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EFFECT OF APPLIED VOLTAGE ON ELECTROPHORETIC DEPOSITION OF NANO-HYDROXYAPATITE COATING ON BIODEGRADABLE AZ31 MAGNESIUM ALLOY AND ITS CORROSION PROPERTIES

C.Y. Chong[1,4], N.A. Fadil[1,2], F.M. Nor[3], T. A. Abu Bakar[1,2,*]

[1]Department of Materials, Manufacturing and Industrial Engineering,
Faculty of Mechanical Engineering, Universiti Teknologi Malaysia (UTM),
81310 Johor Bahru, Johor, Malaysia.

[2]Materials Research and Consultancy Group,
Faculty of Mechanical Engineering, Universiti Teknologi Malaysia (UTM),
81310 Johor Bahru, Johor, Malaysia.

[3]Department of Mechanical Engineering, Curtin University, Miri,
98009 Sarawak, Malaysia.

[4]Maxhub PLT, 7, Jalan Pulai 58, Taman Pulai Utama, 81300 Skudai,
Johor, Malaysia.

*Corresponding Author's Email: tuty@utm.my

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ABSTRACT: Magnesium alloys have recently gained attention among researchers due to their excellent biodegradability. However, rapid corrosion of Mg AZ31 alloys may cause an implant to fail before the bone has been fully restored. This study aimed to enhance corrosion resistance of Mg AZ31 alloy. In this study, hydroxyapatite (HA) powder coatings were prepared by using electrophoretic deposition (EPD) technique on AZ31 alloy for orthopaedic application. In this research, the voltage applied by EPD was increased from 10V to 50V. Coating morphologies, coating structures and corrosion properties were studied. FESEM observation was conducted on the formation of cracks, agglomeration and particle distribution. Corrosion test was performed by using an immersion test. Meanwhile, potentiodynamic test was evaluated by using pH value measurement and Tafel extrapolation. The presence of HA had successfully increased the corrosion resistance of bare AZ31. Through the FESEM observation, applied voltage of 20V had the highest corrosion resistance and least defects found amongst samples. Moderate applied voltage of 20V revealed the least defects and uniform coating layer because of charged particles attraction and repulsion to form a self-arrangement and high packing deposited layer. Therefore, the corrosion properties were increased by acting as an effective barrier to the corrosive environment.

KEYWORDS: *Hydroxyapatite, EPD coating, Applied Voltage, Morphologies, Corrosion Properties*.

1.0 INTRODUCTION

An implant material is a medical device created to replace or support a damaged biological structure. The common metallic implant materials for orthopaedic fixation include Ti-6Al-4V, stainless steel, 316L, cobalt chromium alloy and Co-Cr-Mo [1]. These materials refer to a permanent implant, which offers promising long-term support to the patient. Some chemical substances are added to these materials to support such high corrosion resistance and could harm the human body [2, 3]. A biodegradable implant is a different approach which offers a temporary implant fixation and is expected to decompose gradually after the bone is fully restored. These implants are expected to be dissolved, absorbed, consumed or excreted harmlessly through the human body, thus eliminating the need for a second surgery to remove them [4].

Magnesium (Mg) is proposed as a potential candidate for a biodegradable implant due to its metallic strength properties, biodegradable performance and harmless Mg^{2+} release in the human body [3-4]. Mg is a lightweight metal with density of 1.74g/cm^3. Its elastic modulus is similar to human bone stiffness value, which could avoid the stress shielding effect [5]. However, degradation rate of Mg in the human physiological environment is high. Mg suffers from rapid corrosion in the human body, which limits its clinical application [6]. Surface modification is one of the most simple and effective methods to improve the corrosion resistance of a metal [7]. Hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is a ceramic coating material with high calcium phosphate. Moreover, its bioactive properties favour bone growth [7]. HA is a common material coated on permanent metallic implants to offer excellent biocompatibility properties and enhance corrosion resistance [8]. It could be coated with various methods. However, in many cases, it was commonly found unsatisfactory due to the considerable size of crack formation [9, 10], irregular packing structure [11, 12] and long-term stability issues [13]. Other methods, including EPD and sol-gel coating, were proposed to solve the problem [9, 13]. Electrophoretic deposition (EPD) is a liquid coating method suitable for colloidal processes with ceramic coatings [11, 14]. It is widely used for biomedical coating and extensively for fabricating ceramic coating on a metal surface [15, 16]. The EPD formed a porous coating that favoured biomedical applications [10, 14—16].

