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THE EFFECT OF DIFFERENT SILICA (SiO₂) NANOPARTICLES WEIGHT PERCENTAGE ON THE MORPHOLOGY OF WATER-BASED COATING

Cik Rohaida Che Hak[1], Hishamuddin Husain[1], Nadira Kamarudin[1], Mohd Saari Ripin[1], and Mohammad Aslamilie Mohd Suhil[2]

[1]Malaysian Nuclear Agency
Bangi, 43000 Kajang, Malaysia
[2]Bina Integrated Industries Sdn. Bhd
Taman IKS Seksyen 9, 43650 Bandar Baru Bangi, Malaysia
Correspondence author: rohaida@nuclearmalaysia.gov.my

ABSTRACT

A nano-composite coating was prepared by adding SiO₂ nanaoparticles to a commercial water-based acrylic resin at different weight percents (wt.%). The mixing was done using industrial scale overhead stirrer for about 15 minutes at a moderate speed. The mixture was sprayed to the metallic surface to form a thin layer of matt coating. The surface morphology of the coating was investigated using FESEM and the distribution of SiO₂ was studied using elemental mapping with EDX. As the content of SiO₂ increased from 1 to 3 wt.%, the morphology changed significantly. There were three types of morphology observed on the coating attributed from the nano-composite mixing behaviour. However, from the elemental mapping, SiO₂ particles were homogeneously distributed on the coating. Therefore, the nano-composite coating can be developed using this technique, however the mixing parameters need to optimized to produce a good morphology distribution of surface coating.

Keywords: Nano particles, SiO₂, morphology

INTRODUCTION

Recently, the use of nanomaterials has benefited many industries. In medicine, nanoparticles can be used to deliver drugs efficiently to diseased cells (Xu et al., 2016; Gu et al., 2013), in energy industry the nanomaterials is used to enhance the efficiency of solar cells (Sagadevan, 2013) and in coating industries nano-additives can increase properties of anti-corrosion coatings (Montemor et al., 2007; Montemor et al., 2009) and also enhance the mechanical properties of the coating (Kumar et al., 2015; Wang et al., 2000). There are many types of nanomaterials and the choice of which type is used depends on the desired property. There are nano-sized particles, pigments and fillers, nanopolymer dispersions, and nano-additives that are now commercially available. Among various functional nanoparticles, silica (SiO₂) nanoparticles is one of the promising materials that iswidely used in various industries. SiO₂ is the combination of silicon (46.83%) and oxygen (53.33%) (Azo nano, 2013). In construction industry, SiO₂ are used in tiles, concrete, cement, pipes, glasses, solution and coats (Stat nano, 2018), while in other industries SiO₂ has been successfully used for photocatalysis, as catalyst support in medicine, automotive and corrosion (Capeletti et al., 2018; Mora et al., 2017; Yari et al., 2014; Allahverdi et al., 2012).

Incorporation of nanoparticles in a polymer matrix (coating base materials) can modify the physical and mechanical properties of the matrix leading to several new characteristics which may improve the performance of the coating. In the coating, nanoparticles are expected to improve the existing properties of the coating due to the specific characteristics of its structure such as size, shape and larger surface area. However, the final properties of the coating are affected by many factors such as

the interaction between the nanoparticles and the matrix as well as the degree of nanoparticles dispersion (Rahman & Padavettan, 2012; Kang et al., 2001). One of the biggest challenges in coating industry is the agglomeration of nanoparticles when added into the hybrid matrix. If the nanoparticles agglomerate, the result of the coatings is not good and it become worst when the physical and mechanical properties are affected (Guo et al., 2014). Proper mixing between nanoparticles and matrix is vital to enhance the dispersity or homogeneity nanoparticles on the coating surface and then improve the final desired properties of the coatings. Furthermore, specific characterization techniques are essential in identifying the uniformity of nano particles in the coatings.

