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Carbon-containing-titania coated stainless steel prepared by high voltage powder spray coating and its adhesion phenomena



ORGANIC COATINGS

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ABSTRACT

Nowadays, many studies involve coating materials on stainless steel prepared by various methods, and many approaches have been taken to improve the abrasion resistance of the coatings. Here, the attachment of carbon/ titania (C/TiO₂) on stainless steel and the evaluation of its coating adhesion is reported. The commercially available epoxy resin was used as the source of carbon, and the transformation from epoxy resin to pyrolytic carbon was performed. It is proposed that the incorporation of an inorganic particle will improve the adhesion properties through the reduction of the carbon shrinkage. C/TiO2 was prepared from the mixture of commercialized epoxy resin (Oxyplast PR12®) and anatase TiO2 powder, followed by spraying the mixture onto stainless steel (AISI 304) surface using high voltage powder spray coating (HVPSC). The sprayed powders on stainless steel underwent pyrolysis at several temperatures from 300 to 700 °C for an hour to determine the optimum temperature for excellent adhesion. The physical properties of C/TiO₂ coated samples were characterized by Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FESEM), surface profiler meter and X-ray photoelectron (XPS) spectroscopy. The FTIR analysis of C/TiO2 coating identified the appearance of peaks C-H sp³, C=O, C-O, and Ti-O. It was noticed that the absorption band of C-H sp³, C=O, and C-O slowly disappeared as the pyrolysis temperature increased, indicating that the structure changed from epoxide to pyrolytic carbon. FESEM images showed that the TiO_2 particles were fully covered with the carbon layer, and the thickness was determined to be in the range of $4.8-15.5\,\mu$ m. The abrasive and peel adhesion test was performed, showing no detachment of coated material of C/TiO2 pyrolyzed at 300 °C, suggesting that this temperature produces the best coating adhesion. The carbon-based coating adhesion phenomena were elucidated by XPS analysis of Fe2p, C1s, and Ti2p element peaks. It was demonstrated that the presence of an oxide layer on stainless steel, availability of functional groups, and structure shrinkage were the factors that affect the adhesion of the carbonaceous coating. The structure shrinkage was reduced due to the presence of TiO₂, which is associated with strong coating adhesion. This demonstrated that the carbonaceous coating produced by HVPSC formed an excellent adhesion in the presence of TiO2.

1. Introduction

Coating is a process where a material is deposited on the surface of an object (substrate). The purpose of the coating onto the surface of a substrate depends on its usage. Up till now, many types of coating materials have been used to meet the needs of enhancing durability and efficiency, as well as lower environmental impact ([1], Wen et al., 2017). Based on previous studies, polymeric films, thin films, surface coatings, and metallic coatings on stainless steel have been extensively applied in superhydrophobic coatings [2], solar cells [3], pharmaceuticals [4], photocatalysis [5]; [6], antibacterials [7], and paint films [8]. A coating material may consist of organic, inorganic, polymer, or a combination of any of these materials. Most of these coating materials have been produced by sol-gel process, which is a relatively straightforward procedure to be employed. However, several drawbacks are found for this process, such as the high cost of raw materials and the imperfection of material during the drying process that leads to volume shrinkage and cracking [9]. As a consequence, coatings and films

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fabricated via this method have affected consistency in terms of the physical and chemical-resistant coating.

Apart from the method mentioned above, high voltage powder spray coating (HVPSC) has also been introduced as an alternative preparation method for powder coating. Powder coating is an economical technology for surface treatment [10,11]. It is a simple and effective process that uses powder as the medium of deposition. HVPSC is an established method and the application of HVPSC has long been used in finishing industry and polymer coating [4,10]; [12]. The commonly used powder for coating is thermoset polymer resin, such as vinyl ester, polyester, epoxy, polyurea, phenolic, silicone, urethane, acrylic, and others [11,13]; [14]. Nevertheless, the major drawback of thermoset resin is high curing shrinkage [13]; [14]. After being cured, the resin exhibits low surface area, which limits its application [13]. Besides that, polymer coating is not able to undergo any functionalization after curing process due to its poor adhesion and physical stability.

Therefore, much effort has been made in the fabrication of new coated materials to expand coating usage. Carbon has been applied in a wide range of applications, and it is one of the most selected materials due to its characteristics of high electrical and thermal conductivity, high chemical stability, high lubricity, non-toxicity, and resistivity towards radiation [15]. To date, the main challenge of coating fabrication is the need for developing abrasion-resistant hard coatings. Manufacturers and users play an integral role in overcoming this drawback. It is known that many inorganic and organic materials show low adhesion and abrasion resistance (Wen et al., 1995). For that reason, with the emergence of powder coatings, the same approach can be applied as a strategy to utilize HVPSC to coat a metal surface with carbon-based material. Due to the importance of producing high resistance coating, this research uses carbon to be bonded with titanium dioxide (TiO₂) for carbon-based material coating. The heating process without the interruption of oxygen has been introduced in the formation of pyrolytic carbon coating from epoxy resin. Based on the surface energy point of view, it is beneficial to transform the epoxy surface into pyrolytic carbon to increase the adsorption ability of the coating with a strong adhesion attraction. Previous studies have reported that the surface energy of epoxy resin was in the range of $40-50 \text{ mJ/m}^2$ while the carbonaceous surface possesses $100-150 \text{ mJ/m}^2$ (Wu, 1989; [16-18]). Thus, it is believed that the formation of pyrolytic carbon can significantly increase the surface energy, which will lead to better adsorption. The surface energy of epoxy resin and pyrolytic carbon is illustrated in Fig. 1.

Although carbon is a widely used substance, the enhancement of carbon functionalities is still required. It is expected that the incorporation of additives can enhance the resistance properties of pyrolytic carbon. It is hypothesized that the addition of TiO_2 can act as an



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Fig. 1. Surface energy illustration diagram.

additive to strengthen carbon-based coating, whereas the coated carbon will have excellent adsorption properties; thus, the surface can be easily functionalized towards desired applications. Therefore, the goal of this research is to produce a high resistance coating of carbon/titania (C/ TiO_2) coated on stainless steel prepared using the HVPSC method.

