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Effect of Coating Mild Steel with Polyaniline Added Extracted Silica from Rice Husks and Its Corrosion Behaviour in Hydrochloric Acid Solution

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Abstract

This study was conducted to study the effect of extracted silica content in polyaniline silica composite towards corrosion protection of mild steel in 2 M hydrochloric acid. The silica was extracted from paddy husk by incineration method at 800ºC for 5 hours in a muffle furnace. The white ash formed was then treated with NaOH to obtain trisilicate, which was then treated further with H_2SO_4 to obtain silica precipitate on the top of the solution. Polyaniline (PANI) was prepared by in situ polymerizations of aniline, HCl and potassium dichromate. The polyaniline silica composite (PSC) was prepared by adding the extracted silica, weighing 0.2g (PSC 0.2), 0.4g (PSC 0.4) and 0.6 g (PSC 0.6), into the synthesized PANI. The extracted silica, PANI and PSC 0.6, were characterized by FTIR analysis. The presence of extracted silica is supported by the FTIR analysis. The corrosion protection performance of PANI, PSC 0.2, PSC 0.4 and PSC 0.6 was then compared by immersing the bare mild steel, mild steel coated with PANI and mild steel coated with PSC 0.2, PSC 0.4,and PSC 0.6 in 2 M HCl for 24 hours. The weight loss method was used in this study to investigate the corrosion behaviour of the samples. PCS 0.6 revealed the lowest corrosion rate, which was 0.95 g. The corrosion protection of PSC coating increases directly proportional to the silica contents in PSC. The temperature study showed as the temperature increased, the corrosion rate will also be increased. This occurred due to the rise of kinetic energy as a higher temperature was used. PSC 0.6 showed the best protection even at a high temperature compared to other samples. FESEM analysis was also conducted to observe the surface properties of the sample when immersed in HCl solution.

Keywords: Rice Husk Ash, Extracted Silica, Pani, Weight Loss, Corrosion

Introduction

Previous studies proposed that the corrosion protection performance of polyaniline is reliant on the type of dopants used. However, it was discovered that the oxide layer formed by doped polyaniline has low durability and provides short-term corrosion protection (Fang et al.,2007; Sathiyanarayanan et al., 2007). Recently, researchers had tried to improve the corrosion protection of polyaniline by incorporating polyaniline with fillers. It was found that the incorporation of polyaniline with fillers can improve the corrosion performance of polyaniline. Wu et al (2007) suggested that the better corrosion protection of modified polyaniline is due to the barrier properties of the fillers, which impede the diffusions of the corrosive agent's form reaching the metal surface.

Zinc oxide, titanium oxide and silica are few examples of nano compounds used as fillers in the polymeric coatings. The addition of silica had improved tensile strength, abrasion resistance, hardness, scratch resistance, modulus and weather-ability of the polymer (Zhou et al., 2009). Palraj et al (2015) claimed that silica improved the corrosion barrier performance of the polymeric coating. Thus, in this study, silica will be extracted from rice husks. Rice husk and rice husk ash (RHA) are interesting material sources containing high- quality levels of silica (Real, Córdoba & Alcalá, 2018). Nowadays, silica can be categorized as one of the valuable components and could be applied widely in different fields, such as thebiotechnology field, medical field and raw material for a certain industry. The major factor ofsilica usage in various fields is because of its extremely great performances. Silica is a stable component chemically, physically and thermally (Dulaimi et al., 2011, Chandrasekhar et al 2003). Silica is also present abundantly in a large quantity and according to Chandrasekhar et al (2003), about 0.23 tons of paddy husks were produced as a by-product for each one ton of rice manufactured. Moreover, silica is also compatible with various materials and is relativelycheap (Nandiyanto et al., 2016).

The addition of silica will increase the barrier properties of polyaniline coatings. Several researchers have revealed the effect of commercial silica as barriers in coating but only a few numbers of research discussed extracted silica as a barrier in the coating system. Thus, the focus of this study is to investigate the effect of coating mild steel with polyaniline added extracted silica from rice husks and its corrosion behaviour in hydrochloric acidsolution.