It was reported that the colloidal process is easy to manipulate with the coating process and interparticle force to reduce undesired defects, such as cracks and irregular packing structure [17]. One of the major process parameters is applied voltage (V). The applied voltage was reported to affect the kinetic movement of charged particles and arrangement of deposited layers [11, 12, 18]. This study aims to utilise the EPD method and suitable applied voltage to fabricate a high packing, dense layer, thus increasing the corrosion resistance of AZ31 for biomedical applications. The significance of the study is that it produces an easy and cheap process besides extending knowledge on the EPD process parameters.

2.0 METHODOLOGY

A commercial nanoparticle HA powder that was needle-shaped (supplied by Sigma-Aldrich) and length of ≤40nm was used. As received, AZ31 hot rolled bulk material was cut into 30x10x3mm dimensions as substrate. The substrate was ground to 1200 grit silicon carbide, rinsed through water and ultrasonic bathed in ethanol before being subjected to EPD coating. EPD suspension was prepared by mixing 30g of HA powder and 1 litre of ethanol. The suspension was stirred for 24 h in a tight and sealed bottle. The EPD process was prepared by using graphite as the anode and AZ31 metal plate as cathode. Both electrodes were immersed in a 200 ml suspension with separation of 1cm. The EPD process was conducted at a 1 min deposition time and room temperature. EPD was performed starting from 10V until cracks were observed with the naked eye . After the EPD process, these samples were air dried and heated in a furnace at 400°C for 2 h.

Surface morphologies were characterised by FESEM and XRD (Siemens-D5000) operation with 20kV used monochromatised CuK, radiation, identified powder and coated phases. Corrosion behaviour was investigated by using an immersion test and potentiodynamic test in Hank's Solution. The immersion test was performed by measuring the changes in pH value at the adjacent sample (<1cm) for three consecutive days, while the potentiodynamic polarisation test was carried out by using a potentiodynamic machine (model Parstat 2263). Four electrodes were used: a saturated calomel, SCE as reference electrode, graphite as counter electrode and HA-coated sample as working electrode. These measurements were derived by TAFEL extrapolation to determine the corrosion potential of samples (E_{corr}) and corrosion density (I_{corr}) through software analysis (Versa Studio).

3.0 RESULTS AND DISCUSSION

3.1 Phase analysis results

X-ray diffraction (XRD) analysis was employed to identify and investigate the phase changes before and after coating prepared by EPD of HA on AZ31. Figure 1 shows the XRD pattern of (a) AZ31 substrate, (b) HA powder and (c) coated HA sample coating.

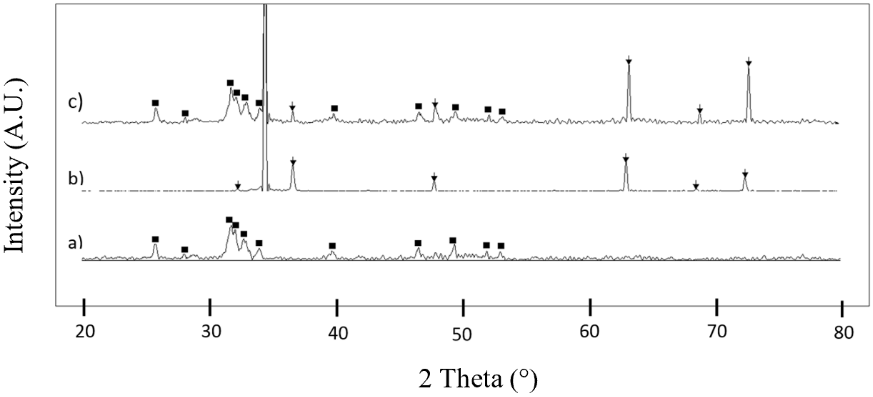


Figure 1: XRD pattern of (a) AZ31 substrate, (b) HA powder and (c) HA coating

As seen, all XRD peaks of HA were designated as '↓' and matched with HA JCPDS: 01-074-0565. Meantime, AZ31 substrate XRD peaks were designated as '■'. All HA coating layer peaks corresponded to HA powder and AZ31 substrate. No significant changes in XRD patterns before and after EPD coating were observed. XRD patterns of coated HA on AZ31 correspond to the peak of HA powder and AZ31 substrate. Therefore, it was suggested that no significant HA phase changes occurred during the EPD coating process. This finding was like that of Ma et al. [19].

