

# Maximizing the functional properties of epoxy coatings using milled Al for enhanced mechanical strength and corrosion resistance

Research Article

Ubair Abdus Samad<sup>1</sup>, Jabair A. Mohammed<sup>1</sup>, Mohammad Asif Alam<sup>1</sup>, Saeed M. Al-Zahrani<sup>2</sup>, El-Sayed M. Sherif<sup>1</sup>, Asiful H. Seikh<sup>1\*</sup>, Hany S. Abdo<sup>1</sup>

<sup>1</sup> Center of Excellence for Research in Engineering Materials (CEREM), King Saud University, Riyadh, Saudi Arabia

<sup>2</sup> Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia

Received 07 October 2024; Accepted 13 November 2024

**Abstract:** Herein, epoxy coatings modified with milled aluminum (Al) were tested for their mechanical strength and corrosion resistance. First, milling was performed on the as-received Al powder for 70 h. The obtained powder postmilling was added to DGEBA-type epoxy resin and cured with an amine-based D450 hardener. The milled Al powder was added in varying weight percentages (1, 2, and 3%). Different types of panels were coated using an automatic film applicator to obtain controlled film thickness and left for curing. Morphological characterization was done using field emission scanning electron microscopy and X-ray diffraction. Thermal stability of the coatings was evaluated using thermogravimetric analysis. Mechanical properties were measured using conventional testing techniques as well as nanoindentation. The analysis results suggest that milling of Al alters the structure of powder postmilling. The milling operations also have an effect on the mechanical and anticorrosion properties of the materials. The results obtained for the prepared modified coating suggest that addition of 2 wt% in the epoxy resulted in balanced mechanical and anticorrosion properties.

**Keywords:** Epoxy coatings • Powder milling • Corrosion • Nanoindentation • EIS • Mechanical properties

## 1. Introduction

Corrosion is an intricate issue associated with metallic structures, especially in hostile weather, and failure of these structures due to corrosion leads to massive financial loss. Applying coatings to protect metallic structures from corrosion is a widely utilized process. Coatings protect metallic surfaces from corrosion and are extensively employed in miscellaneous industries like oil and gas, aviation, and automobile sectors [1,2]. Coatings act as a barricade separating the metallic structures from the surroundings and shielding the material from moisture, UV deterioration, and mechanical wear [3]. Although protecting the metallic substrates against corrosion is the crucial function of a coating, the type and material of the substrate, quality of the coating, and surroundings are

some of the factors that influence the efficiency of the coating.

Developing new coating formulations to improve their electrochemical properties has gained much attention recently. Epoxy-based coatings exhibit better corrosion resistance, superior insulation, and high adhesive properties, and because of these properties they are one of the most commonly used coating materials [4,5]. By using specific curing agents such as hardeners, the epoxy resin is converted from the liquid phase to the solid phase. The curing rate of an epoxy resin–hardener blend increases as the hardener concentration increases, making it prone to reaction with primary amines. The ideal hardener-to-resin ratio should be close to the stoichiometric ratio to avoid having any unstable epoxy network that can result from a higher epoxy-to-hardener ratio. The chemical properties of epoxy-based coatings are improved by selecting a suitable hardener depending on its penetration time and

\* E-mail: aseikh@ksu.edu.sa

wettability. These coatings can also be used as adhesive materials to repair cracks and crevices. However, the major constraint with epoxy-based coatings is their brittleness, which causes defects by mechanical wear [6]. Under corrosive conditions, they deliver excellent barrier properties. However, after prolonged exposure to corrosive conditions, they tend to deteriorate, which can be observed by a considerable increase in the coating's electrical conductivity. With prolonged exposure, the adhesive properties of the epoxy coating also diminish. The pores on the coating surface represent a weak point since they allow the moisture and the corrosive electrolyte to penetrate the upper barrier layer to react with the metal. As a result, significant delamination of the coating and also corrosion on the metal substrate occur [7].