Before the extraction of silica from paddy husk, the paddy husk will be processed in several steps. First, the rice husk will be pre-treated before the extraction of the silica. Then, the rice husk was converted into rice husk ash (RHA) by incineration at a high temperature of the husk. Polymerization of aniline is carried out by oxidative polymerization conducted in the presence of the oxidant. Then, the extracted silica will be mixed with polyaniline and the corrosion performance of mild steel when coated with polyaniline composite silica will be investigated using the weight loss method.

Method

In this research, rice husks (RHs) were washed and rinsed separately three times withdeionized water so that unwanted materials could be removed. The RH was heated with an oven with a temperature of 60°C for 1 day so it can fully dry, then, they were grounded and sieved (48 mesh). Finally, 50 g of each variety of grounded RH was placed under magnetic agitation in 500 mL of a solution of 1 M HCl at room temperature for a day (Chandrasekharet al., 2006) to remove impurities. Subsequently, the mixture was filtered under vacuum with deionized water until a

constant pH will be achieved, and then, it was inserted into the ovenat a temperature of 60°C for a day so it could dry (Costa & Paranhos, 2018).

The thermal treatment was performed to optimize the calcination time and temperature for obtaining the RHAs. The calcination was performed in a furnace with a heating rate of 5ºC min^{-1}. It was burnt off at a temperature range between 800-850ºC with the help of a digital temperature probe. Heating was continued until white ash was formed. The total time required for burning the husk is about 2 hours. After the white ash was formed, it was weighed (Costa & Paranhos, 2018).

The silica was extracted by using the caustic. In this process, the ash was extracted, thus, forming a sodium silicate solution. The solution was filtered for any residual by using a filter paper. The clear filtrate that was obtained from the filtration process will undergo precipitation. The round bottom flask was continuously heated by using a heating mantle withan installed temperature probe. Then, the solution was filtered out from carbon impurities thatmight be produced from the heating process earlier by using a filter press. The residue obtained was weighed and recorded. Meanwhile, the clear filtrate solution obtained was heated in an oven with a temperature around 100-150ºC in a period of 1 hour until it was concentrated. The concentrated solution obtained will be jelly-like, which will be gelatinous sodium silicate and will be weighed. The gelatinous sodium silicate will be inserted in a 200 ml beaker and concentrated H_2SO_4 was added until acidic medium was achieved. This will lead to a chemical reaction that would precipitate the silica and leave sodium sulfate at the bottom of the beaker. A small quantity of water (10 mL) was added to reduce the high exothermic temperature. The solution is cooled for 30 minutes. After that, the precipitate of the solution is filtered to obtain the silica (Todkar et al., 2016).

Next, polymerization of aniline (vacuum-distilled) was conducted by utilizing classical oxidative polymerization operated in the presence of potassium dichromate as the oxidant. The reaction was conducted under 4°C in aqueous 1.0 M HCl with 0.1 M aniline. Aniline was dissolved in 1.0 M HCl and cooled to 0°C. A solution of oxidant in HCl (1.0 M) was added to the mixture dropwise below 4°C (Palaniappan & Shekhar, 2004). Next, the mixture was stirred continuously for 4 hours so that the solution fully reacts. The precipitate was formed in a form called emeraldine. It was cleaned and washed using distilled water and methanol. It will then undergo drying and extraction process using ethanol so that oligomers can be removed (Lukasiewicz et al., 2007). Finally, the resulting salt was washed by acetone and dried by using an oven at 110°C (Palaniappan & Shekhar, 2004). The same steps as in section 3.3 were used to prepare polyaniline composite silica. However, after the addition of oxidant, 0.2 g silica was added into the mixture and let stir for 4 hours. The steps were repeated for the preparation of polyaniline containing 0.4 grams and polyaniline containing
0.6 grams of silica. Polyaniline composite silica was analyzed using FTIR.

The PANI obtained was mixed with acrylic paint. The ratio of acrylic paint: solvent: PANI was 2.5:6:1.5 (Dulaimi et al., 2011). The mixed coating solutions were applied onto mild steel using a coating applicator and were cured for 2 hours at 90°C (Bescher & Mackenzie, 2003). The thickness of the coating will be measured using a microprocessor coating thickness gauge.