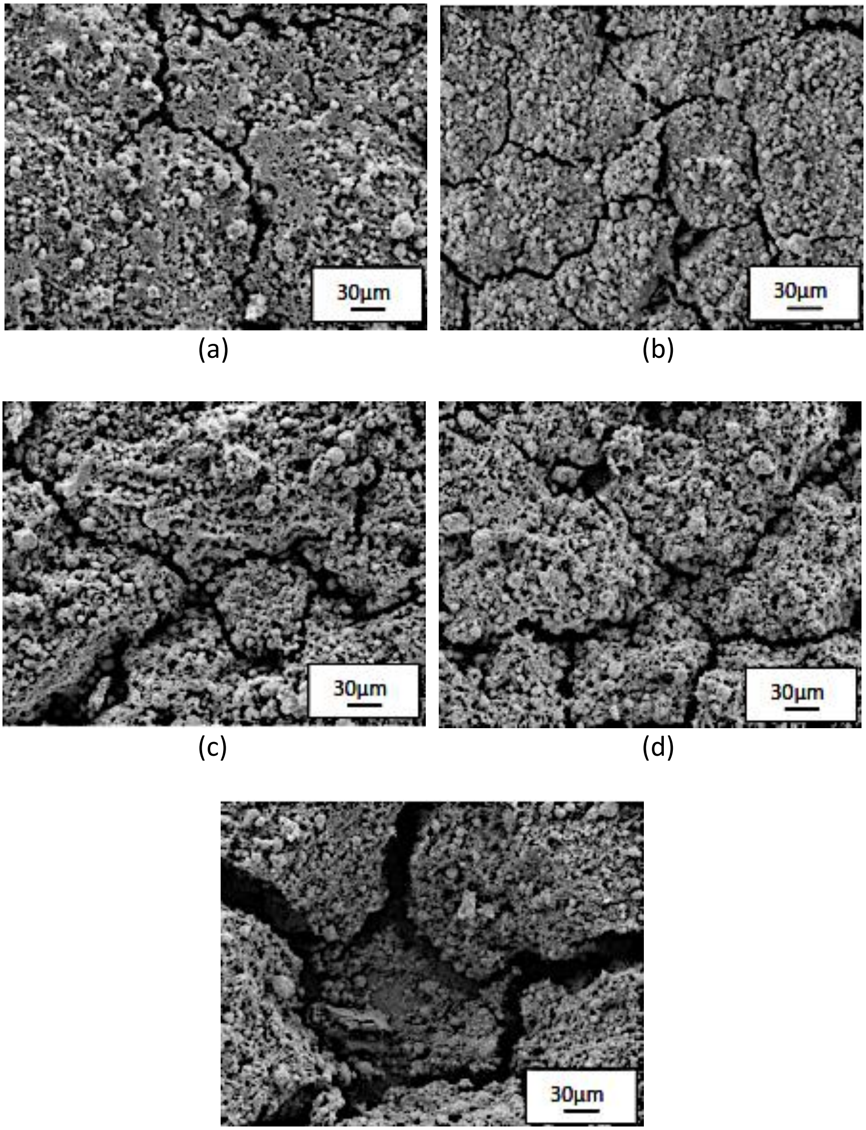
3.2 HA coating behaviour

Higher magnification observation by using FESEM, as shown in Figure 2 (a), had found micro cracks on the surface of some coated layers. Micro crack formation had gradually increased from sample 10V to 50V, as shown in Figure 2 (a) to Figure 2 (e).

The 20V sample coated with moderate applied voltage was sufficient to form a fully covered coating on the AZ31 surface. Surface morphologies observed in Figure 2 (b), 20V had smaller crack than the 30V sample. However, as it increased to 40V, a higher degree of irregular surface layer was found. Relatively high electrophoretic mobility caused agglomeration on coating, thus creating an irregular coated layer. This finding was similar to the micrographic studied, supporting the concept of self-arrangement of particles near metal surfaces [11, 12, 17, 18, 20]. A flocculation mechanism near metal disrupted the self-arrangement mechanism of attraction and repulsion of particles as a higher voltage was applied. As a result, accumulation happened.