With the development of novel coating formulations, researchers in the public and private sectors are already motivated to improve the efficiency of the current epoxy coatings and limit the level of volatile organic compounds [8]. They have successfully enhanced the adhesion and corrosion behavior of the coatings by incorporating appropriate additives and pigments [9]. The size, distribution, type, and adaptability of the pigments used determine the quality of the epoxy system. Micrometer-sized chromium- and lead-based pigments are commonly used to protect the metal surfaces against corrosion. These pigments protect metallic substrates from corrosion by forming an anti-corrosive layer on their surface. However, their inclusion in epoxy coatings improved corrosion resistance at the expense of impact and abrasion properties [10]. Moreover, these pigments are known to be extremely dangerous to the environment and are inherently toxic. As a result, extensive research is in progress to create novel, eco-friendly anticorrosive pigments. Nano-size pigments have recently been preferred over micro-size pigments due to their improved particle–matrix interaction [11].

Nanocomposite coatings as compared to micro-size particle-incorporated coatings have exhibited better barrier characteristics and corrosion resistance [12]. Aluminum (Al) [13] and zinc [7] powders are two popular metallic pigments used for these coatings. Incorporating these nanoparticles into epoxy resins yields eco-friendly coatings. After the epoxy coating hardens, the nanoparticles fill the tiny holes caused by local shrinkage, increasing the cross-linking density and forming a consistent and homogeneous layer between the external environment and the substrate. As a result, this significantly enhances the barrier characteristics of nanoparticle-pigmented coatings [14].

The development of Al-rich coatings for enhancing corrosion resistance under extremely hazardous conditions represents a significant breakthrough in nano-composite coatings.

Al, a non-hazardous substance [15], is incorporated into the epoxy coating matrix while adhering to environmental protection regulations. This integration causes the formation of oxide and hydroxide layers of Al over the coatings, which provides strong corrosion resistance [16]. Moreover, its glossy look, high scratch resistance, cost-effectiveness, and enhanced electrical and mechanical properties make Al an effective filler material in various industries such as automotive, plastic, and painting [17]. The cathodic protection mechanism of Al is an additional advantage, further preventing corrosion. Properties of the barrier for the coatings in contradiction to the electrolyte's permeability can be further boosted by effectively plugging the polymeric coating's pores using corrosion product precipitate. Furthermore, adding Al powder to epoxy coatings strengthens their corrosion resistance by causing corrosion products to form on steel surfaces [13]. Incorporating the Al pigment into zinc-rich coatings has also been confirmed to improve corrosion resistance while simultaneously reducing the cathodic sacrificial behavior [18,19]. Researchers have investigated the electrochemical behavior of nanocomposite epoxy coatings with nano-Al pigments, leading to the conclusion that these coatings demonstrate heightened resistance to corrosion due to the formation of oxide and hydroxide layers of Al, which act as barriers, preventing corrosive fluids from permeating the matrix [20,21].

In our previous published work, the behavior of different epoxy formulations has been studied [22] with the addition of as-received Al powder [23]. In the present study, we have incorporated nano-crystalline Al powder into the best epoxy formulation. The ball-milled Al (MAL) pigments with different wt% were incorporated into the amine-cured DGEBA epoxy coatings. This process modified the Al-milled particles. The Al-milled particles were homogeneously distributed in the epoxy matrix using an appropriate coupling agent. The prepared coating mixture was then applied to the substrate surface, and it was characterized using a variety of techniques. The morphology of prepared formulations before and after the incorporation of Al particles was examined using field emission scanning electron microscopy (FE-SEM). Nano-indentation was used to analyze the mechanical characteristics. Finally, electrochemical impedance spectroscopy (EIS) method was implemented to evaluate the electrochemical behavior of the coated substrates.

