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Epoxy Primer Coating Filled Microcrystalline Cellulose Treated with Silane Coupling Agent on Metal Substrate

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ABSTRACT

Epoxy resin was incorporated with microcrystalline cellulose (MCC) for the production of the primer coating. Various sonication times were applied for the purpose of determining the ideal sonication period that provides the best barrier performance. The coatings were also added with various 3-Aminopropyltriethoxysilane (APTES) loadings in order to improve the mechanical and corrosion resistance properties. Fourier Transform Infrared (FTIR) Spectroscopy analysis was carried out to examine the chemical interactions and diffusion between MCC, APTES, and epoxy resin. After nine days of immersion in a 5 % sodium chloride (NaCl) solution, the ideal sonication period was found to be 30 minutes, with no corrosion occurring aggressively and no flaking or blistering appears on the coating. The anti-corrosive qualities of the primer coating were eventually enhanced by the addition of MCC modified with APTES. The addition of APTES had improved the interaction between MCC and epoxy, hence achieving better compatibility and promoting a uniformly dispersed MCC throughout the

epoxy resin matrix. The Tafel polarization results found that the addition of APTES up to 9 % gave the lowest corrosion rate at 0.004 mm/year and the highest polarization resistances at 198.69 kΩ. This is explained by the fact that enough MCC-APTES can serve as a physical barrier and obstruct the paths used by corrosive agent to diffuse. Therefore, the MCC-Epoxy treated APTES coupling agent for metal corrosion protection has thus been successfully created.

Keywords: Epoxy; Microcrystalline Cellulose; 3-Aminopropyltriethoxysilane (APTES); Sonication

INTRODUCTION

The corrosion of metals exposed to the atmosphere is determined by the corrosive interaction of the metal with the corrosion resistance of the aqueous electrolyte to the material on the surface of the material [1]. Corrosion is a dangerous and extremely costly problem. Because of it, buildings and bridges can collapse, oil pipelines break, chemical plants leak, and bathrooms flood. The International Measures of Prevention, Application, and Economics of Corrosion Technology (IMPACT) report, issued today by National Association Corrosion Engineers International (NACE), estimates the global cost of corrosion to be US$2.5 trillion [2]. Many methods have been used in combating corrosion such as the selection of the right material for construction, inhibitors, proper equipment design, electrical protection, and surface coating. The coating is a layer of material deposited onto a substrate to enhance the surface properties for corrosion and wear protection [3]. Hence, the coating can be considered as a low-cost and practical approach to combat corrosion in metal structures. Primers provide superior adhesion to pre-treated metal surfaces as well as corrosion resistance, especially for ferrous surfaces. Epoxy primers are utilized for a wide range of materials because of their great adhesion, mechanical ability, and chemical resistance in wet and high-humidity settings [3]. The thickness of an epoxy primer coating determines its ability to resist corrosion; the thicker the epoxy primer layer, the better the protection [3]. For good corrosion protection, good adhesion of the coating to the steel is required. But it has been observed that epoxy primer aging in the presence

of water can cause it to lose its tack, especially at high temperatures (60 or 80 °C). Hence, the addition of fillers has a great impact to compensate for the mentioned disadvantages of epoxy primer coating. The adherence of polymeric coatings to metal substrates, permeability, thickness, and chemical and mechanical resistance in harsh environments are all factors that influence their corrosion performance [1]. Addition of filler into the epoxy can improve the protective characteristics of epoxy coatings.

There are many types of filler in epoxy primer coatings such as aluminum as metallic filler, aluminum oxide as chemical filler, and nanofiller such as microcrystalline cellulose (MCC). Cellulose micro and nanofiber have a wide range of applications due to their high aspect ratio, crystallinity, and Young's modulus [4]. Low density, biodegradability, and the fact that it comes from renewable sources are all key qualities of cellulose. However, an unmodified MCC-epoxy composite was reported to have poor adhesion between the epoxy and metal. Therefore, the treatment of fillers in epoxy binders will improve their dispersibility and increases the mechanical properties of the cured resin. The adhesion between MCC-epoxy primer resins and metal substrate can be improved by the introduction of a silane coupling agent to epoxy primer. Amine functional silanes can also be used for filler pretreatment or mixed with a hardener fraction. It was reported that the addition of γ-aminopropyltriethoxysilane (APS) into the epoxy-based coating by the wet chemical deposition method produces the greatest adhesion strength to 60 MPa [5]. Dealing with small particles requires a proper preparation procedure because it has a direct impact on the strength and functional properties of the coatings. The dispersion of nanoparticles in the polymer matrix can be made by several techniques such as ball milling, shear mixing, extrusion, calendaring, and sonication. Ultrasonic mixing is a method of distributing the filler in the epoxy coating. According to Kaboorani et al, the ultrasonication technique has the advantage of being easy to operate in the experiment and having a quick synthesis time [6].