2. Experimental

2.1. General procedure

This study aims to introduce a new method using powder deposition technique to prepare carbon-based material attached with TiO₂, to produce a firm and durable coating adhesion, and to study its interfacial interaction. The results obtained by various instruments were analyzed and compared with one another to explain the effect of pyrolysis temperature on the characteristics of C/TiO₂. Besides that, the experiments conducted in this study investigated the optimum composition of added TiO₂ and the best pyrolysis temperature to produce wear-resistance coating on the substrate. C/TiO₂ coating adhesion strength and durability were tested using abrasion and peel adhesion tests. Based on the experimental results, the best C/TiO₂-coated sample was identified. A carbon-coated sample was also produced at the same optimum temperature in order to achieve excellent coating performance.

This research is mainly focused on the powder deposition method using electrostatic interaction for carbon-based material on a conductive substrate. The coating materials of carbon and C/TiO₂ were prepared using a technique through high voltage powder spray coating (HVPSC) followed by pyrolysis. The pyrolysis temperature was varied from 300 to 700 °C. The physicochemical properties of the C/TiO₂ and carbon were studied to investigate the behavior of each material and to determine the best coating produced. The interfacial interaction phenomenon of carbon-based material was then elucidated by XPS, followed by clarification with DFT and structure volume calculations.

2.2. Chemicals and materials

In this research, the chemicals used to synthesize carbon, C/TiO₂, and C/TiO₂/Ag were epoxy resin powder (Oxyplast PR12[®]), commercial TiO₂ powder (Sigma–Aldrich), ethanol (99.8%, Qrec), and acetone (Qrec). The material and apparatus utilized in this research were stainless steel (AISI 304), 0.45 μ m nylon membrane (Sigma–Aldrich), molecular sieve beads (Sigma–Aldrich), sand and double-sided adhesive tape (Unicorn double-sided foam tape, GP-99).

2.3. Preparation of carbon and carbon/titania coating using High Voltage Powder Spray Coating (HVPSC)

The coating of carbon and C/TiO₂ onto the stainless steel substrate was conducted using HVPSC. HVPSC as an electrostatic charging method uses high voltage gun that produces electric force to ensure that the powders emitted from the nozzle can reach the grounded metal substrate's surface by electrostatic interaction [10]. First, the experiment was started by synthesizing C/TiO₂ coating material to find the optimum composition, followed by the synthesis of carbon material. To produce carbon-based material coating, epoxy resin was used as the precursor of carbon and circuitously as adhesive for TiO₂. The experiment of C/TiO₂ took place by preparing epoxy resin containing TiO₂ powder to be sprayed using HVPSC and curing process under pyrolysis condition. The commercial epoxy resin powder and TiO₂ powder were physically-mixed by grinding the powders in mortar and pestle with the assumption that the TiO₂ powder will be mixed homogenously with the epoxy resin powder. After the mixing, the epoxy resin powder containing TiO₂ was loaded into the spray bottle equipped with the HVPSC machine.

For coating purposes, stainless steel plates were cut into the size of $6\text{cm} \times 2.5 \text{ cm}$. Prior to the coating, the plates were cleaned with

ethanol and acetone to remove any contaminant substances on the plates' surface. The plates were grounded into the machine with a voltage of 50 kV, and the prepared powders (in the spray bottle) were sprayed onto the plate's surface with a distance of 10 cm. The plates that have been successfully coated with epoxy resin powder containing TiO₂ went through the curing process by pyrolysis at the temperature range of 300 °C-700 °C for an hour. The curing process of epoxy resin powder usually occurs at 200 °C for 10 min; therefore pyrolysis temperature at the range of 300–700 °C were selected inorder to study the effect of pyrolysis temperature on the strength of carbon-based coating adhesion and to determine the optimum temperature. The same procedure was applied to synthesize carbon coating by using only epoxy resin powder loaded into the sprav bottle. Carbon/TiO₂-coated stainless steel after pyrolysis samples were labelled as C/TiO₂ 300, C/TiO₂ 400, C/TiO₂ 500, C/TiO₂ 600, and C/TiO₂ 700, where numbers 300, 400, 500, 600 and 700 indicate the pyrolysis temperatures in degrees Celsius.

2.4. Instrumentation

The high voltage powder spray coating (HVPSC) machine used to prepare C and C/TiO₂ coating materials was Encore[®] LT Powder Spray Systems (Nordson Corporation). The physicochemical properties of the synthesized materials were studied using Fourier transformed infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FESEM), surface profiler meter, X-ray photoelectron (XPS) spectroscopy, and DFT calculation.

3. Results and discussion

3.1. Carbon/titania coating

Finding the best mixture composition of TiO₂ and epoxy resin powder is crucial since too high TiO₂ composition will affect the efficiency of the coating performance. Therefore, to synthesize carbonbased coating, various compositions of TiO₂ in epoxy resin powder were prepared, starting from 1% to 30%. However, increasing TiO₂ composition caused difficulties in the spraying process. At 30% of TiO₂ composition, the powder could not be sprayed uniformly onto the stainless steel due to the difficulty for the powder to flow out through the nozzle. After the trials with different TiO₂ compositions were completed, 20% of TiO₂ composition was chosen for this research as it was the maximum composition that could be easily prepared and sprayed from the HVPSC's nozzle. The stainless steel samples before and after coating with C/TiO_2 (after pyrolysis) are shown in Fig. 2. From the visual observation, the appearance of coating at the normal curing temperature (200 °C) was transparent, whereas black colour was observed at higher pyrolysis temperatures (300-700 °C), which differed from the original white-coloured powder samples.

For this research, the maximum TiO_2 composition of 20% and 80% of epoxy resin was chosen as it could be easily sprayed from the HVPSC's corona gun. The attachment of TiO_2 with carbon coatings was characterized using FTIR, FESEM, and XPS. These results were used to study the effect of pyrolysis temperature on the formation of carbon from epoxy resin based on the availability of functional groups, the identification of elements in the coating structure, as well as to observe the appearance of carbon and TiO_2 , together with the location of TiO_2 , in the coating structure through morphology studies.