Considering that the influence of certain factors, e.g. particle size, mixing process and coating formulations, the objective of this work is to examine the influence of SiO_2 nanoparticles to the surface morphology of coating materials. The field emission scanning electron microscope (FESEM) is the most suitable instrument to characterize the distribution of nanoparticles in the coating materials via surface texture and roughness. With the narrow electron probe from the field emitter gun, in combination with electromagnetic objective lens, the high resolution imaging can be performed on the thin coating surface to determine the size of the nanoparticle. Moreover, the integrated energy dispersive x-ray (EDX) spectrometer can determine the chemical element of the particles. Both FESEM-EDX offer physical and chemical information about the nanoparticles and coating.

METHODOLOGY

Sample Preparation

For raw materials there are two types used in this study: (i) base coating materials which is emulsion A - a clear water-based acrylic resin (supplied by Bina Integrated Industries Sdn. Bhd.) and (ii) commercial SiO_2 nanoparticles – additive that was added to the emulsion. These raw materials do not require any special sample preparation.

For coating sample, it requires sample preparation as follows: (i) preparation of coating substrate (mild steel), (ii) preparation of coating solution and (iii) application of coating onto the substrate. The mild steel was cut into size of 2.5cm x 2.5cm, grinded using 700 grit sandpaper, water rinse and then air dried to obtain a clean, flat and rust-free surface. The base material of coating comprise of emulsion A and other additives (without nanoparticles) was mixed using an overhead stirrer at 1200 rotation per minute (rpm) speed for 15 minutes. The base material was then filtered using 20 micron filter mesh to remove any foreign matters or non-mixable resin. Then, the SiO_2 nanoparticles were added into the base materials from 1 to 3 wt % to form a coating solution, and the stirring continued for another 10 minutes at the same speed. The formulations of the coating solution is shown in Table 1. A dispersing agent was also added in one of the sample. After that, the coating solution was sprayed onto the mild steel substrate and let to dry at room temperature for 30 minutes

Characterization

In this study, the morphology studies and elemental analysis were carried out on both the raw materials and coating samples. The morphology was observed using FESEM , GeminiSEM 500, Carl Zeiss at low and high resolution imaging, whereas chemical element was determined using EDX, X-Max 80, Oxford Instrument. Image analysis was carried out using SmartTiff software by Carl Zeiss and the elemental analysis was done with Aztec software by Oxford Instrument. SiO_2 nanoparticles were scattered on carbon tape and were imaged as it is, while emulsion A was dropped onto a glass

slide, and let to dry at room temperature. Platinum coating was used to aid the imaging process of the emulison A and coating samples.

Table 1: Water based coating composition

Category	Percentage of weight (%wt)
Nano Particle (SiO_2)	0, 1, 2, 3
Dispersing agent	0.3
Base mixture for clear coat (Resin, solvent and additives)	Remaining

RESULT AND DISCUSSION

Analysis of raw materials

Figure 1 (a) shows the micrographs of SiO_2 nanaoparticles at magnification 50,000 times. The micrograph shows two types of morphology; heavily agglomerated and less agglomerated particles. The agglomerates that bulges made the shape and the size of the particles difficult to be determined. However, if we look at the area with a small blob, the shape of the SiO_2 particle is a sphere. Figure 1 (b) shows that when the image in Figure 1 (a) is magnified up to 100,000 times, it is confirmed that SiO_2 nanoparticles are spherical and the size is in the range of 13–19 nm. Figure 1 (c) shows the EDX spectrum of nanoparticles which identified by the two main peaks recognized as silicon (Si) and oxygen (O). The content of Si and O elements determined using qualitative analysis based on factory standard is 30.7% and 69.3% respectively.The unlabeled peak is the carbon element (C) of the adhesive tape. This confirms that the particles used in this study are pure SiO_2 and are in the nano sized range.
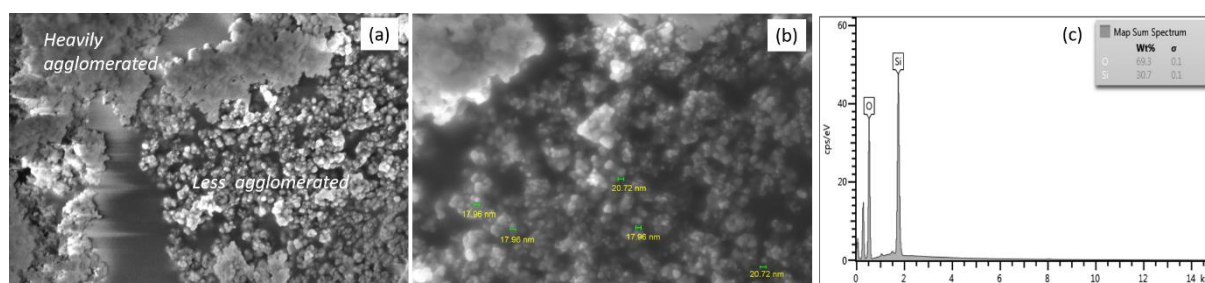

