Electrochemical Impedance Spectroscopy Study on Corrosion Protection of Acrylate Nanocomposite on Mild Steel Doped Carbon Nanotubes

M R Mahmud 1,2, M M Akhir 1,2, M S Shamsudin 1,2, A N Afaah 1,2, A Aadila 1,2, N A M Asib 1,2, Salman A H Alrokayan 4, Haseeb A Khan 4, M K Harun 1, M Rusop 2,3 and S Abdullah 1

1Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
2NANO-SciTech Centre, Institute of Science, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
3NANO-ElecTronic Centre, Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
4Research Chair of Targeting and Treatment of Cancer Using Nanoparticles, Department of Biochemistry, College of Science, King Saud University (KSU), Riyadh, Saudi Arabia

E-mail: mrashidmahmud@yahoo.com

Abstract. Acrylate:carbon nanotubes (A:CNTs) nanocomposite thin film was prepared by sol-gel technique. The corrosion coating protection of acrylate:carbon nanotubes (CNTs) nanocomposite thin film has been coated on mild steel characterised by electrochemical impedance spectrometer (EIS) measurement and equivalent circuit model are employed to analyse coating impedance for corrosion protection. In this study, 3.5 w/v % sodium chloride (NaCl) solution was immersed the acrylate:carbon nanotubes nanocomposite thin film. As the results, the surface morphology were found that there formation of carbon nanotubes with good distribution on acrylate-based coating. From EIS measurement, A:CNTs nanocomposite thin film with 0.4 w/v % contain of CNTs was exhibited the highest coating impedance from Nyquist graph after immersed in sodium chloride solution and may provide the excellent corrosion protection. The Bode plots have shown the impedance is high at the beginning from the time at high frequency and slightly decreases with value of frequency become smaller.

1. Introduction
The coatings corrosion protection has been used widely in industries due to possess protection from any defects or corrosion activity [1, 2]. Corrosion occurs in metal due to the surface exposures to the environment changes and moistures such as solution. Polymers anti-corrosion protection have been used to avoid corrosion activity from penetrate to the coated materials. This study using acrylate as polymer materials to coat surface of mild steel [3]. Polymeric materials known as acrylate based coating possess excellent mechanical strength and adhesion for several substrates. Acrylate provides excellent coatings protection for home appliances, aircraft, marine instrument, ships, oil planter and others metal materials avoid from corrosion activity [4-6]. In this research, mild steel substrate was used as coated materials.
for thin films of acrylate. Carbon nanotubes discovered by Sumio Iijima in 1991 which has invented carbon nanotubes (CNTs) using arc-discharge method in powder form [7-11]. CNTs possess versatile nanofillers for blend with polymer-based such as acrylate due to tremendous properties in mechanical, electrical, thermal and structure [12, 13].

Acrylate:carbon nanotubes (A:CNTs) nanocomposite thin film used for coating protection on coated mild steel by provides coating barrier between the metal coated and exposure medium such as sodium chloride solution used in this characterisation. Furthermore, Sol-gel technique was prepared of A:CNTs nanocomposite thin film provide a cost effective and easy way to incorporating the polymers composite and nanomaterials in order to obtain well dispersion and homogeneously distributed [4, 14].

Electrochemical impedance spectrometer (EIS) has used for evaluation corrosion performance on coating metal materials that exposure to the aqueous solution and non-destructive testing for corrosion of the coating protection [15]. In term of organic coatings, possess tremendous and effective protection of metals coated and as corrosion inhibitors to the materials. Furthermore, metals substrate and intermediate layer of coating protection naturally can be determine the protection characteristics of the coated materials. All coating protection influence the response of impedance to the metal coated that extracted by analysis used of EIS spectra. Polymeric materials exposed to the environment changes and given protection to the coated metal but it influence to the polymeric are potentially permeable to corrosion activity such as oxygen, water and ions [16]. Macedo et al. has discussed anomalous impedance variations on the samples coated as a function of time exposure in a sodium chloride solution with approach used the five-electrode system [15, 17]. However, most of the popular method for measured the coating corrosion protection was used electrolyte as an solution to exposure the coated metal by using composition of the sodium chloride (NaCl) around 3.5 w/v % of NaCl [18-20], the results from EIS measurement are typically fluctuated from different samples through the coating defects or pinholes in solution. In this present work, were prepared acrylate:carbon nanotubes nanocomposite thin film by doped with varies amount of weight percentages that increment of 0.2 w/v % of CNTs into acrylate such as 0.2 w/v %, 0.4 w/v %, 0.6 w/v %, 0.8 w/v % and 1.0 w/v % to determine the coating corrosion protection of the A:CNTs nanocomposite thin film.