## 2. Experimental procedures

### 2.1 Materials

Pure Al powder with 99.5% purity and 2  $\mu\text{m}$  average particle size was sourced from Alfa Aesar, located in Massachusetts,

USA. Epikote 1001-X-75 from Hexion Chemicals was used as the main matrix resin. Aradur D-450 from Huntsman Advance Materials was used as the curing agent. Acetone, MIBK (methyl isobutyl ketone), and xylene were purchased from the local market. Additives such as leveling agent, dispersing agent, and air release agent were procured from BYK-Chemie GmbH, Wesel, Germany.

## 2.2 Preparation of coating

This high-purity Al powder was subject to mechanical milling in a planetary ball milling machine from Fritsch, Pulverisette, P7 model. During the milling process, the Al powder plus 10 mm stainless-steel balls were placed in cylindrical stainless-steel containers. The powder to ball weight ratio was carefully maintained at 1:10 to ensure effective milling. The milling process was carried out for a total duration of 70 h, with the ball mill operated at a rotational speed of 150 revolutions per minute (rpm). To prevent cold welding and agglomeration of the Al particles during milling, a process control agent (PCA) such as 1 wt% stearic acid was used. Additionally, to manage the heat generated inside the milling jars, the machine was paused periodically throughout the milling process. This intermittent pausing is necessary to dissipate heat and prevent excessive temperature rise, thereby ensuring the stability and uniformity of the milling conditions.

The preparation of the formulations began by sonicating the ball-milled nano-Al powder with acetone in a small beaker. The precise quantity of required Al powder, indicated in Table 1, was carefully measured and then dried at 100°C for 24 h using an oven to remove any residual moisture before its addition to the formulation. To ensure effective dispersion of the particles, the required amount of silane was added to acetone. This silane–acetone mixture was then sonicated continuously for 3 min to promote thorough mixing. Following that, the silane–acetone solution was added to the dried Al powder, and sonication was continued for an additional 15 min to ensure uniform dispersion of the Al particles throughout the solution. Meanwhile, the required quantity of the resin was

placed into a dried beaker. This resin was then diluted with small quantity of xylene with the help of a mechanical stirrer to facilitate the homogeneous mixing of particles.

Post-sonication, the treated particles were incorporated into the diluted resin and thoroughly mixed using a mixer operated at a speed of 5,000 rpm. This high-speed mixing ensured proper dispersion of the particles within the resin and also helped in the solvent removal in order to maintain the application viscosity. Once the mixture was thoroughly blended, the formulation underwent a degassing process to eliminate any remaining solvent and trapped air bubbles, which could otherwise affect the quality and consistency of the coatings. Following the degassing step, the formulation was allowed to stabilize at room temperature for 10 min, ensuring that it reached a uniform state before further processing. Subsequently, the appropriate quantity of a hardener, specifically polyamidoamine, was precisely added to the mixture and mixed gently to avoid air trap in the resin, and the final coating mixture was then applied to metal substrates for characterization. This application was carried out using a bird applicator with 120 µm gap size, in conjunction with a Sheen automated film applicator, to achieve a uniform coating on the substrates. Table 1 provides details of all the ingredients used in the formulation, including their respective percentages, ensuring a clear understanding of the composition of the mixture. The coating properties were evaluated after 7 days of application on the panels to ensure complete curing at room temperature.

## 2.3 Measurements

The morphological and structural analyses of the prepared coatings were performed using a field emission scanning electron microscope, model JSM-7400F (JEOL, Japan) and XRD analysis was carried out using a D8 Discover from Bruker, Germany, to verify the incorporation of particles and the corresponding changes in the prepared coatings in the scanning range of 10°–70°; the scans were performed at a slow scan rate of 0.2°/min.

The thermal characteristics of the coatings were measured using thermogravimetry analysis (TGA) using an

| Sample | Resin (g) | MIBK (ml) | Xylene (ml) | Silane | MAI powder wt% | Additives* | PA-450 (g) |
|--------|-----------|-----------|-------------|--------|----------------|------------|------------|
| MAI-1  | 83.34     | 8         | 8           | 2.0    | 1.0            | 1.0        | 15.90      |
| MAI-2  | 83.34     | 8         | 8           | 2.0    | 2.0            | 1.0        | 15.90      |
| MAI-3  | 83.34     | 8         | 8           | 2.0    | 3.0            | 1.0        | 15.90      |

\*Additives: Dispersing agent, leveling agent, and air release agents (similar quantity).