The surface morphological structure of epoxy resin, TiO_2 , and synthesized samples of C/TiO₂ after pyrolysis was analyzed by FESEM, as illustrated in Fig. 3. Fig. 3 shows that TiO₂ particles had spherical to irregular shape with the size range of 68.2–92.7 nm. The epoxy resin's surface morphology (Fig. 3 (b)) had an uneven and fractured surface. The FESEM images of synthesized C/TiO₂ samples at different temperatures were magnified for 40,000 times and presented in Fig. 3 (c), (d), (e), (f), and (g), respectively. The images confirmed that TiO₂



Fig. 2. Stainless steel (a) before coating and (b) after coating followed by pyrolysis.

particles were successfully attached to the carbon on stainless steel after the pyrolysis process.

From Fig. 3 (c), for pyrolysis at 300 °C, some particle fragments could be observed on the carbon layer's surface, and they were identified as TiO_2 particles. The thickness of the carbon layer caused the other TiO_2 particles to be embedded under the thick carbon layer. Based on Fig. 3 (d)–(f), the samples had a similar trend, where the images showed that the carbon layer entirely covered the TiO_2 particles. Pyrolysis temperature affected the formation of carbon layers since no thick carbon layer was observed (Fig. 3 (d)–(f)).

3.2. Functional group analysis of carbon/titania coating

FTIR was used to identify the types of bonding vibrations and functional groups present in C/TiO₂ coatings prepared from epoxy resin and TiO₂ powder by HVPSC. The FTIR spectra of epoxy resin and C/ TiO₂ at pyrolysis temperatures of 300-700 °C are depicted in Fig. 4. Based on Fig. 4, the FTIR spectra indicated the presence of the main functional group bands of epoxy resin and C/TiO2 and clearly showed the differences in peak intensity for these functional groups. The characteristic bands of epoxy resin in the spectrum (Fig. 4 (a)) were in accordance with previous studies, were clearly observed functional groups were assigned as follows: C-H sp³ stretching vibration at 2967 and 2969 cm⁻¹, conjugated C=O vibration at 1713 cm⁻¹, C-H sp³ bending vibration at 1473 and 1460 cm⁻¹, C–O vibration at 1265 and 1101 cm⁻¹, and rocking CH₂ at 727 cm⁻¹ [13]. The epoxy resin used in this research contained nitrogen (N) compound. Since the types of N compounds were not disclosed, therefore the small peak around \sim 1640 cm⁻¹ detected in the spectrum attributed to C=N bond was assumed as the N compound in the epoxy resin structure. The broad peaks observed around $520 - 783 \text{ cm}^{-1}$ in Fig. 4 (b) corresponded to the Ti–O bond vibration in TiO₂ [19].

Spectrum (c) showed the absorption bands of C–H sp³, C=O, and C–O. This could be explained by the tendency of epoxy resin to form pyrolytic carbon at the temperature as low as 300 °C through the sighting of peak reduction of C–H sp³, C=O, and C–O, which was in agreement with a previous report [20]. Referring to Fig. 4.3 (d)–(g), as pyrolysis temperature increased, the absorption peaks of C–H sp³, C=O, and C–O slowly disappeared. For the spectra of C/TiO₂ at



Fig. 3. FESEM images of (a) TiO₂, (b) epoxy resin, and C/TiO₂-coated stainless steel after pyrolysis at (c) 300, (d) 400, (e) 500, (f) 600, and (g) 700 °C.



Fig. 4. FTIR spectra of (a) epoxy resin, (b) commercial titania, and C/TiO₂-coated stainless steel at pyrolysis temperatures of (c) 300, (d) 400, (e) 500, (f) 600, and (g) 700 °C.

 Table 1

 Thickness of C/TiO₂-coated samples.

Sample Thickness (μ m) \pm (
$\begin{array}{ccc} C/TiO_2 \ 300 & 15.55 \\ C/TiO_2 \ 400 & 11.55 \\ C/TiO_2 \ 500 & 8.58 \\ C/TiO_2 \ 600 & 4.82 \\ C/TiO_2 \ 700 & 4.75 \end{array}$	

400–500 °C, it could be seen that the peak intensity of C–H sp³ stretching reduced, while other peaks vanished. All principal bands disappeared in the spectra of C/TiO₂ at 600–700 °C, as the epoxy resin has been completely removed in the pyrolysis process, and structural changes took place. As shown in Fig. 4 (a) and (b), a very small absorption peak of C=N bond was observed in the spectra of epoxy resin and C/TiO₂ 300 °C. With increasing pyrolysis temperature of 400–700 °C, the peak can be clearly detected. The intensity peak of C=N started to increase from the temperature of 400 °C and above that could be due to the carbon layer getting thinner and higher distribution of C=N. The presence of TiO₂ in the C/TiO₂ coating after pyrolysis was confirmed by the broad peak that appeared around 500–783 cm⁻¹. More quantitative analysis was carried out as supplementary studies in determining the pyrolytic carbon and TiO₂ in C/TiO₂-coated samples.

The thickness of the synthesized C/TiO₂-coated stainless steel at pyrolysis temperatures of 300-700 °C using HVPSC samples was measured using a surface profiler meter. The results are given in Table 1.

From the data, the thickness of all the C/TiO₂-coated samples were in the range of 4.7–15.5 μ m. The thickness of C/TiO₂ samples pyrolyzed at 300, 400, 500, 600 and 700 °C were 15.55, 11.55, 8.58, 4.82, and 4.75 μ m, respectively. Currently, fabrication of thin films and coatings is essential in many applications. The thickness of thin films and coatings is commonly obtained in nanoscale and microscale, respectively. In this study, C/TiO₂ coatings were measured in micrometre unit as coating thickness was moderately higher compared to thin film. This is due to the method of preparation and deposition. To form a very thin layer of film, common deposition techniques are carried out in liquid deposition medium [21], [22]. In this work, HVPSC introduced electrostatic charging using powder deposition. As the materials were prepared in powder form, it was impossible to obtain such a thin layer of coating similar to normal thin films.

From Table 1, coating thickness decreased as the pyrolysis temperature increased. This relates to the tendency of coating to peel off due to high-temperature heating. Since epoxy resin curing process occurred at 200 °C for 10 min, therefore there was no breakdown of any chemical bonds in C/TiO₂ structure at temperature lower than 300 °C. In addition, at low temperature, the possible reactions that happened were the changes of chemical interaction and physical properties of epoxy resin. Coating thickness was lower at higher temperatures. At 700 °C, the structure of epoxy resin structure has been completely decomposed and converted into pyrolytic carbon. Hence, high-temperature heating has the tendency to reduce the thickness of the pyrolytic carbon layer.