2. Experimental

The chemicals of sodium chloride (NaCl) powder was used in order to produce 3.5 w/v % of NaCl electrolyte. The contact area of mild steel was then polished with high graded sand paper and cut into small size with 2 cm x 2 cm dimension. In other hand, the carbon nanotubes (CNTs) was synthesised by chemical vapour deposition (CVD) technique. Camphor oil and ferrocene as a precursor and catalyst were used in this research, respectively [7]. CVD were employed with 180 °C for the pre-cursor temperature (first furnace) and 800 °C for the deposition temperature (second furnace) takes around 60 minutes duration for deposition time. The experimental set up of CVD can be found in our previous paper [21-24]. The acrylate:carbon nanotubes (A:CNTs) nanocomposite was prepared by sol-gel technique. The acrylate was dissolved in organic chloroform solvent with ratio of 1:5 (acrylate:chloroform). Then, the CNTs were introduced by 0.2 to 1.0 w/v % with 0.2 w/v % increment in each acrylate solutions. The sonochemistry technique was employed in order to ensure CNTs mix well in acrylate solution by using ultrasonic probe processor (Sonotrode H3UP 400S, Hielscher) with parameter sonication time is 60 minutes. After that, spin-coater with speed around 5000 rpm for deposition time is 60 second for 10 drops were used for A:CNTs nanocomposite deposited on mild steel substrate. Then, the sample have been dried for 10 minutes with 100 °C to remove the residual from substrate.

Characterisation parameter on immersed in NaCl solution by using EIS analysis with initial frequency (50 kHz) and final frequency (0.015 Hz). Samples exposure area to the solution is 2.85 cm² with AC voltage 10 mVrms. EIS measurement were performed by Gambry Instrument for this corrosion behavior and used Gambry Echem Analyst software for corrosion analysis in this study. Hence, field emission scanning electron microscope (FESEM) were observed for surface morphology studies of
acrylate/carbon nanotubes nanocomposite thin film with 5 kX magnification and working distance is 5.4 mm.

3. Results & Discussion

![Equivalent circuit model used for EIS measurement of the samples immersed in 3.5 w/v % NaCl solution.](image)

**Figure 1.** Equivalent circuit model used for EIS measurement of the samples immersed in 3.5 w/v % NaCl solution.

![The Nyquist graph has shown EIS measurement of the uncoated mild steel.](image)

**Figure 2.** The Nyquist graph has shown EIS measurement of the uncoated mild steel.
Figure 3. The Nyquist graph on EIS measurement for acrylate:carbon nanotubes nanocomposites for several weight percentage between 0.2 w/v % - 1.0 w/v % of CNTs contain with increment of 0.2 w/v %.

Figure 4. The Bode plot for the uncoated mild steel.

Figure 5. The Bode plots of acrylate:carbon nanotubes nanocomposites thin film on mild steel with increment 0.2 w/v % of CNTs contains (a) 0.2 w/v %, (b) 0.4 w/v %, (c) 0.6 w/v %, (d) 0.8 w/v % and (e) 1.0 w/v %.

Figure 1 has shown the equivalent circuit model are employed to analyze the corrosion protection of the coatings under percolation of sodium chloride, (NaCl) solution. Basically, The electrochemical impedance spectroscopy (EIS) were performed in this research well-known for investigated the coating corrosion protection for the acrylate:carbon nanotubes (A:CNTs) nanocomposite thin films [25]. Hence, \( R_s \) is solution resistance; \( C_c \) is coating capacitance; \( R_{po} \) is pore resistance; \( C_{dl} \) is double layer capacitance; \( R_{ct} \) is charge transfer resistance. Where, \( \omega \) is angular frequency; \( \alpha \) is a dimensionless parameter; \( Y \) is a parameter with dimensions \( \Omega^{-1} \) s\(^\alpha\) representative for constant phase element (CPE). Commonly, \( 0 < \alpha < 1 \); when \( \alpha=1 \) and \( Y=C \), CPE function like ideal capacitor with capacitance, \( C \); when \( \alpha=0 \), a resistance is presented. It also resemblance equivalent circuit model founded to stimulate the degraded behavior of organic coating in existence publication [17, 26].
Employing EIS results, the impedance spectroscopy were analyzed using Gambry software (Gambry Echem Analyst) which is used initial frequency 50 kHz and final frequency 0.015 Hz under continuous immersion in 3.5 w/v % NaCl solution probably half an hour. In figure 2, obtained the Nyquist graph of uncoated mild steel corresponding to the natural corrosive activity apparently happen due to there is no coating protection on the metal surface. In addition, the graph shown single capacitive loop at high frequency at the starting measurement. The protection of the coating being attributed to the solution protection in the conductive paths of the sol-gel coating and corrosion activity only occurring in the layer of free coating protection [14].