It could be observed that on the 50V sample (Figure 2 (e), whereby the obtained surface was irregular with considerable crack size. Ferrari et al. [12] explain the concept of charged particle arrangement, whereby the particles were packed in electrophoretic and their arrangement on the electrode surface can be altered by an electric field such as applied voltage. High applied voltage with high kinetic motion of particles tended to agglomerate as it was deposited on the working electrode due to turbulence formed on the metal surface before it was deposited. The self-arrangement of particles was due to the evolution of potential energy and the particle distance for surface dispersion by an electrostatic mechanism [12]. As the electrophoretic motion of particles was too high, the particle separation did not form a close-packed with self-arrangement particle separation. Particles deposited with a high mobility rate had relatively low repulsion energy to deposit with a self-arrangement position to the adjacent particles. Therefore, low packed density and agglomerate surface were formed.

The research also works with the EPD multilayer approaches. Compared with the HA single-layer coating, the HA multilayer coating has successfully enhanced the coating compactness by filling up the previous coating layer's defects, producing a high-density layer and uniform structure without cracks and hump structure.



(a) (b)

(c) (d)

(e)

Figure 2: Surface morphologies of HA coating sample at various applied voltage: (a) 10V, (b) 20V, (c) 30V, (d) 40V and (e) 50V.

3.3 Corrosion Behaviour

The coating structures fabricated by applied voltage of 10V-50V were tested in immersion and potentiodynamic tests to understand their corrosion properties. Immersion test results were measured by pH value changes in Hank's solution, as illustrated in Figure 3. pH values increased rapidly from pH 7.4 to 8.8 in the initial immersion test and increased gradually until the end of the test. Increasing pH values adjacent to physiological conditions were involved in the corrosion reaction by involving OH-OH-releasing during the process. The more active the reaction, the higher pH value changes were measured. The chemical reaction was depicted as follows:

Anodic Reaction : $Mg \rightarrow Mg^{2+} + 2e$ (1)
Cathodic Reaction : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (2)
Thin film formation : $Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$ (3)
Thin film is loose and solute. : $Mg(OH)_2 + Cl^- \rightarrow MgCl_2 + 2OH^-$ (4)

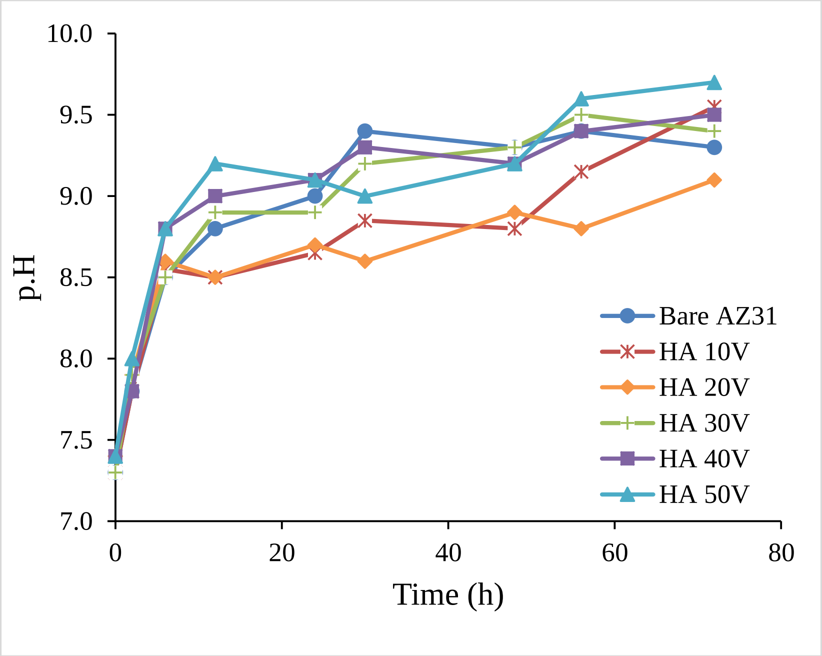


Figure 3: The changes of pH values during immersion time 72 h of HA coated sample from 10V to 50V applied voltages