**Table 1.** Formulating ingredients of the prepared epoxy coatings fabricated with MAI particles.

SDT Q600 (TA Instruments, USA). The coatings were subjected to thermal decomposition at an elevated temperature of up to 600°C in an inert gas environment (nitrogen) to evaluate the thermal stability of the prepared coatings. The mechanical characteristics of coatings were analyzed using conventional mechanical testing such as pendulum hardness according to ASTM D-4366, impact according to ASTM D-2794, and scratch resistance according to ASTM D-7027. Pendulum hardness is the measure of the number of oscillations on a coated surface. The scratch resistance was measured using a stylus with increasing load against the movable bed of the sample holder, with the stylus facing the sample surface. In the case of measuring the strength of the impact, a standard fixed weight was dropped on the sample surface with variable height in order to determine the impact strength of the sample.

The mechanical properties of the prepared coatings were measured using a Nanotest platform from Micromaterials, Wrexham, UK, with a Berkovich-type indenter employed to extract the elastic modulus and hardness values. The coating's characteristics were examined using a Berkovich-type indenter utilizing the load control program. For nanoindentation, the coated samples were exposed to deformation using an indenter, and coatings were subjected to a maximum load of 250 mN for a period of 60 s to nullify the effect of creep (because of the viscoelastic nature of polymers). Then, unloading was performed to extract the modulus of samples. Both the loading and unloading were performed at a similar rate of 1 mN/s.

The Oliver and Pharr method is a widely recognized technique for interpreting nanoindentation data, which facilitated the measurement of mechanical properties such as hardness and elastic modulus of materials. This method provides a systematic approach to analyze load–displacement data obtained during indentation tests. The nanoindentation process begins with a sharp indenter, typically made of diamond, which is pressed into the surface of the material under a controlled load. The indenter is driven into the material to a predetermined depth, and the load ( $P$ ) and displacement ( $h$ ) are recorded continuously throughout the loading and unloading phases. These data form the basis for subsequent analysis. The hardness ( $H$ ) of the material is defined as the ratio of the maximum load applied to the projected area of the indentation at that load. The formula for calculating hardness is given by  $H = P_{\max}/A$ , where  $P_{\max}$  is the maximum load applied during the indentation and  $A$  is the projected area of the indentation. The projected area can be derived from the geometry of the indenter and the depth of penetration, and it is typically determined using the following equation:  $A = \pi/2(h_{\max} - h_t)^2$ , where  $h_{\max}$  is the maximum depth of penetration and  $h_t$  is the depth at which the unloading begins.