In other side, figure 3 shows that the Nyquist graph of acrylate:carbon nanotubes nanocomposite for several samples with different contains of CNTs such as (a) 0.2 w/v %, (b) 0.4 w/v %, (c) 0.6 w/v %, (d) 0.8 w/v % and (e) 1.0 w/v % with increment of weight percentage 0.2 w/v % of CNTs. From the table 1 obtained that the sample with 0.2 w/v % of CNTs shows the highest impedance value compared to the rest has possess $Z_{\text{real}} = 4.454 \ \text{k}\Omega$ and $Z_{\text{imaginary}} = 1.439 \ \text{k}\Omega$, respectively. Then, the coating impedance slightly decreases interm of $Z_{\text{real}}$ and $Z_{\text{imaginary}}$ from 0.8 w/v % (1.804 kΩ and 450 Ω), 0.6 w/v % (1.689 kΩ and 369.2 Ω), 1.0 w/v % (1.374 kΩ and 226.1 Ω), 0.2 w/v % (1.051 kΩ and 182.1 Ω) of CNTs contain and the lowest impedance is uncoated mild steel (371.8 Ω and 89.59 Ω). The most excellent corrosion protection of acrylate with contain 0.4 w/v % of CNTs may due to highest coating impedance that can retained coating from the NaCl solution to pass through the coated mild steel. Thus, addition of carbon nanotubes (CNTs) in acrylate improve the corrosion protection of the coating due to formation of CNTs as conducting materials would trap the ions from directly penetrate the mild steel and provides increment of barriers in the coating. Besides that, the barrier phenomenon can be related to the avoiding or blocking of the the free metal surface and decreasing the corrosion rate. In theory, abatement values of potential during measurement has shown scattered of electrolyte and corrosion activity occurs take place on defects or pin holes of the mild steel which is existed in the surface of the coated metal. According to A. Mostafaei et al. [27] state that the potential was shifted occurs due to the formation of the passive layer film on carbon steel substrate with assistance of conducting polymer.

Figure 4 has shown the Bode plot that evolutions of impedance modulus for uncoated mild steel with high value of impedance at the high frequency and slightly decreases in term of value of impedance at the low frequency. It is may due to the penetration of NaCl solution into the mild steel substrate without coating protection of acrylate:carbon nanocomposite thin film. Besides that, figure 5 shows that the Bode plots of the samples for fives different contain of CNTs found that almost similar with uncoated mild steel where coating thin film started at high frequency with highest impedance and after a few times it is slightly decreases with frequency and the coating impedance become lowest at the end of immersed in NaCl solution. But, there is shifted for the sample contain 0.2 w/v % of CNTs which is highest in impedance at the lowest frequency then also decreases after a few times with frequency become smaller. In literature, the presence of nanoparticles in polymer coating comes with incorporating between filler and matrix can improve the barrier between coated metals and exposure solution that can protect from corrosion activity [28].

As shown in figure 6, optical photographs shows sample surface after was immersed in 3.5 w/v % of NaCl solution for investigation of corrosion performance of the coated mild steel. Circular surface around 2.85 cm$^2$ area exposure to the solution has been formed corrodes due to the electrolyte slightly penetrate the coating material and surface of mild steel started defect with no longer protected by the A:CNTs nanocomposite thin film. For the surface morphology of (A:CNTs) nanocomposite thin film were observed by using field emission scanning electron microscope (FESEM) with 5.00 kX magnification before this sample was immersed in 3.5 w/v % of NaCl solution. As shown in figure 7 has found that the formation of CNTs as filler is well distributed into acrylate but not even homogeneous and CNTs formed with black colour with tubes-likes and acrylate in colourless form.
Table 1. The impedance value ($Z_{\text{real}}$ and $Z_{\text{imaginary}}$) that refer to the figure 2 and figure 3 of acrylate:carbon nanotubes nanocomposite thin film coated on mild steel

| Contain of CNTs, (w/v %) | $Z_{\text{real}}$, (Ohm, $\Omega$) | $Z_{\text{imaginary}}$, (Ohm, $\Omega$) |
|--------------------------|------------------------------------|----------------------------------------|
| Uncoated mild steel      | 371.8                              | 89.59                                  |
| 0.2                      | 1.051 k                             | 182.1                                  |
| 0.4                      | 4.454 k                             | 1.439 k                                |
| 0.6                      | 1.689 k                             | 369.2                                  |
| 0.8                      | 1.804 k                             | 450                                    |
| 1.0                      | 1.374 k                             | 226.1                                  |

Figure 6. The sample of acrylate:carbon nanotubes nanocomposite thin film deposited on mild steel after immersed in 3.5 w/v % of NaCl solution.

Figure 7. FESEM image of acrylate:carbon nanotubes nanocomposite thin film coated on mild steel.
4. Conclusion
As the conclusion, the acrylate:carbon nanotubes (A:CNTs) nanocomposite thin film were successful prepared by sol-gel technique and the results has shown addition of carbon nanotubes into acrylate improve the coating barrier and increase coating impedance that coated on mild steel. Electrochemical impedance spectrometer found that acrylate:carbon nanotubes nanocomposite thin film with 0.4 w/v % of CNTs contain possess the highest coating impedance provide good corrosion protection on coated mild steel that prevent from NaCl solution to pass through the substrate. Furthermore, the surface morphology were observed by FESEM shows that CNTs was formed in acrylate with good distribution but not even homogeneous. There is good improvement in corrosion protection properties in term of varies doped weight percentage of carbon nanotubes blended with acrylate and lengthen the corrosion protection on coated materials.

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