3.3. Adhesion performance of carbon/titania coating

Abrasion test is a method used to examine the strength of a coating on a surface. This test requires the process of scuffing, scratching, or rubbing away the coating with controlled process steps using an abrasive material. In this present work, abrasion test was carried out using the same abrasive material in rubber wheel test and manually tested with some modifications of Taber abrasion test [14]; [23]. Film or coating interface, thickness, and coating adhesion are important aspects in coating studies. Abrasion test was performed to assess the efficiency of coating and the results are shown in Table 2. Molecular sieve and sand were the two abrasive materials used. Table 2

Abrasion test data of C/TiO_2 -coated stainless steel using molecular sieve and sand as abrasive materials.

Sample	Weight loss using molecular sieve (%)	Weight loss using sand (%)
C/TiO ₂ 300 °C	0	0
C/TiO2 400 °C	0	0
C/TiO2 500 °C	0	0
C/TiO2 600 °C	0.6	0.6
C/TiO $_2$ 700 °C	1.8	2.0

After 7 h of milling, the weight losses of the coated samples were recorded in the range of 0.6–2.0%. Two different abrasive materials were used to study the strength of coating. These materials were selected for the milling process due to their roughness and robustness. As HVPSC is a new method for coating carbon-based material on stainless steel, the durability of C/TiO_2 coating is vital because high resistance coating is essential. From the data, C/TiO_2 at pyrolysis temperatures of 300–500 °C showed zero percentage of weight loss, which validated that the adhesion of C/TiO_2 coating pyrolyzed at 600 and 700 °C suffered some weight loss. It is believed that coating thickness influences the coating durability. In addition, no physical changes of C/TiO_2 -coated samples were observed with naked eyes before and after the test, as shown in Fig. 5.

3.4. Peel adhesion test of carbon/titania-coated stainless steel at pyrolysis temperatures of 300–700 $^\circ C$

In this work, the attachment of the carbon-based material onto stainless steel was further investigated using peel adhesion test by Rouw [11] but with some modifications. Fig. 6 (a) shows the coating material prior to the peeling test and Fig. 6 (b) presents the results after the peeling test with the application of an adhesive double-sided tape.

Peel adhesion test was performed by covering the coating surface with an adhesive double-sided tape for 5 min and then the tape was pulled out. From the images in Fig. 6, C/TiO_2 coating at 300 °C showed



Fig. 5. Images of C/TiO₂ coated on stainless steel at pyrolysis temperatures of 300–700 $^{\circ}$ C (a) before and (b) after abrasion test.



Fig. 6. Images of C/TiO₂ coated on stainless steel (a) before and (b) after peel adhesion test.

Table 3 Abrasion test data of C/TiO_2 coating using molecular sieve and sand as abrasive materials.

Sample	Weight loss using molecular sieve (%)	Weight loss using sand (%)
C+TiO ₂ 300 °C	0	0
TiO ₂ +C 300 °C	0	0

the best result, where none of the coatings were attached to the surface of the double sided-tape. Starting from C/TiO_2 coating at 400–700 °C, the amount of coating detached increased gradually. This result is in accordance with the weight loss percentage observed in abrasion test. Overall, from the results of peel adhesion test, the quantity of coating attached on the surface of double-sided tape was not too substantial. Therefore, it is relevant to state that the performance of C/TiO_2 is convincing.

Based on the results obtained, the formation of C/TiO₂ coated on stainless steel using HVPSC at 300 °C showed the best coating adhesion. Therefore, this study produced carbon coating with the same condition as C/TiO₂ pyrolyzed at 300 °C. This was done to study the effect of the addition of TiO₂ on coating properties. Based on abrasion and peel adhesion tests, the best coating between carbon and C/TiO₂ was identified at pyrolysis temperature of 300 °C. The incorporation of TiO₂ onto carbon-based coating was further studied to determine whether TiO₂'s location on the coating affected the coating performance or not.

3.5. Study on the effect of TiO2 location in C/TiO2-coated stainless steel at pyrolysis temperature of 300 °C

As discussed in Section 3.4, C/TiO₂ coating at 300 °C showed the best result compared to pyrolysis at 400, 500, 600, and 700 °C, in which no C/TiO₂ coating was detachable from the stainless steel surface. It can be hypothesized that TiO₂ particles attached to the stainless steel surface were contributed to strong coating adhesion. The following

experiments were carried out to identify whether the location of TiO₂ on the coating of C/TiO₂ pyrolyzed at 300 °C influence coating adhesion or not. TiO₂ location of the coat was modified for further investigation in determining the best coating performance of C/TiO₂ at a pyrolysis temperature of 300 °C. The sample preparation was done at two different locations as follows: spraying with the sequence of (1) the first layer of epoxy resin followed by TiO_2 layer (C + TiO_2 300 °C) and (2) the first layer of TiO₂ followed by epoxy resin layer (TiO₂ + C 300 °C). The samples were subjected to pyrolysis at 300 $^\circ\text{C}$ with N_2 gas supplied for 1 h. The results of abrasion and peel adhesion tests for both samples are shown in Table 3 and Fig. 7. By referring to Fig. 7, C+TiO₂ 300 °C sample had a smoother and more homogeneous surface of the coating. For $TiO_2 + C$ 300 °C, the coating was quite rough and non-homogeneous. This is because, during the spraying process, TiO₂ powder was coarser than epoxy resin; thus, the first layer of TiO₂ powder was not sprayed evenly on the surface of the stainless steel plate and subsequently affected the coating after heating.

For abrasion test with a milling machine, no weight loss was detected for both coated samples (refer to Table 3). This proves that the coatings on the stainless steel plate are sturdy and able to withstand even after 7 h of abrasion test. For peel adhesion test, Fig. 7 shows the captured images of $C+TiO_2$ 300 °C and TiO_2+C 300 °C samples. No coating was observed on the double-sided tape after the tape was applied on the surface of coating for 1, 5, and 60 min. Surprisingly, these results are consistent with C/TiO₂ coating at pyrolysis temperature of 300 °C. Therefore, the position of TiO₂ does not influence and affect the strength and durability of coating. From this study, it can be seen that good coating performance can be achieved by the presence of TiO₂ without being influenced by the location of TiO₂ on the coating. To verify the factor and interactions that attributed to strong adhesion and high resistance coating, the coating was subjected to XPS analysis, as presented in the following section.