Figure 1: Morphology and elemental analysis of SiO_2 nanoparticles (a) agglomeration of particles; (b) nano-sized SiO_2 particles with spherical shape; and (c) EDX spectrum of SiO_2

Figure 2 (a) shows the micrographs of emulsion A at magnification 10,000 times. Inset shows that emulsion A is composed of spherical particles, uniformly arranged and not clumped. Figure 2 (b) shows that at magnification of 50,000 times, the particles are close to each other without coalesce, this allows the particle size to be calculated easily. The diameter of the particles is in the range of 98 - 143 nm.
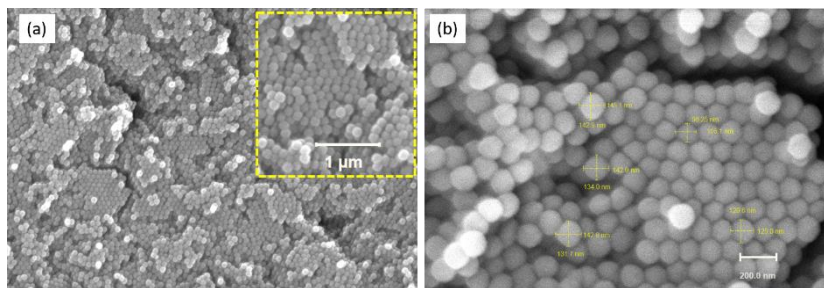
Figure 2: Morphology of emulsion A at different magnifications; (a) 10,000x and (b) 50,000x.

Figure 3 shows the EDX analysis of emulsion A using point and ID mode. The analysis was done on a single particle taken at 4 different spots labeled as spectrum 16 – 19 as shown on the micrograph. All spectra indicate the presence of a main peak identified as carbon element (C) and a weak peak identified as zinc (Zn). Spectra 17 and 18 show the weak peak for sulfur (S) is also identified. Thus, the main element of emulsion A is carbon with a concentration of 99.5 wt% and traced elements Zn and S with a concentration of less than 0.5 wt%.
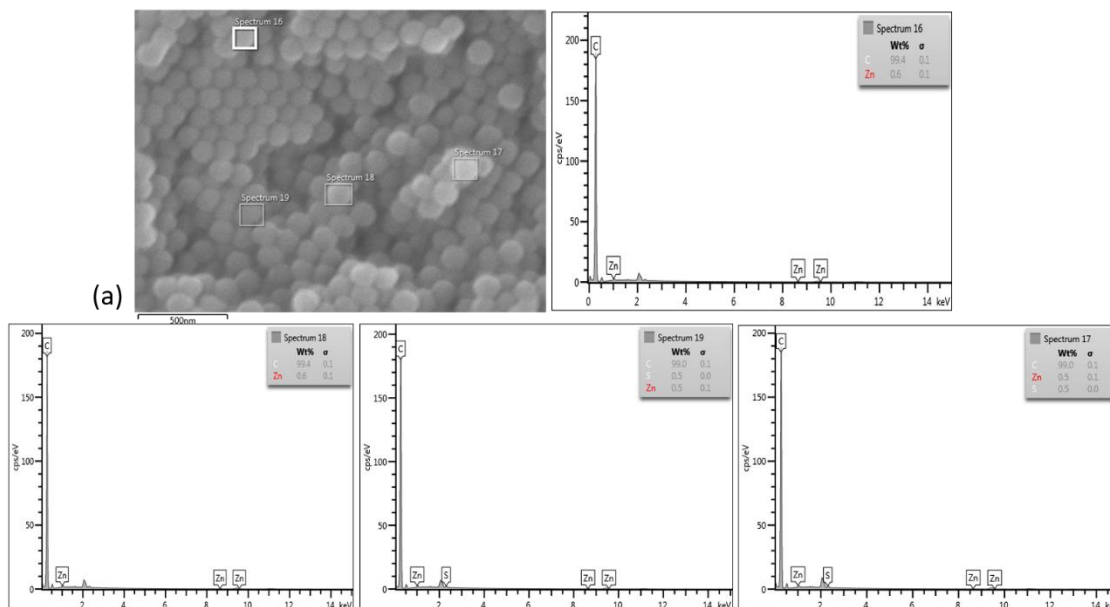