As Mg in physiological conditions, anodic and cathodic reactions are shown in Equation (1) and Equation (2). As mg dissolution, H_2 and OH^- were by-products of corrosion reaction. OH^- ions release increased the pH value of surrounding area. The reaction rose rapidly by releasing more OH^- and was saturated after 6 h of immersion. Similar trends were observed by Hornberger et al. [9] and Wang et al. [22]. as compared to bare AZ31, relatively slow pH value changes were observed on the coated sample. This suggested that HA coating has successfully decreased the corrosion reaction on metal surfaces. Amongst HA-coated samples, the 20V coated sample showed the lowest slope, whereby the pH value increased from 8.6 to 9.1 after 6 h. On the other hand, samples coated with other applied voltages reached a higher pH value at the end of immersion, which was from 9.4 to 9.7. As mentioned, applied voltages determined the particle distribution and surface morphologies. A highly compact and dense surface morphologies coating layer protected the Mg substrate more effectively. Therefore, lower pH value results were obtained on sample 20V.

On the other hand, relatively high applied voltage samples, 40V and 50V, performed less corrosion resistivity in the immersion test than insufficient, not fully covered samples (10V). This may be because of the thick coating layer tended to form cracks on the coating layer. Moreover, these two samples observed more coating dissolution at the end of immersion test. A thick coating layer was believed to be easily felt during the corrosion test. Therefore, a thick layer sample showed a higher slope of pH value changes with more substrate exposure to the corrosive environment.

Mg dissolution and formation $Mg(OH)_2$ as the precipitation (Equation 3). This layer was soluble and reacted with Cl^- from Hank's Solution to form $MgCl_2$, as shown in Equation 4, and thus further increased local pH. If HA coating dissolution, it will form PO_3^{-4} and Ca^{2+}. These ions reacted with OH^- in the solution. At the same time, PO_3^{-4} and Ca^{2+} in the solution also reacted with OH^- to form hydroxyapatite [21]. This reaction increased the local pH value, corrosion resistance and mechanical stability [23].

Similar results were obtained by potentiodynamic test. The immersion test proved a short-term corrosion measurement of the changes, while potentiodynamic provided long-term corrosion data by calculating its corrosion rate (mmpy). Corrosion rates were obtained by Tafel Extrapolation. Figure 4 shows the potentiodynamic polarisation curves of bare AZ31 and HA-coated samples from 10V—50V in Hank's Solution. Parameters are listed in Table 1 with corrosion potential (E_{corr}), corrosion current density (I_{corr}), and anodic Tafel constant (βa), cathodic Tafel constant (βc) extracted by Tafel region extrapolation. Rp, polarisation resistance obtained from the Stern-Geary equation was an essential evaluation of coating resistivity. The The significant of Rp value to this study lies in its role as a critical parameter for evaluating the resistivity and performance of coatings in corrosion protection. A high Rp value indicates that the coating effectively resists ionic movement, preventing the electrochemical reactions that lead to corrosion. Conversely, a low Rp value suggests reduced protection and potential coating defects. Besides, it provides quantitative measure of corrosion rate by determining the corrosion current density, which directly correlates with the material's corrosion rate. This provides a numerical basis for comparing the protective efficiency of different coatings. The equation shows as follows:

$$R_p = \frac{\beta_a \beta_c}{2.31\, i_{corr}\, (\beta_a + \beta_c)} \tag{5}$$

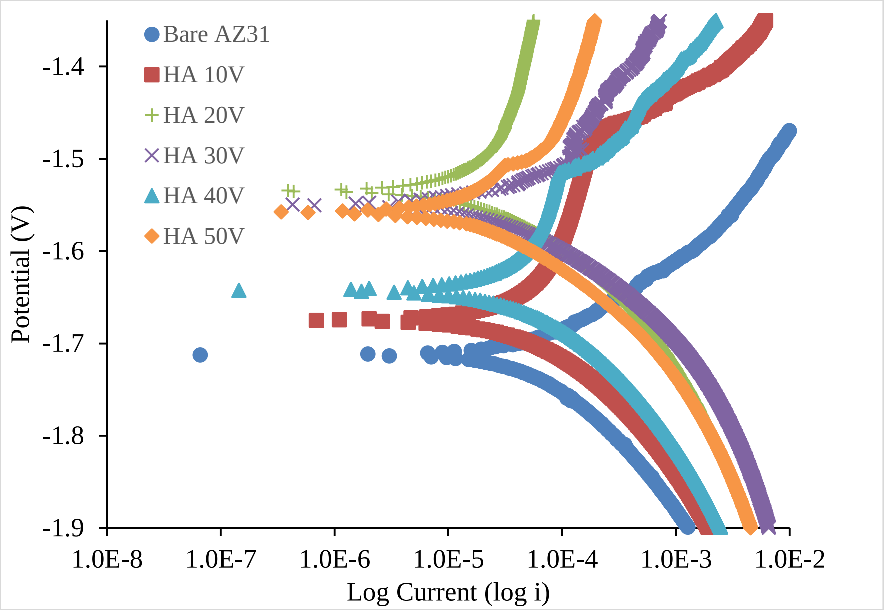


Figure 4: Potentiodynamic polarisation curves of the HA-SV group vary from 10V to 50V with a scanning rate of 1mV/s in Hank's Solution.

Although potentiodynamic polarisation curves of the bare AZ31 showed a clear difference in the positive shift of corrosion potential (E_{corr}) of the HA-coated sample, The current density (I_{corr}) of HA coating was lower than bare AZ31. These results showed that HA increased the corrosion resistance of bare AZ31. The corrosion rate calculated and shown in Table 1 found that sample 20V had significantly improved the corrosion resistance by only 4.4733 mmpy, while the bare sample was 33.435 mmpy. Rp, polarisation resistance of 20V showed the protectiveness layer obtained by Stern Equation with the information obtained from polarisation test shown in equation 5. Sample 20V, with the least surface defects observed from surface morphologies regarding cracks and agglomeration, acted as a high protective layer against the corrosive environment. Therefore, the Rp values were higher than other coated samples.

Table 1: Electrochemical data for bare AZ31 and HA-coated samples from potentiodynamic polarisation tests

Applied Voltage (V)	E_{corr} (V)	i_{corr} (μA/com^2)	βα (mV/ decade)	βc (mV/ decade)	R_p (Ωcm^2)	Corrosion rate (mmpy)
Bare AZ31	-1.752	348600	478.394	770.677	-	33.435
HA 10V	-1.658	1380	395.961	585.47	0.0744	13.243

HA 20V	-1.519	466.41	364.224	370.577	0.1712	4.4733
HA 30V	-1.529	1644	723.928	596.962	0.0865	15.772
HA 40V	-1.623	1216	446.551	549.393	0.0881	11.671
HA 50V	-1.562	833.064	498.446	425.215	0.1198	7.9898

These corrosion results suggested that appropriate applied voltage during EPD could provide relatively higher corrosion protection to magnesium alloy in physiological conditions. A dense, least micro-cracks coated sample obtained by self-arrangement particles under suitable applied voltage was more favourable against a corrosive environment.

4.0 CONCLUSION

Hydroxyapatite deposited on magnesium alloy by using the electrophoretic deposition technique increases corrosion resistance. Relatively high corrosion resistance results are obtained from a highly compact and optimum self-arrangement particle deposited layer with an applied voltage of 20V. In the short-term immersion test in Hank's Solution, HA 20V has the lowest slope of pH value increment in 72 h of immersion. In the potentiodynamic test, the corrosion rate of 4.4733 mmpy and Rp of 0.1712 Ωcm^2 calculated from Tafel extrapolation and Stern Equation show positive results on HA-coated layer corrosion resistance. A moderate applied voltage could prevent considerable crack size formation and accumulation and form a highly closed-packed layer. Therefore, it provides a better barrier to separate a corrosive environment from the substrate. The HA multilayer coating approach is also believed useful for this application.

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AUTHOR CONTRIBUTIONS

C.Y. Chong: Conceptualization, Methodology, Writing- Original Draft Preparation; N.A. Fadil. Author: Data Analysis, Validation; F.M. Nor: Data Analysis; T.A. Abu Bakar: Result Validation, Writing-Reviewing, Editing and supervision.

CONFLICTS OF INTEREST

The manuscript has not been published elsewhere and is not under consideration by other journals. All authors have approved the review, agree with its submission and declare no conflict of interest on the manuscript.

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