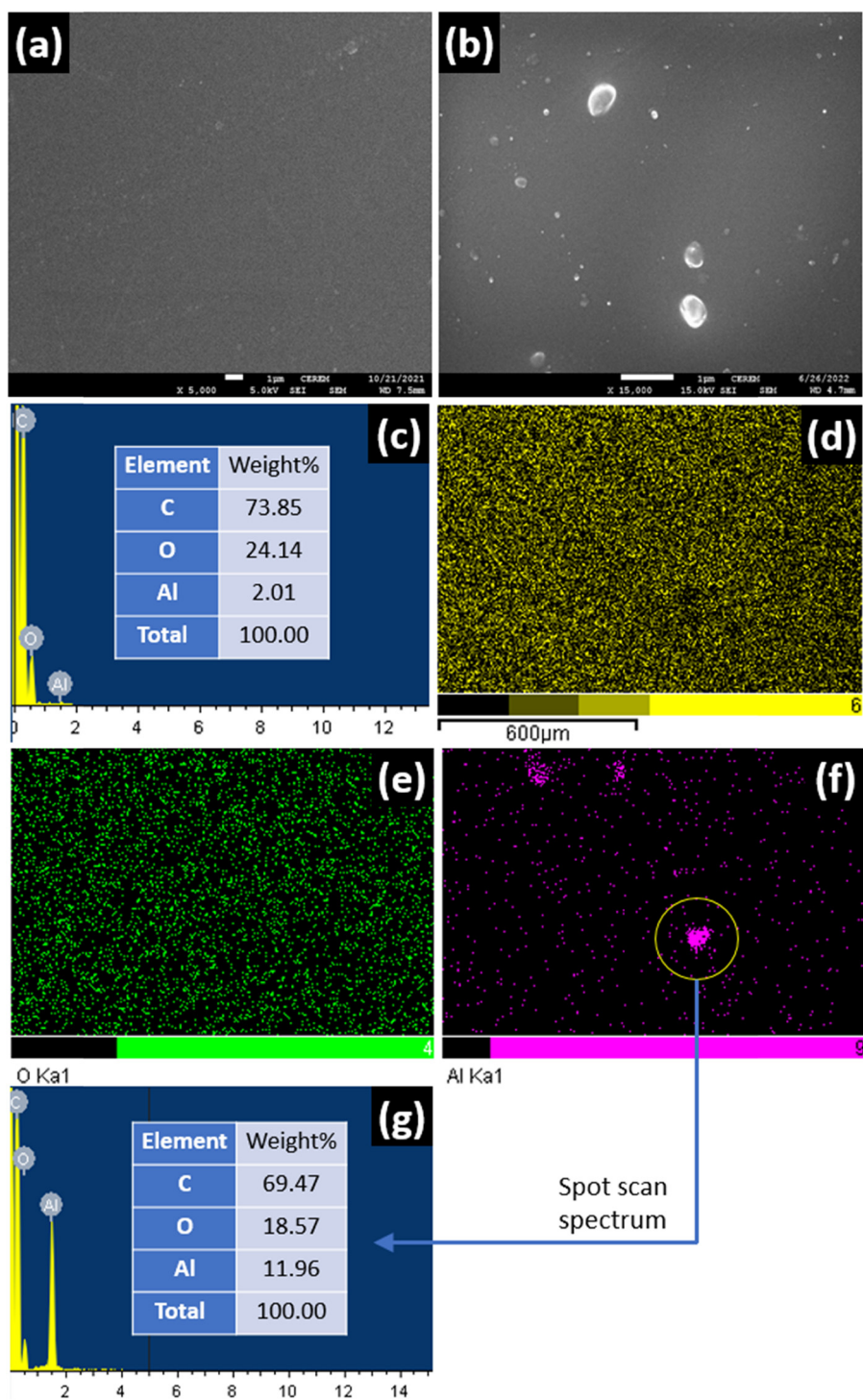
The elastic modulus ( $E$ ) is obtained from the unloading curve data. During the unloading phase, the relationship between the contact stiffness ( $S$ ) and the elastic modulus is used, which is expressed as  $E = \beta(A/S)$ , where  $\beta$  is a geometric factor that depends on the indenter shape. The contact stiffness ( $S$ ) is defined as the slope of the unloading curve at the maximum load, and it is calculated from the load–displacement data.

The corrosion behavior of the coated panels was evaluated by EIS, the measurements were done by using a three-electrode cell of the Autolab PGSTAT 30 from Metrohm, The Netherlands. In a three-electrode configuration, the setup consists of three distinct electrodes – working electrode: this electrode is typically a coated panel under investigation. Reference electrode: this electrode provides a stable potential. In our case, we used a common Ag/AgCl reference electrode. Counter electrode: the counter electrode completes the electrochemical cell electrical circuit. It is typically made of an inert material; herein, we used a platinum electrode. The coating surfaces were exposed to 3.5 wt% NaCl solution ranging from 1 h to 30 days. All the tests for different exposure periods were conducted under similar conditions in a frequency range of  $1 \times 10^5$  to 0.1 Hz using a  $\pm 5$  mV wave perturbation.