Figure 3 : Elemental analysis of emulsion A using point and ID mode

Analysis of coating samples

Figure 4 shows the morphological changes of the surface of mild steel before and after coating. Figure 4 (a) shows that surface of mild steel is porous and has scratches on it resulting from the grinding process. Whereas Figure 4 (b) shows that coating covers the entire surface of the mild steel, but it is uneven and the surface appeared rough and has textured on it. Figure 4 (c) shows the surface of the coating become more uneven and rougher with addition of 1 wt% SiO_2 nanoparticles. Figure 4 (d) shows the surface of the coating with 1 wt% SiO_2 when added with 0.3 wt% dispersing agent. It is not much different when compared to morphology without addition of dispersing agent. Figure 4 (d-f) show the surface of the coating becomes more uneven and rougher with an increase in the amount of SiO_2 from 1 to 3 wt%.
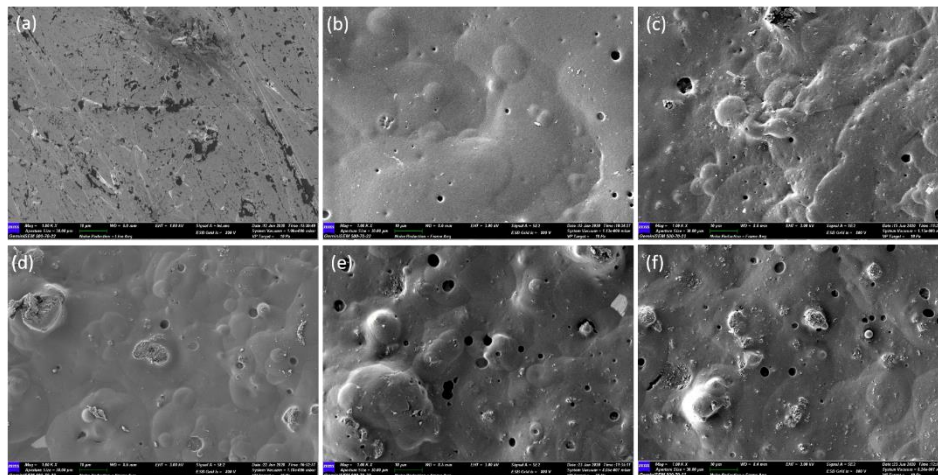
Figure 4 : Morphology changes of different surface; (a) mild steel (substrate); (b) coating without SiO$_2$; (c) coating with 1 wt% SiO$_2$; (d-f) coating with SiO$_2$ at 1, 2 and 3 wt% SiO$_2$ respectively in the presence of 0.3 wt% dispersing agent.

Elemental mapping analysis using EDX was conducted to investigate the distribution of Si element in the coating surface. This is to confirm the presence of SiO$_2$ nanoparticles in the coating material. Figure 5 shows the distribution of Si on the coating surface is homogenous throughout the surface of the coating regardles with and without dispersing agent.
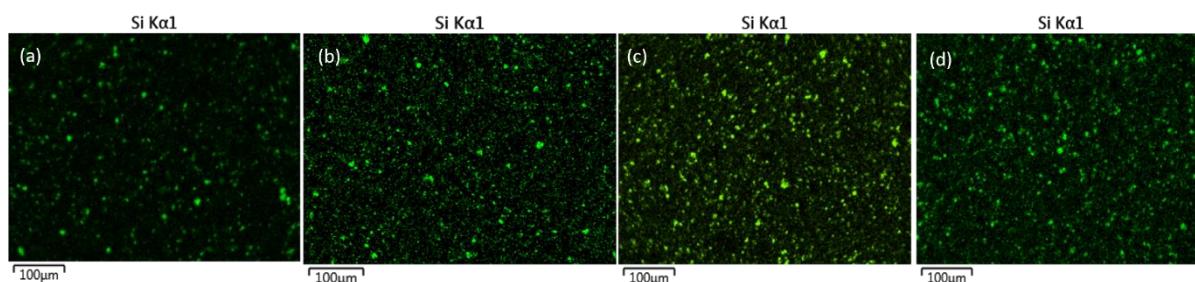