In this work, epoxy resin was utilized as the precursor of carbonbased coating. From the analysis, it is confirmed the transition of epoxide structure to pyrolytic carbon started at the pyrolysis temperature



Fig. 7. Images of (a) C+TiO₂ 300 °C coating and (b) TiO₂+C 300 °C coating after 1, 5, and 60 min of peel adhesion test.

range of 300–700 °C. Since the coating underwent pyrolysis process without the presence of oxygen, the carbonaceous coating was known as pyrolytic carbon. The formation of pyrolytic carbon was proven from the colour change, functional groups, and XPS analysis. The visual observation observed showed that the colour of epoxy resin powder was white in colour, then changed to transparent at curing temperature and the colour turns to black after the pyrolysis process. Moreover, pyrolytic carbon formation from epoxy resin was identified with the reduction and disappearance of C–H, C–O and C=O peaks as temperature increased.

Further confirmation of pyrolytic carbon was studied in C—C interaction of C1s spectra. To summarize thus far, the samples of C/TiO₂coated stainless steel at pyrolysis temperatures of 300–700 °C were successfully prepared using HVPSC method. The morphology showed that TiO₂ particles were coated with carbon. The coated carbon layer decreased with increasing pyrolysis temperature. As an evidence, the measured particles size was smaller. The results also indicated that the carbon layers were reduced and less thick as the temperature increased. Thus, pyrolysis temperature affected the structure and carbon content in C/TiO₂-coated samples.

The best adhesion performance of C/TiO₂-coated samples was observed at pyrolysis temperature of 300 °C. The coating adhesion of C/ TiO₂-coated samples at 400–700 °C was convincing because only very little detachments were observed and approximately 2% of weight loss was detected. On the other hand, the only carbon-coated sample experienced a weight loss of approximately 3%. Besides that, it was also observed that a high volume of carbon coating was detached from the stainless steel plate. The result emphasises that the incorporation of TiO₂ in carbon-based coating is significant for coating adhesion. The performance of carbon coating was poorer than that of C/TiO₂ probably due to the shrinkage of coating structure during heating. The heating process shrunk the long chain of epoxy resin and produced compact pyrolytic carbon structure, which changed to a smaller chain structure. This explains that shrinkage that occurred as the structure changes from epoxy resin to pyrolytic carbon with increasing temperature. Besides that, the addition of TiO_2 has reinforced the coating adhesion in C/TiO_2 where it works by reducing carbon shrinkage and acts as a stabilizer in the structure. Since the location of TiO_2 may affect the attachment of carbon on the stainless steel surface, the clarification of its location is important. It was demonstrated that the location of TiO_2 , whether at the interphase between carbon and stainless steel or the outer layer of carbon, did not affect coating adhesion. The shrinkage of carbon coating was reduced in the presence of TiO_2 . The clarification for the presence of TiO_2 is described in the following sections.

3.6. Interfacial interaction studies through X-Ray photoelectron spectroscopy analysis

A study on the interaction of chemical bonding, functional groups, and chemical state of carbon and C/TiO₂-coated samples was performed using XPS. In this work, a depth profiling study was carried out for all samples through XPS measurement in order to study the composition and bonding interaction before and after etching. Besides, the effect of pyrolysis temperature from 300 °C to 700 °C was studied to find the relation to the interfacial interaction of coated samples.

3.6.1. Surface of stainless steel plate

The stainless steel plate was examined using XPS analysis to determine the presence of oxide layer on its surface. The wide-scan spectrum of stainless steel is shown in Fig. 8.

The species detected in the stainless steel were iron (Fe), oxygen (O), and carbon (C). The stainless steel used in this work is AISI 304, which consists of 74% Fe, 16% chromium (Cr), and 10% nickel (Ni). However, Cr and Ni elements were not detected in this analysis most probably due to the low amount in the stainless steel plate. Since Cr and Ni elements were not detected, therefore it was confirmed that only iron oxide layer was present on the stainless steel surface. C element was observed at 284.6 eV due to the carbon available from the



Fig. 9. Fe2p depth profiling XPS spectra of stainless steel at the (a) innermost surface, (b) third layer surface, (c) second layer surface, and (d) outermost surface.

environment [24]. Thus, as an internal reference, the binding energy of C1s at 284.6 eV was used for XPS spectrum calibration. To study the chemical bonding of stainless steel, the Fe2p peak spectra of stainless steel are presented in Fig. 9.

The high-resolution XPS spectra of Fe2p comprise of three overlapping bands allocated to oxidized Fe species. The binding energy of Fe metals was observed at approximately ~708 eV [25]. The first convolution peak in Fig. 9 (a) shows the highest binding energy at 707.94 eV, which accounted to the strong Fe metal interaction. The interaction became weaker at the outermost surface of stainless steel. The binding energy around ~709 eV was assigned to Fe²⁺ oxidation state, which ascribed to the ferrous oxide (FeO) layer of stainless steel [25]. Fe³⁺ oxidized species detected at the binding energy centred at approximately ~712 eV, was attributed to ferric oxide (Fe₂O₃) ([25] [26];). Hence, the XPS spectra have proven the presence of iron oxides layer on the stainless steel surface. This is in good consistent with previous reports ([27] [26];). These oxides layer can be considered to help in improving the coating adhesion.

The O1s peak spectra of the stainless steel are shown in Fig. 10.



Fig. 10. O1s depth profiling XPS spectra of stainless steel at the (a) innermost surface, (b) third layer surface, (c) second layer surface, and (d) outermost surface.

From the figure, the XPS spectra of O1s were further deconvoluted into three bands. The lowest binding energy at ~530 eV could be accredited to the lattice oxygen of FeO [25]. The second convolution graph with binding energy ~532 eV was attributed to the O bonding of Fe₂O₃ oxide [25]. The third convolution peak showed the binding energy approximated at ~533 eV and was assigned to the O adsorbed on the stainless steel surface [28]. These results are also consistent with the result of the Fe2p XPS spectra in Fig. 9.

The distribution amount of O and Fe elements is summarized and illustrated in Fig. 11. From the XPS spectra of the stainless steel, the overall trend showed that the quantity of O decreased, while the



Fig. 11. Atomic percentage of Fe and O in stainless steel XPS spectra.



