vitro cytotoxicity assessment of selected nanoparticles using human skin fibroblasts. *AATEX,* 14 (Special Issue): 397-400.

Fabian, E., Landsiedel, R., Ma-Hock, L., Wiench, K., Wohlleben, W., & Van Ravenzwaay, B. (2008). Tissue distribution and toxicity of intravenously administered titanium dioxide nanoparticles in rats. *Archives of Toxicology,* 82(3): 151-157.

Hamid, R., Rotshteyn, Y., Rabadi, L., Parikh, R., & Bullock, P. (2004). Comparison of alamar blue and MTT assays for high through-put screening. *Toxicology in vitro,* 18(5): 703-710.

Hou, J., Zhu, G., Xu, J., & Liu, H. (2013). Anticorrosion Performance of Epoxy Coatings Containing Small Amount of Inherently Conducting PEDOT/PSS on Hull Steel in Seawater. *Journal of Materials Science and Technology,* 29(7): 678-684.

Inzelt, G. (2011). Rise and rise of conducting polymers. *Journal of Solid State Electrochemistry,* 15(7-8): 1711-1718.

Patil, R., & Radhakrishnan, S. (2006). Conducting polymer based hybrid nano-composites for enhanced corrosion protective coatings. *Progress in Organic Coatings,* 57(4): 332-336.

Pujalté, I., Passagne, I., Brouillaud, B., Tréguer, M., Durand, E., Ohayon-Courtès, C., & L'Azou, B. (2011). Cytotoxicity and oxidative stress induced by different metallic nanoparticles on human kidney cells. *Particle and Fibre Toxicology, 8*(1): 10.

Radhakrishnan, S., Siju, C., Mahanta, D., Patil, S., & Madras, G. (2009). Conducting Polyaniline–nano-TiO_2 composites for smart corrosion resistant coatings. *Electrochimica Acta,* 54(4): 1249-1254.

Ramya, S., Anita, T., Shaikh, H., & Dayal, R. (2010). Laser Raman microscopic studies of passive films formed on type 316LN stainless steels during pitting in chloride solution. *Corrosion Science,* 52(6): 2114-2121.

Ruhi, G., Bhandari, H., & Dhawan, S. (2015). Corrosion Resistant Polypyrrole/Flyash Composite Coatings Designed for Mild Steel Substrate. *American Journal of Polymer Science,* 5(1A): 18-27.

Wen, N., Tang, Q., Chen, M., & Wu, L. (2008). Synthesis of PVAc/SiO 2 latices stabilized by silica nanoparticles. *Journal of Colloid and Interface Science,* 320(1): 152-158.

Yah, C. S., Iyuke, S. E., & Simate, G. S. (2012). A review of nanoparticles toxicity and their routes of exposures. *Iranian Journal of Pharmaceutical Sciences,* 8(1): 299-314.