Figure 5: Elemental mapping for Si on the coating surface; (a) 1 wt% SiO$_2$; (b-d) 1, 2, 3 wt% SiO$_2$ in the presence of 0.3 wt% dispersing agent respectively.

The concentration of Si on the coating was calculated quantitatively using the Aztec software and the results are shown in Table 2. The content (wt %) of Si increase with the increasing amount of SiO$_2$ nanoparticles added into the emulsion. There is a slight increase of the Si content when the dispersing agent was added. These results confirmed that the roughness of the surface of the coating is attributed from the SiO$_2$ nanoparticles. This is also indicating that the dispersing agent does not help to disperse the SiO$_2$ in the emulsion during stirring process. Table 2 also shows that element C increases significantly while element Fe decreases exponentially when the coating is applied to the mild steel. Element C comes from the emulsion, while Fe is from the mild steel. Thus, it proves that the coating has covered almost the entire surface of the mild steel although Fe still can be observed using EDX.

Table 2: Elemental mapping analysis of the coating

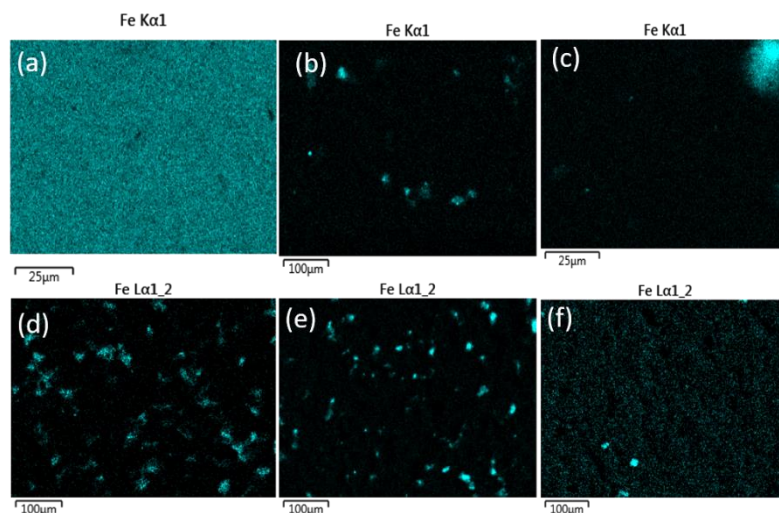| Element (wt%)	Substrate	Coating without SiO₂	Coating with 1 wt% SiO₂, no dispersing agent	Coating with dispersing agent		
				1 wt% SiO₂	2 wt% SiO₂	3 wt% SiO₂
C	5.33	84.09	79.85	85.05	78.32	75.74
O	1.22	13.56	16.73	12.67	15.94	16.37
Fe	93.45	1.14	1.33	5.27	3.41	1.55
Si			1.16	1.21	2.28	3.04
Zr		1.2	0.93			2.87

Figure 6: Elemental mapping analysis for Fe on different surface; (a) mild steel; (b) coating without SiO₂; (c) coating with 1 wt% SiO₂; (d-f) coating with 1, 2 and 3 wt% SiO₂ respectively in the presence of 0.3 wt% dispersing agent.

Further investigation on the distribution of Fe element on the coating surface was carried out using elemental mapping. Figure 6 shows that Fe still appeared after coating is applied with or without addition of SiO₂. Instead, the addition of dispersing agent reveals more Fe (Figure 6 d-e). This explains that the coating has a non-uniform thickness. The different thickness of these coating layers can be clearly seen in Figure 4 (b and d). Locations with thin layer coating reveal the Fe element from the mild steel, whereas location with thicker coating will not reveal Fe but only C from the emulsion. It is also found that C decreases with increasing of SiO₂, clarifying that the added nanoparticles are seating on the surface of the coating. The higher the amount of SiO₂ added, the more uneven the surface of the coating as shown on Figure 4 (d-f).