Fig. 12. C1s spectra of (a) surface C/TiO₂ 300 (before etching) and (b) bulk C/TiO₂ 300 (after etching).



Fig. 13. C1s spectra of (a) surface C/TiO₂ 400 (before etching) and (b) bulk C/TiO₂ 400 (after etching).

quantity of Fe increased in the depth of the coating. This shows that iron oxides layer exist on the surface of stainless steel. As the depth of coating became deeper, it can be noticed that the amount of oxides decreased, which is also relevant to the higher distribution of Fe. A previous work reported that the surface chemisorbed oxygen is a highly active species during chemical reaction [29]. Accordingly, in this study, it is believed that surface-adsorbed oxygen and the presence of oxide layer assisted and improved coating adhesion.

3.6.2. C1s peak of carbon/titania coating before and after etching

To further understand the interaction of C element, the XPS spectra of surface and bulk C1s element of C/TiO_2 300 are compiled in Fig. 12. The C1s convolution peaks showed C–C, C=O, and C–O bonds. A very low amount of N is observed in the wide-scan spectrum of C/TiO_2 at 300 °C (see Fig. 12 (a)) explained the reason for undetected C=N and C–N bonding. The peaks did not appear because the distribution of C–C bonding was higher than that of C=N bonding. Furthermore, for C/TiO₂-coated samples at pyrolysis temperatures of 400–700 °C, the N1s peak appeared with the detection of C=N and C–N bonds. This was attributed to the low distribution of C–C bonding compared to those of

C=N and C-N bonding. Hence, it can be assumed that the compound containing N in the structure was stable at these temperatures, while the carbon compound was less stable, hence it tended to decompose. As shown in Fig. 12, it was observed that C-C bonding was shifted to lower binding energy from the inner to the outer surface of C/TiO₂. The shift was due to the structure changes of carbon from polymer to pyrolytic carbon. A strong interaction of C-C bonds at the bottom of C/TiO₂ coating explained that the carbon structural changes started near the stainless steel surface. Thus, the shifting of C-C bonding explained that the chemical bonding in C/TiO₂ was influenced by heating and underwent structural changes.

The stainless steel used as the substrate in this study is a great conductor material in which electricity and heat can flow through it. Therefore, during heating, it is expected that high heat transfer occurs at the surface of stainless steel. Hence, the C/TiO_2 coating adjacent to the stainless steel surface would be more likely to undergo structural changes compared to the surface of C/TiO_2 coating. During heating, the carbon located near to the stainless steel surface had higher tendency to transform easily. It was deduced that pyrolytic carbon started to form at the inner surface of C/TiO_2 coating. It was clearly observed that C/TiO_2



Fig. 14. Functional group distribution of C/TiO₂-coated samples.

had a different structure at the inner and outer surfaces. The same trend was also observed for C1s spectra of carbon coating at 300 °C before and after etching (see Supplementary material).

The C1s convolution peaks of C/TiO₂ at pyrolysis temperature of 400 °C are shown in Fig. 13. The convolution peaks showed C–C, C=N, and C–N bonds. The C=N and C–N peaks were observed for C/TiO₂ at 400 °C due to the high bonding distribution after pyrolysis. The C=N and C–N distribution increased parallelly with the increase in pyrolysis temperature, while no C=N and C–N peaks were observed in the epoxy resin and C/TiO₂ at 300 °C, caused by a very low amount of N1s bonding in the structure. Interestingly, at pyrolysis temperature of 400 °C, the shifting of C–C bonding was less significant and there was only a slight shift. This proved that there was not much difference in the structure before and after etching, and it was considered that the structure changed to pyrolytic carbon. Besides that, similar trends were also observed for C/TiO₂ coating at 500–700 °C and carbon coating at 500–700 °C (see Supplementary material).

The distribution of pyrolytic carbon and other functional groups (C-O and C=O) of C/TiO_2 and carbon coating is presented in Figs. 14 and 15, respectively. From the data, pyrolysis temperature affected the distribution amount of pyrolytic carbon. Higher distribution of pyrolytic carbon was achieved at higher pyrolysis temperature. From Figs. 14 and 15, epoxy resin powder had a lower distribution of carbon (C-C bond). This conveys that the epoxy resin structure had more functional groups of C–O and C=O, which is in good agreement with the FTIR spectra (see Fig. 4). In addition, the changes from low to high distribution of carbon with increasing temperature explained the





Fig. 16. C1s spectra of (a) epoxy resin and carbon coating at (b) 300, (c) 400, (d) 500, (e) 600, and (f) 700 $^{\circ}$ C.

structural change from C–C chain (epoxy resin) to pyrolytic carbon C–C chain with the presence of C=N and C–N. However, for C/TiO_2 and carbon coating at 300 °C, the distribution of pyrolytic carbon after etching (bulk) was lower than before etching (surface). This might be caused by inhomogeneous composition in the sample spot area during analysis. It was determined that the maximum carbon functional group percentage started at pyrolysis temperature of 400 °C, which is the stable form of carbon and was optimally formed at this temperature.

3.6.3. C1s peak of carbon/titania and carbon coating

As shown in Figs. 14 and 15, the functional group distribution between surface and bulk coating of all the samples was similar, suggesting that the structure of carbon and C/TiO₂ coating also followed the same pattern. Therefore, C1s element spectra of surface carbon and C/TiO₂ samples are depicted in Figs. 16 and 17, respectively, in order to further study the carbon-metal interaction. The epoxy resin C1s spectrum in Fig. 16 (a) showed a low intensity of C–C and C=O bonding



Fig. 17. C1s spectra of (a) epoxy resin and C/TiO_2 coating at (b) 300, (c) 400, (d) 500, (e) 600, and (f) 700 $^\circ C.$

but a high intensity of C–O bonding. This indicated that the C–O bond interaction was dominant in the structure. For the confirmation of pyrolytic carbon structure, C1s spectra in Figs. 16 and 17 could be classified into three main peaks at approximately ~284.8, ~285.9, and ~ 287.5 eV [25]. The strong peak at ~284.8 eV was assigned to graphitic carbon (sp² hybridized carbon), indicating carbon atoms were arranged in a conjugated honeycomb lattice [25,30]. These peaks are similar with the peaks of pyrolytic carbon reported in previous studies [30,31]. Besides that, at pyrolysis temperature of 400–700 °C (Figs. 16 and 17 (c) – (f)), no carbonyl species peak was detected around 289 eV, which confirmed that the epoxy resin has been successfully converted into pyrolytic carbon and in good agreement with the FTIR spectra (Fig. 4).