The corrosion behaviour of polyaniline composite silica was determined by the weight loss method. The weight loss method was used in this study because of the simplicity of this method in identifying the corrosion rate of the metal. The metal sample was polished by emery paper to remove any rust that formed on the surface of the metal (Dulaimi et al., 2011). The coating of

the metal was measured at three random places on the coating by using a coating thickness gauge. The thickness of the coating was maintained at~50 to 60 microns.It is important to measure the metal coating to prevent the influence of the coating thicknessto the corrosion rate of the sample. Since the purpose of the study is to observe the effect of conducting polymer for corrosion protection, it is significant to maintain a uniform thickness of the coating. Thus, all mild steel was coated using a coating applicator. Figure 1 shows the example of coating on PSC 0.6.

Figure 1: Mild steel is coated with PSC 0.6.

The metal was weighed at the interval of 30 min, 1 hour, 3 hours, 6 hours and 24 hours of immersion. The weight loss was calculated by using Equation (1) (Motlatle et al., 2018):

Weight loss= initial weight-final weight ÷ (initial weight) (1)

For the corrosion study, the mild steel was immersed in the solution of polyaniline composite silica coating at room temperature. Then, all the samples were fully immersed in 2M of HCl solution. The exposure of this metal inside the HCl solution was studied for a totalof one day and the weight of the metal was taken at 30 min, 1 hour, 3 hours, 6 hours and 24hours intervals and the data was recorded to indicate the weight loss by the metal. Then, theeffect of temperature on the corrosion performance of the samples was investigated. All thesamples were fully immersed in 2 M of HCl solution at different temperatures ranging from 298 to 328 at 10 K intervals in 2 M hydrochloric acid for 24 hours.

FESEM analysis was conducted to observe the surface morphology of mild steel and mild steel coated with PANI composite coating. The FESEM analysis was performed at 20 000 X with an electron beam voltage of 15 kV at room temperature. The FESEM imageswere recorded by using HITACHI S4500 with EDAX software Genesis.

Results and Discussion

The characterization of the Silica, PANI and PANI composite silica (PSC) was conducted using FTIR. Figure 2 shows the FTIR of the samples.

From Figure 2, the presence of silica peak can be seen. The most significant peaksthat are present in the spectrum were 3432 cm^{-1}, 797 cm^{-1}, and 1089 cm^{-1}, which indicate the presence of silica in the white ash that has been burnt off at 800°C for 5 hours. According to Tyagi (2017), the peak that ranges from 1070 cm^{-1} to 1095 cm^{-1} indicates the presence of Si- O- Si bonds and the peak ranging from 700 cm^{-1} to 900 cm^{-1} indicates the presence of Si-C bonds.

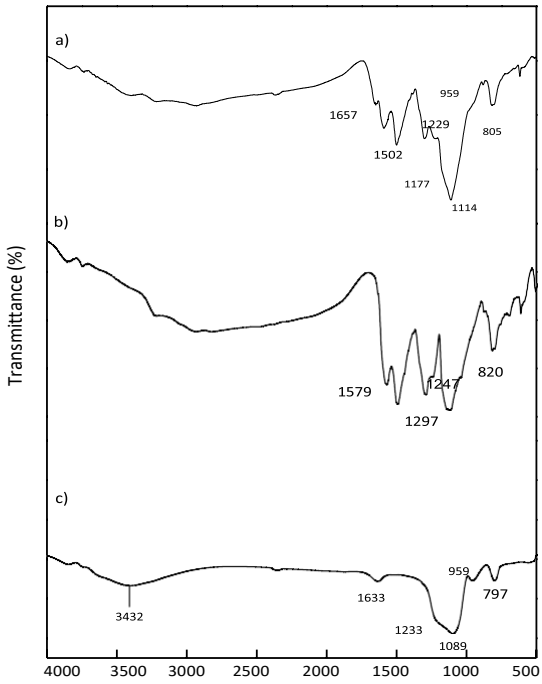

Figure 2: The absorbance of a) PSC 0.6, b) PANI and c) silica, respectively.

In the PANI spectrum, peaks at 1579 and 1496cm^{-1} could be observed. These bands represent the vibrational and stretching of the PANI, corresponding to C=N and C=C stretching and indicating quinoid and benzenoid ring (Tehseen et al., 2016). For PSC, the presence of peaks at 1657 cm^{-1} indicates the presence of Si-O from the silica compound (Gao et al., 2016). A well-defined peak of Si-O-Si was observed at 1114 cm^{-1} (Liu et al., 2004). This band has merged with the band due to (-NH+=) of polyaniline.