In this study, the preparation of epoxy filled with MCC primer coatings with various concentrations of silane coupling agents was studied. The loading of MCC to the epoxy primer coating was specified as 5 wt%. Ultrasonic mixing was used in this study as the mixing method. The prepared coating was tested on its mechanical, physical, and corrosion properties. The sample was characterized by ATR-FTIR. Finally, the corrosion properties

of the primer coating were analyzed through the immersion test and Tafel Polarization method.

EXPERIMENTAL

Determination of the Optimum Sonication Time

First, 0.25 g of MCC was weighed and poured into the epoxy primer coating. The mixture was then stirred for 10 minutes using a mechanical stirrer. Next, the mixture was mixed and dispersed over various sonication times which are 0, 30, 60 and 90 minutes using ultrasonicator at a constant temperature of 27 °C. This homogenized mixture was then coated on the metal substrate. The corrosive properties of the coating were further analyzed.

Surface Treatment of MCC

0.25 g of APTES was measured and dissolved in a mixture of 80/20 (v/v) ethanol/water solvent. The mixture was then stirred using a magnetic stirrer for 1 h which further became hydrolyzed to form reactive silanol groups. 0.25 g of MCC was added to this solvent mixture and further stirred for 2 hrs. Ethanol was removed through evaporation by exposing it to ambient temperature for 24 hrs. This grafted MCC was subsequently kept in the oven at 100 °C for 2 hours for curing followed by thorough washing with water to remove the last traces of ethanol then drying at room temperature. The treated MMC powder was used for further study. This process was repeated using different loading of APTES which are 5 %, 7 % and 9%, as shown in Table 1.

Table 1: Formulation for different loadings of APTES

Microcrystalline Cellulose 5 wt.% (g)	APTES (g)	Percent loading (%)
0.25	0.25	5
0.25	0.35	7
0.25	0.45	9

The Study on the Effect of Silane Coupling Agent on the Coating's Properties.

0.25 g of treated MCC was weighed and poured into the epoxy primer coating and subsequently stirred for 10 minutes using a mechanical stirrer. The mixture was mixed and dispersed over 30 min sonication time using ultrasonicator at a constant temperature of 27 °C. This homogenized mixture was then coated on the metal substrate and the mechanical and corrosive properties of the coating were further analyzed.

CHARACTERIZATION.

Fourier Transform Infrared (FTIR) Spectroscopy was used to identify and analyzed the chemical structure of epoxy primer coatings. FTIR is a method of absorbing radiation and converting it into energy, which is then reflected by sample molecules based on their structure and interaction. The samples were scanned over a wavelength ranging from 4000 cm^{-1} to 650 cm^{-1}, which was used to identify the sample's molecular fingerprint.

Corrosion Testing.

Immersion test

The immersion test was carried out according to ASTM G3712. Firstly, each plate that has been coated with epoxy primer coating was scratched with an 'X' mark and was then immersed in a corrosion environment containing 3.5 % NaCl solution. The plate was left for 9 days in an open environment and at room temperature. Observation on coating condition for corrosion rate of the plate was observed at three days intervals.

Tafel polarization method.

Tafel polarization was carried out according to ASTM G5997. This method was used to measure the corrosion rates. The formulated epoxy primer-coated steel plate was immersed in 3.5 % NaCl solution at room temperature while observed by the Tafel plot. Autolab Potentiostat instrument was used to carry out the polarization analysis of the coating plates. Two plates were tested for each compound.

RESULTS AND DISCUSSION

Fourier Transform-Infrared Spectroscopy (FTIR) Analysis.