Interestingly, the shifting of C1s peaks for carbon and C/TiO₂ samples showed a similar trend. The change of C–C bond in the coated samples was due to the change of epoxy resin structure during the pyrolysis process. The C–C convolution peak of carbon and C/TiO₂ at 300 °C was shifted to higher binding energy compared to C–C bond of the epoxy resin. This showed that structural changes occurred during heating. The highest binding energy of carbon-coated and C/TiO₂-coated samples was observed at approximately \sim 285 eV starting at



Fig. 18. C—C binding energy of carbon and C/TiO_2-coated samples with the results from adhesion test.

pyrolysis temperature of 400 °C. The high binding energy due to the strong interaction of carbon bonding indicates the change in structure with the formation of pyrolytic carbon [30,31]. In addition, a less significant shift of C–C convolution peaks can be seen from pyrolysis temperature of 400–700 °C, which indicated that the structure was adapted to pyrolytic carbon.

The binding energy of carbon-coated and C/TiO₂-coated samples are plotted in Fig. 18. From the figure, carbon at pyrolysis temperature of 300-700 °C and C/TiO₂ at pyrolysis temperature of 400-700 °C showed high binding energy, which led to high interaction of C-C bonding. It is hypothesized that the stronger interaction of C-C bonding exhibits more pyrolytic carbon behaviour, which may lead to the occurrence of higher shrinkage. Therefore, the higher interaction of C-C bond contributed to the high possibility of carbon shrinkage, which resulted in poor coating adhesion on the stainless steel. Unlike C/ TiO_2 coated at 300 °C, the sample had the lowest binding energy of C–C bond, which explained the low interaction of C-C bonding associated with low shrinkage and resulted in good adhesion performance. Besides that, the low interaction of C-C bonding might have been affected by the incorporation of TiO₂ in the structure. As evidence, the results of adhesion performance were correlated with C1s interaction, which showed 2.5% weight loss of carbon coating at 300 °C. In contrast to C/ TiO₂ at 300 °C, no weight loss was detected and no coating detachment was observed.

3.6.4. Ti2p element peak of C/TiO_2 coating

The Ti2p XPS spectra of C/TiO₂ coating samples are presented in Fig. 19. Commercial TiO₂ (Fig. 19 (a)) showed two major peaks associated with Ti2p_{1/2} located at 463.77 eV and Ti2p_{3/2} located at 458.03 eV [32]. However, no significant peak of Ti2p could be observed for C/TiO₂ at pyrolysis temperature of 300 °C. The morphology of C/TiO₂ at 300 °C (see Fig. 3) showed that the TiO₂ particles were embedded in the thick carbon coating. Therefore, it produced a very low atomic percentage of Ti (< 1%) in the XPS survey spectrum, which could not be detected in high-resolution Ti2p spectrum. The binding energy of Ti2p convolution peak for C/TiO₂-coated samples is depicted in Fig. 20.

Decreased Ti2p binding energy was observed for C/TiO₂-coated stainless steel pyrolyzed at 400–700 °C in Fig. 19. The shift of Ti2p was due to the change in the oxidation number of Ti. The Ti2p peak of TiO₂ at 458.03 eV demonstrated the highest oxidation state of Ti^{4+} . Then, the oxidation number was reduced to Ti^{3+} at 457.37 eV and continued to decrease to Ti^{2+} when the binding energy was reduced to 455.58 eV.



Fig. 19. Ti2p spectra of (a) TiO_2 and C/TiO_2 at pyrolysis temperatures of (b) 400, (c) 500, (d) 600, and (e) 700 °C.



Fig. 20. Ti2p and C—C binding energy of C/TiO₂-coated samples at different pyrolysis temperatures.

These results are in good agreement with a previously reported study [32]. However, it was very difficult to relate the relationship between oxidation number and binding energy of Ti with the adhesion properties of C/TiO₂, since the adhesion of carbon-based coating is between carbon and stainless steel, not with Ti. Besides that, coating adhesion depends on the interaction of carbon and stainless steel. Therefore, TiO₂ is not directly associated to bonding but related to the shrinkage. The incorporation of TiO₂ in C/TiO₂-coated sample will prevent the carbon layer from detaching and help in reducing the carbon shrinkage. The shrinkage that occurred was proven by density functional theory (DFT) calculation.

3.7. Factors affecting the carbon-based coating on the surface of stainless steel

This study aims to produce good adhesion coating. Several tests and

12

analyses have been performed to identify the factor that contributes to good coating quality. This is to study the effect of using epoxy resin as the precursor of carbon-based material and the addition of TiO₂ in the formation of the carbon-based coating. Based on the analysis, the adhesion of carbon and C/TiO₂ coated on stainless steel was influenced by three factors: oxide layer on the surface of stainless steel, functional groups of carbon-based coating, and carbon shrinkage. It has been proven that the stainless steel used in this study had oxide layers. Besides that, the functional group of carbon-based coating plays an essential role since more functional groups in the coating structure leads to higher abrasion resistance. Another critical factor that affects the bonding of carbon-based coating is the shrinkage of carbon. In this study, heating process was applied to obtain a carbonaceous coating on the surface of the stainless steel. As confirmed by spectroscopic analyses, the carbonaceous coating was pyrolytic carbon. It is expected that the shrinkage occurred during heating since the pyrolytic structure was more compact compared to epoxy resin. The shrinkage process weakens the adhesion of the carbon-based coating on the stainless steel surface.

The stainless steel used in this study was analyzed and the presence of oxide layer on the stainless steel surface was confirmed by XPS analysis. The existence of oxide layer is crucial, thus, some works have used glass as a substrate and performed surface treatment to create oxide layer ([33,34] [35];). It is believed that the oxide layer has contributed to the coating adhesion. The probability of this phenomenon is that the carbon may be attracted to the oxide layer on the stainless steel's surface and it tends to form physical interaction. The physical interaction force between the oxide layer and carbon in C/TiO₂ structure will lead to stronger adhesion.