The corrosion performance of the samples was determined by the weight loss method.As can be seen in Figure 3, at 24 hours, the weight loss value of the coated metal was lower compared to the uncoated metal. When mild steel is coated with PANI, the weight loss value was 1.6 g. However, after the addition of extracted silica, the weight loss value dropped to 1.16 g for PCS 0.2. PCS 0.6 showed the lowest weight loss value, which was 0.95 g. This indicates that PCS 0.6 has the best protection against compared to other coatings.

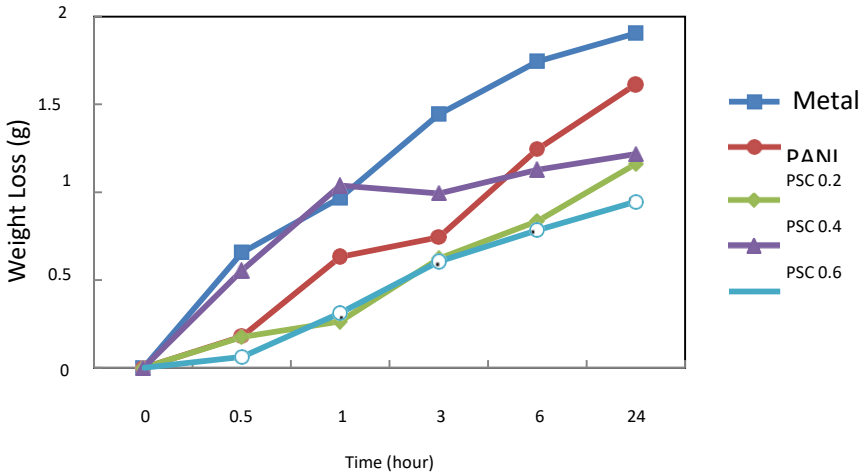

Figure 3: Weight loss of the metal and coated metal against time

In terms of corrosion rate, we could see that there is a decrease in the corrosion rate asmore silica amount was added into PANI. The corrosion rate represents the corrosion of metal mm per year. A lower weight loss value reveals that the corrosion rate is slow. From the observation, the corrosion rate is highest on the blank sample and lowest at PCS 0.6. These occurred due to the presence of the protective coating on the mild steel surface while the blank does not have any protection against 2 M HCl. The presence of silica in the PANI also enhanced the anticorrosion properties. The corrosion rate is higher for the blank sample followed by PANI, then, PSC. This finding was in line as reported by Kumar et al. (2013). The study found that PANI composite has the highest effect on anticorrosion properties onthe coating of the metal. Furthermore, the corrosion protection capability of the coating was enhanced by increasing the amount of silica and PSC 0.6, which shows the most exceptional anti-corrosive properties rather than PSC 0.2 and PSC 0.4. It can be deduced that the corrosion protection properties of all coatings could be due to the presence of the extracted silica in polyaniline. The SiO_2 particle that presents in the PANI chains enhanced the PANI chains, which resulted in a decrease in the degradation of the polymer chain whenever the chain is exposed to an acidic condition (Kumar et al., 2013). Thus, increasing the corrosion protection of the PANI.

The weight loss of mild steel at different temperatures was measured to observe how temperature affects the corrosion rate of mild steel. The weight loss experiments were performed at different temperatures ranging from 298 to 328 at 10 K intervals in 2 M hydrochloric acid. The result reveals that the corrosion rate increased with increasing temperature and reduced when more extracted silica was added into PANI (Figure 4). The corrosion rate increased because of the rise in temperature, which is due to the increase in the average kinetic energy of the coating, indicating that temperature is directly proportional with kinetic energy (Olasehinde et al., 2016). PCS 0.6 revealed the best corrosion protection due to the lower value of weight loss. The decrease in the corrosion rate arising from the increment of extracted silica in PANI is due to the barrier properties of the coating (Lei et al., 2019).