### 3. Results and discussion

The surface morphology of the prepared coatings analyzed using SEM is presented in Figure 1. As can be seen in Figure 1a, the epoxy without any added particles possesses a very smooth and clear surface. In Figure 1b, the addition of milled particles is quite clearly visible as white marks on the coating surface, well distributed all across the coating sample. This suggests the addition of particles is homogeneous all over the sample. The addition of MAI particles does not create any voids in the coating as there are no signs of cracking in the sample's image. Some bigger size particles are clearly visible in the SEM image due to the fact that with prolonging the milling of Al powder the particles tend to fuse again. As reported in the literature, the elongated milling hours expose the powder to cold weld [24]. Elemental analysis by energy-dispersive X-ray (EDX) spectroscopy was also performed on this sample, which confirms the presence of Al particles in the coating, as can be seen in the obtained EDX graph presented in Figure 1c along with obtained weight percentages.

Figure 2 presents the XRD spectra of plain epoxy, unmilled, and MAI powder and of epoxy coatings modified with MAI powder. Figure 2a shows the spectrum of epoxy without any modification. It can be seen that the obtained

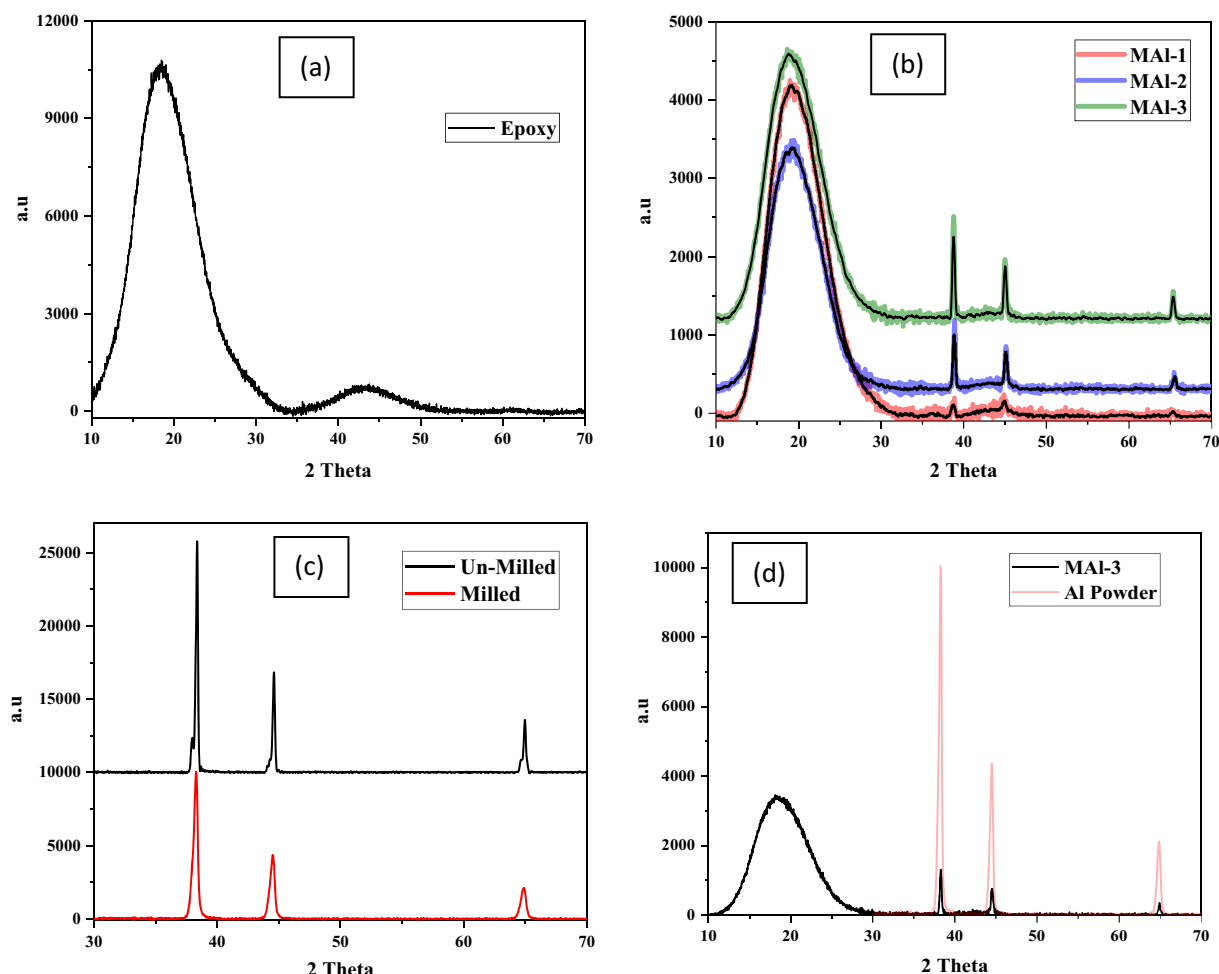


**Figure 1.** (a) SEM image of epoxy coating without any particles, (b) epoxy coating with the addition of 2 wt% MAI, (c) obtained EDX spectral scan with corresponding elemental percentages of epoxy coating added with 2 wt% MAI, (d–f) mapping for the C, O, and Al elements, and (g) the EDX spot scan spectrum of the agglomerated Al particles encircled in (f).

spectrum is completely amorphous as epoxy itself is amorphous. The addition of MAL is clearly evident from the modified coatings' spectra (Figure 2b), in which the crystalline peaks of the added material can be clearly witnessed in comparison to the amorphous epoxy material. The intensity of the peak appearance is also seen to increase with the increasing percentage of added milled powder. The wide peak in the  $2\theta$  range of  $10^\circ$ – $30^\circ$  is due to the