From the FTIR spectra, C/TiO₂ at 300 °C consisted of C–H, C=O, C–O, and Ti–O functional groups. Meanwhile, these functional groups diminished for C/TiO₂-coated samples at pyrolysis temperatures of 400–700 °C, except for Ti–O. Interestingly, C/TiO₂ at 300 °C exhibited more functional groups compared to other coated samples and showed the best coating adhesion performance. This emphasizes that the availability of functional groups present in C/TiO₂'s structure affects the abrasion resistance of coating. In addition, increasing pyrolysis temperature changes the structure of epoxy resin to pyrolytic carbon. Hence, it can be stated that the presence of less functional groups in C/ TiO₂ exhibits pyrolytic carbon criteria and results in low adhesion.

In this work, the epoxy resin used had the spinal structure of epoxide with the chain of C–C bond and pyrolytic carbon was formed with cyclic C–C structure [31]. This study predicts that the formation of pyrolytic carbon affects coating adhesion. The main reason for this phenomenon can be due to the shrinkage within carbon structure. The FTIR and XPS data clearly showed that as temperature increased, more pyrolytic carbon was formed and C–C interaction becomes higher. This formation shortens the structure from the long chain C–C of epoxy resin to compact aromatic C–C. The adjustment of structure causes shrinkage within the carbon structure due to the formation of aromatic C–C. The structural shrinkage caused by C–C interaction enables coating to be easily removed from the stainless steel's surface.

This prediction is in good agreement with the results of adhesion performance test, which showed weak adhesion of C/TiO_2 coating starting from pyrolysis temperature of 400–700 °C. Furthermore, the correlation study of carbon and C/TiO_2 coating at 300 °C demonstrated that the incorporation of TiO_2 in carbon-based coating assisted in minimizing structure shrinkage and improved coating adhesion on stainless steel. However, utilization of 20% TiO_2 in C/TiO₂-coated stainless steel. Therefore, this work concerns carbon interaction towards the adhesion of carbon-based coating.

To clarify the correlation between the interactions of C–C towards structure shrinkage, density functional theory (DFT) method was performed to calculate the binding energy, and the shrinkage of coating was measured. In order to study the changes of epoxy resin structure with heating, two model structures (epoxy resin and pyrolytic carbon)



Fig. 21. The effect of pyrolysis on the coating adhesion of carbonaceous coating on stainless steel.

with a similar amount of carbon atoms were used for the calculations. The DFT calculation showed high binding energy difference between epoxy resin and pyrolytic carbon. The former had a binding energy of 211.35 eV, while the latter had a binding energy of 213.57 eV. These results suggest that a compact structure of pyrolytic carbon has a strong C–C bond and affects the volume of the structure. In order to confirm the relationship between the binding energy of C–C bond and the shrinkage of the structure, the volume of the shrinkage was calculated by Avogadro software. The volume of epoxy resin and pyrolytic carbon was 322.75 Å³ and 184.47 Å³, respectively. This result clarifies that the structure shrunk with a high amount of shrinkage of approximately ~148.5 Å³. It shows that a strong interaction of C–C leads to higher shrinkage.

From the analysis and calculation, it could be concluded that as the pyrolysis temperature increased, more pyrolytic carbon was formed with strong C—C interaction associated with the possibility of high shrinkage of the carbonaceous coating. This eventually resulted in weak

adhesion of carbon on the stainless steel's surface. The effect of pyrolysis on the coating adhesion of carbonaceous coating on stainless steel is illustrated in Fig. 21.

4. Conclusions

In this research, by using the powder coating deposition technique, carbon/titania (C/TiO₂) coated on stainless steel has been successfully carried out with high voltage powder spray coating (HVPSC). The physicochemical properties of C/TiO₂-coated stainless steel have been studied. The results from the study proved that the pyrolysis temperature plays an important role in the structural transition of epoxy resin to pyrolytic carbon. The structural change had affected the adsorption properties and adhesion resistance. The results indicate the higher pyrolysis temperature of C/TiO₂-coated stainless steel, the weaker the adhesion of the coating. The optimum pyrolysis temperature with convincing adhesion performance has been determined at the pyrolysis

temperature of 300 °C. The incorporation of TiO₂ in carbon-coated stainless steel had a significant impact on the coating durability, as it was still firmly attached even after the removal of the adhesive tape. Results from the study showed that three factors affect the carbon-based coating; the oxide layer on stainless steel, functional groups, and structure shrinkage. The stainless steel (AISI 304) used in this work was confirmed to contain oxides layer on the surface, which is FeO and Fe₂O₃. These oxide layers assisted the carbon-based coating durability through physical interaction. The results have also shown that the functional groups present in the carbonaceous coating have an effect on the adhesion of the coating. More functional groups in the coated sample structure resulted in lower formation of pyrolytic carbon, which led to good adhesion. The connection of pyrolysis temperature towards structural changes and its effect on adhesion resistance was studied by the interfacial interaction of the carbon-based coated stainless steel. The analysis suggests increasing pyrolysis temperature has a high tendency to shrink the carbon structure because the chain of C-C epoxy resin structure was compressed to cyclic C-C of pyrolytic carbon. The shrinkage has been associated with the strong interaction of the C-C bond. C/TiO₂-coated sample at the temperature of 300 °C exhibited the best adhesion performance with low C-C interaction, indicating low structure shrinkage with the presence of TiO₂. Furthermore, the DFT calculation was done to clarify the phenomena between C-C interaction and structure shrinkage. The higher binding energy that was calculated for pyrolytic carbon explains the strong interaction of C-C bonding in C-C aromatic structure compared to the C-C chain structure (epoxy resin). Moreover, a convincing amount of shrinkage measuring about ~148.5 $Å^3$ clearly explains that the structure has shrunk and possesses high shrinkage formation.

Author declaration

We wish to draw the attention of the Editor to the following facts which may be considered as potential conflicts of interest and to significant financial contributions to this work. [OR]

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

CRediT authorship contribution statement

Farah Syuhada Abdul Halim: Conceptualization, Methodology, Data curation, Formal analysis, Writing - original draft, Visualization. Sheela Chandren: Writing - review & editing, Supervision. Hadi Nur: Conceptualization, Methodology, Writing - review & editing, Funding acquisition, Visualization, Supervision.

Declaration of Competing Interest

No potential conflict of interest was reported by the authors.

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Appendix A. Supplementary data

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