Figure 7 shows the different morphological types of coating when added with 1 wt% SiO₂ and 0.3 wt% dispersing agent taken at various magnification. Figure 7 (a) shows that at 1,000 time magnification, the coating has rough and uneven surface. Three red circles marked on Figure 7 (a) represent three different morphology. Figure 7 (b) represents circle b at 10,000 times magnification, comprise of a large cluster of SiO₂ particles, which suggests that it is very likely the dispersing agent reacts with the particles cluster and coats it causing the size of the cluster to increase. On the other hand, Figure 7 (c) which represents circle c at magnification of 20,000 times, the SiO₂ particles is seen to remain nano-sized and clustered to each other. This suggests this is the area where the dispersing agent is most likely not to react with SiO₂ particles and does not coat it. Thus, the morphology of SiO₂ is just the same as it is observed before added to the coating solution. Both circle b and c showing that SiO₂ particles are seated on the coating surface. Figure 7 (d) which represents

circle d at magnification of 50,000 times, showing two different morphologies. One is the area with agglomerated particles and the other area is a uniformly arranged particles with larger diameter. Comparing to the micrographs of raw materials, the agglomerated particles could be the SiO_2 and the uniformly arranged particles could be the emulsion A. This micrograph (Figure 7d) suggests that the agglomerated SiO_2 nanoparticles are embedded in the coating surface.
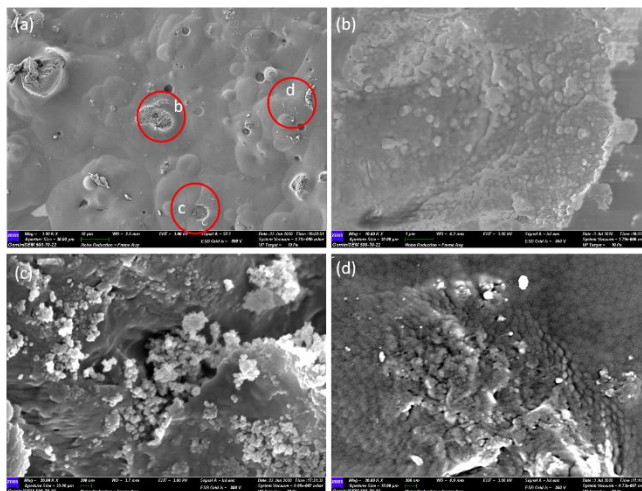

Figure 7: Morphology of coating with 1 wt.% SiO_2 in the presence of 0.3 wt% dispersing agent at different magnifications; (a) 1,000x; (b) 10,000x; (c) 20,000x; (d) 50,000x

These finding suggests that the mixing parameter is likely not suitable to produce a good surface coating. Perhaps, longer mixing time or slower rpm is required to get the additives (nanoparticles and dispersing agent) to be more homogenously mixed with the emulsion. The use of different dispersing agent which more compatible to SiO_2 nanoparticles can be considered to ensure the reaction is more likely to happen. Lastly, further study of the ratio between dispersing agent and nanoparticles is a must to ensure all particles can be coated and then dispersed uniformly on the coating surface. Other studies such as type of impeller for stirring process, sequence of mixing, new base materials formulations are also interesting for future work.

CONCLUSION

In conclusion, the mixing process between base materials, dispersing agent and SiO_2 nanoparticles resulting in different particle distribution on the coating which affects the surface morphology. There are many large-sized SiO_2 particles that are uniformly dispersed on the coating surface representing a cluster of particles that coated with dispersing agent. At the same time, there are also SiO_2 particles that are not coated with the dispersing agent that scattered on the surface of the coating and remained within the nano range sized. There are also SiO_2 particles embedded in the coating and their size remains in the nano range. It is the result of these 3 different morphologies that contribute to the uneven and rough coating layer after being sprayed on the mild steel surface.

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