The spectra were evaluated on samples of epoxy, microcrystalline cellulose (MCC), APTES, MCC-Epoxy, and MCC-Epoxy-APTES. This analysis is to study and understand the characterization of the interaction of the primer coating. Figure 1 shows FTIR spectra of epoxy, MCC and MCC treated 3 % APTES epoxy (MCC-Epoxy3). The functional group of epoxy was observed in regions 1000-1250 cm^{-1} indicating the presence of the C-O-C ether or C-O(H) in the material. The peaks appear at 1606 cm^{-1}, 1507 cm^{-1}, and 1457 cm^{-1} indicate the -C-C stretching vibration in aromatic ring. A peak at 912 cm^{-1} was attributed to the C-O deformation of the oxirane group. The peaks in the range of 3000 cm^{-1} and 3100 cm^{-1} indicate the presence of the symmetrical and asymmetrical C-H stretch in aromatics. The hydroxyl groups on the MCC surfaces might interact with the epoxide group. The broad band in the range of 3000 cm^{-1} and 3500 cm^{-1} indicates the hydroxyl group (O-H) which may indicate the presence of MCC in the epoxy resin. It was confirmed that MCC contains a lot of hydroxyl groups in the cellulose chains and can form potential hydrogen bonds with epoxy by the absorption bands of stretching vibrations of O-H bonds caused by hydrogen bonds at the range 3500 cm^{-1} to 3250 cm^{-1}. A bond C-O-C stretch was shifted from 1029 cm^{-1} to 1032 cm^{-1} demonstrating the bonding of the MCC and epoxy resin. An ether group and a hydroxyl group would be produced if an epoxide group reacted with an MCC hydroxyl group.

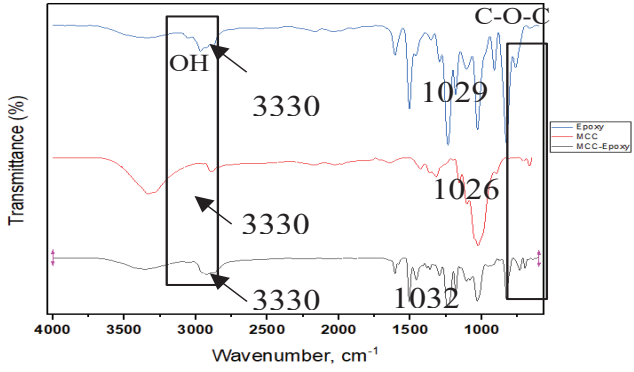


Figure 1: FTIR spectra of epoxy, MCC and MCC-Epoxy3

Figure 2 shows the FTIR spectra of MCC-Epoxy-APTES7. The samples displayed the microcrystalline cellulose bands at 3370 cm^{-1} (O-H stretching vibration) the epoxide group and the hydroxyl groups on the MCC surfaces may interact. The hydroxyl group (O-H) was observed at the bandwidth between 3000 and 3500 cm^{-1}, reveal the existence of MCC in the epoxy resin. The peak observed at 2966 cm^{-1} and 2875 cm^{-1} was attributed to the stretching vibration of C–H, displaying the presence of 3-APTES C-H group. The C-O-C stretch was shifted from 1029 cm^{-1} to 1032 cm^{-1} to indicate the interaction between MCC-Si and epoxy. Due to the enhanced compatibility between the ingredients, the significant affinity of silanol groups for epoxy have increased the interaction and dispersion of MCC-Si into the resin. The bending of -CH_2 and O-C-H was attributed to the peak at 1457.84 cm^{-1}. Affirmation of the Si-O-C band was found at 738.91 cm^{-1}. A successful coating system is when the MCC's small particles dissolve into an epoxy resin and may form an H-bond with the epoxy matrix. The outcomes demonstrated that the 3-APTES alteration of MCC in epoxy resin was accomplished.