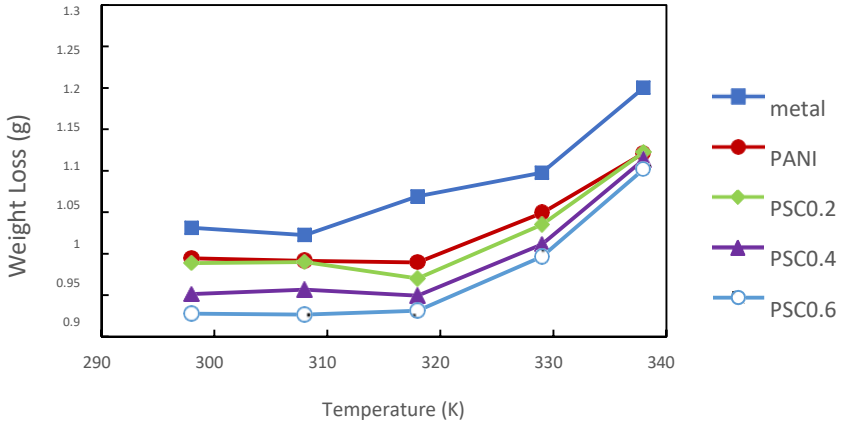

Figure 4: Effect of temperature on the weight loss of mild steel in 2 M HCl

FESEM analysis was conducted to observe the surface morphology of bare metal, uncoated and coated mild steel. Figure 4 shows FESEM image of bare mild steel, uncoated mild steel in 2 M hydrochloric acid and coated mild steel in 2 M hydrochloric acid at 24hours at 10 000 X. As shown in Figure 5 (a), the bare mild steel surface has a very smooth surface. However, a rough surface was observed when the bare mild steel was immersed in
2.0 M hydrochloric acid for 24 hours. This rough surface indica$_c$tes that the mild steel sample was highly corroded. Figure 5 (c) shows the surface morphology of mild steel treated with PCS 0.6. A smooth surface of mild steel can be observed. The smooth surface indicates the presence of a coating on the mild steel surface.

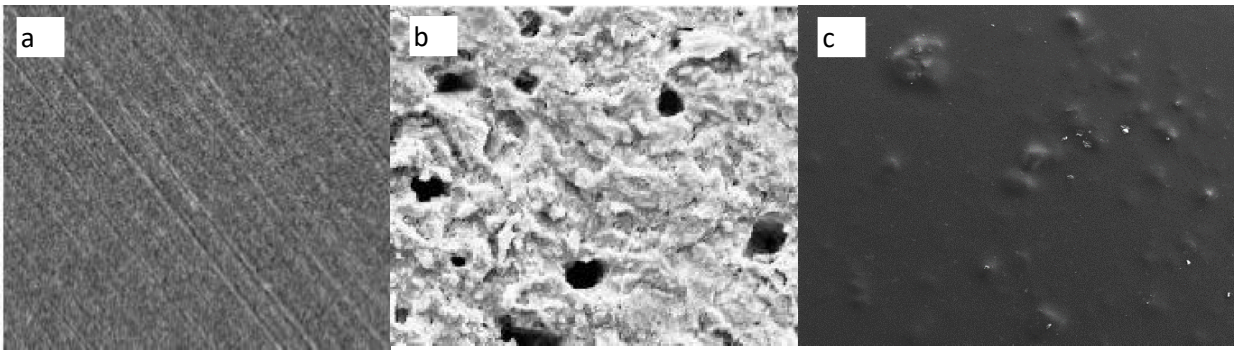

Figure 5: FESEM Analysis a) bare mild steel at 10 000X, b) uncoated mild steel in 2.0 M sulphuric acid at 24 hours at 10 000X, and c) coated mild steel in 2.0 M sulphuric acid at 24 hours at 10 000X

Conclusion

Silica was successfully extracted using NaOH solution. A series of PCS was prepared by *in situ* chemical polymerization with different weight of extracted silica. FTIR peak at 1657 cm^{-1} suggested the presence of extracted silica in the PANI chain. Corrosion results revealed that PCS 0.6 showed the best protection with 0.95 g weight loss. The corrosion study on

temperature effect showed that the corrosion rate increases when temperature increased. The rise in temperature was due to the increase of kinetic energy of the coating. However, the corrosion rate dropped as more silica was added into PANI. This result suggested that there was an increase in the activation barrier of the corrosion process when more silica was incorporated in PANI.

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