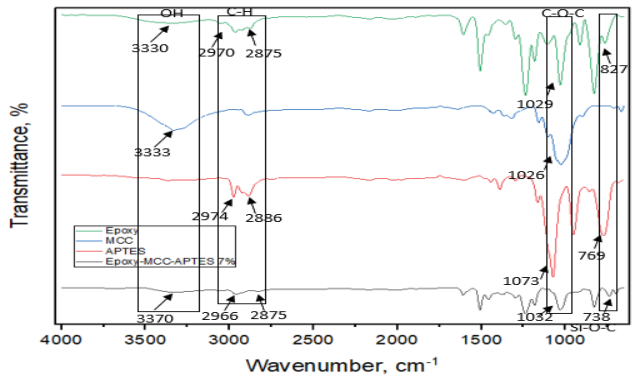


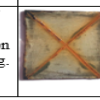
Figure 2: FTIR spectra of epoxy, MCC, APTES and MCC-Epoxy-APTES7

Immersion Test

Table 2 shows the observation and results of the immersion test in 5 % NaCl solution for 3, 6, and 9 days. An immersion test was used to identify the type of failures such as blisters, rusting, cracking, flaking, and delamination of coatings. The samples began to corrode on day 3 while on day 6, the corrosion happened because the reaction existed and on day 9 the corrosion was completely present on the metal plate. When the surface

of the coating got scratched or exposed to the environment, corrosion will happen. The introduction of 'X' mark on the coating have exposed the substrate, hence causing the corrosion to easily form. It was observed that, the increased in sonication time up to 90 minutes, have increased the corrosion to a higher extent and the corrosion also spreads throughout the coating surface. This is due to the fact that, the increased in sonication time have decreased the crystallinity of MCC, thus reducing the tendency of the coatings to resist corrosion. It was reported that prolonged or intense ultrasonication can cause the aggregation of nanomaterials, particularly carbon nanotubes [7]. The chain mobility in the coating was restricted by the nanoparticle agglomeration, and it also caused a small crack in the coating as a result of the localized stress brought on by the degradation of their properties [8]. Because of the poor dispersion, the anticorrosion properties of the coatings deteriorated with an increase in MCC sonication time, leading to coating defects, proving that the MCC's dispersion was crucial to the coatings' ability to protect against corrosion. Agglomeration in the coating due to poor dispersion resulted in the formation of coating surface flaws. These flaws served as the routes for the electrolyte's diffusion, which eventually led to the metal coating interface and led to the corrosion of the metal [9]. The 30 min of sonication time gives the optimum result when the corrosion does not aggressively happen. The uniform dispersion of MCC filled the holes in the coating making the coating resistant to corrosion. Since the fine particles dispersed in coatings can fill cavities and result in crack bridging, crack deflection, and crack bowing, the addition of MCC to epoxy resins offers environmentally friendly ways to improve the integrity and durability of coatings, therefore, the coatings were protected against a corrosive element [10]. As a result, the improvement in MCC dispersion benefits from an ultrasonication time of 30 minutes leads to a compact coating surface with flaws.

Table 2: Observation on 'X' mark result of immersion test various sonication time

Sample	Immersion time (days) 3		6		9	
MCC-Epoxy0		Visible corrosion.		Higher amount of corrosion.		Higher amount of corrosion. Corrosion started to spread on the surface coating.
MCC-Epoxy3		Visible corrosion but not all the "X" mark has corrosion.		Corrosion with flakes on the same spot.		Corrosion on the "X" mark. Flakes on the same spot.
MCC-Epoxy6		Visible corrosion, almost all areas have corrosed.		Higher amount of corrosion.		Corrosion on the "X" mark is much higher. Corrosion started to spread on the surface coating.
MCC-Epoxy9		Visible corrosion, almost all areas have corrosed.		Higher amount of corrosion. and it started to spread on the surface coating.		Higher amount of corrosion. Almost all areas have corroded.

Tafel Polarization

Table 3 displays the corrosion rate and polarization resistance of MCC-Epoxy produced by various sonication time. It was observed that, MCC-Epoxy3 shows the lowest corrosion rate with the highest degree of polarization resistance. Therefore, it can be concluded that higher sonication time destroyed the crystallinity of the MCC thus making the particle size too small as they increase in the surface area of MCC hence the longer sonication time made the particles agglomerate. The increased in sonication time up to 90 min, have increased the corrosion rate to 40.199 mm/year and decreased the polarization resistance to 15.5720 Ω. Based from the results, it is apparent that the optimum sonication time was found at 30 min. The destructive of the crystallinity, particle size and crystal size of MCC gives effect to the epoxy incorporated with filler as a result it decreases the corrosion abilities of the epoxy. The coating's ionic resistance, which is inversely related to the rate of corrosion, is what determines polarization resistance. Therefore, coatings lose resistance to corrosive elements as their rates of corrosion increase. Table 3 shows that the optimum sonication period for Epoxy-MCC results in the lowest corrosion rate (0.5901 mm/year) and the highest polarization resistance (148.060 Ω). This is because stable passivation of the coatings' surface resulted from the formation of a compact oxidation protecting sheet. Epoxy-MCC coating's ability to operate

as a barrier to the primary coating surface and thwart coating delamination was demonstrated by a 30-minute sonication process [11]. This is also because MCC was properly mixed into epoxy resin, which enhances the coating's ability to fend off corrosive substances.

Table 3: Corrosion rate analysis Epoxy-MCC coatings prepared by various sonication time

Sample	Corrosion rate (mm/ year)	Polarization resistance (Ω)
MCC-Epoxy0	1.91	556.58
MCC-Epoxy3	0.59	148.06
MCC-Epoxy6	27.04	30.59
MCC-Epoxy9	40.19	15.57

Table 4 displays the corrosion rate and polarization resistance of MCC-Epoxy-APTES with various APTES loadings. It was discovered that, MCC-Epoxy-APTESS9 shows the lowest corrosion rate. Therefore, it can be concluded that the increased in APTES loadings has enhanced its mechanical, physical, and corrosion characteristics. The comparison of the corrosion rate value for MCC-Epoxy3 with MCC-Epoxy-APTESS9 shows the decrease from 0.59 mm/year to 0.004059 mm/year and an increased in polarization resistance from 556.580 Ω to 198.69 kΩ. Polarization resistance is determined by the coating's ionic resistance, which has an inverse relationship with the rate of corrosion. Therefore, as corrosion rates rise, coatings become less resistant to corrosive elements. Based from the results obtained, the increased in APTES loadings have improved the corrosion resistance of epoxy-based coating. Furthermore, the coatings' ability to inhibit corrosion was improved by the well-dispersion of MCC-APTES at a 30 minutes' sonication in the epoxy resin. As a result, when the coating was exposed to the corrosive environment, it was entirely protected. This is explained by the fact that enough MCC-APTES can serve as a physical barrier and obstruct the paths used by corrosive species to diffuse. The coating's well-distributed characteristics improved the coating's corrosion resistance by reducing MCC-APTES aggregation [12]. However, 5 % and 7 % loading of APTES was not sufficient to enhance the corrosion properties of the coating even though the 30 minutes of sonication time gives the best result to disperse MCC-APTES. Due to the improved interaction between

MCC-APTES and epoxy resin, the high pencil hardness testing at 5H for 7 % and 9 % of APTES loading shows less corrosion in the Tafel measurements test. By being robust enough, the coating is protected against the diffusion of corrosive elements when it has a high hardness strength.

Table 4: Corrosion rate analysis for Epoxy-MCC-APTES coatings containing various APTES loadings

Sample	Corrosion rate (mm/ year)	Polarization resistance (Ω)
MCC-Epoxy	1.91	556.58
MCC-Epoxy-APTES5	4.02	54.48
MCC-Epoxy-APTES7	0.78	131.08
MCC-Epoxy-APTES9	0.004	198.69

CONCLUSION

In general, the mechanical and corrosion properties have been successfully analyzed to study the prospective use of MCC in epoxy primer coating. When used as a filler, MCC shows good compatibility with epoxy resin, as shown by the FTIR study. The epoxide groups' attraction for the hydroxyl group of MCC causes a considerable contact and dispersion of the MCC in the epoxy. It was found that the epoxy primer coating's corrosive capabilities were enhanced by the addition of MCC. Therefore, silane coupling agents can enhance the corrosion resistance of epoxy resins. Based from the immersion test, the compounds sonicated at 30 minutes produced less corrosion on the substrate. The uniformly dispersed MCC in the epoxy have increased the coating resistance to corrosion. For instance, Tafel polarization result revealed that the addition of 9 % APTES produced the lowest corrosion rate with the highest polarization resistances. This was due to the fact that MCC-APTES served as a physical barrier and obstructed the diffusion pathways of the corrosive species. In conclusion, the MCC reinforced epoxy resin primer coating was successfully produced to protect the metal from corrosion. It was also found that 30 minutes of sonication was the ideal time period to dispersed the MCC uniformly.

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