amorphicity of the epoxy; the peak also loses its intensity with milled powder addition, imparting a slightly crystalline behavior. The effect of postmilling can be seen in Figure 2c, which compares the XRD spectra obtained pre- and postmilling operations. The obtained postmilling spectrum suggests a decreasing crystal size, evident from the broadening of peaks in  $2\theta$  ranges corresponding to the spectrum of unmilled powder. Such broadening after milling reflects the transition of the crystallographic structure of the

powder from crystalline to polycrystalline. The broadening, along with the decrease in peak intensity, gives a reliable indication of the grain size reduction in the material [25]. The peak conformation on the obtained XRD spectra was also made by overlapping the spectrum obtained for the MAL powder with the modified coating spectrum made with the highest percentage of 3 wt% MAL. It can be seen in Figure 2d that the peaks are overlapping at the corresponding position of appearance, same as that of the MAL powder sample (JCPDS card number 96-431-3218) at  $2\theta$  values of  $38.27^\circ$ ,  $44.51^\circ$ , and  $64.90^\circ$ , respectively.

The TGA curves for the epoxy as well as modified epoxy coatings with different percentages of MAL are presented in Figure 3. The obtained curves suggest an improvement in the thermal characteristics of the prepared coatings. The weight loss for all the coatings started around  $100^\circ\text{C}$  with the removal of solvent traces in the epoxy complex network



**Figure 2.** XRD spectra of (a) neat epoxy, (b) different percentages of MAL filled coatings, (c) as-received (un-milled) and MAL spectra, and (d) MAL-3 along with MAL powder (overlapping).

structure. The initial decomposition of the material started at temperatures above 200°C, which corresponds to the decomposition of loose chain, un-participated reactants. The main degradation of the chain starts above 300°C.

The obtained data from the graphs, as shown in Table 2, suggest significant enhancement in the epoxy thermal characteristics as the modified coatings are capable of withstanding higher temperatures than the clear epoxy coating. By incorporating MAI particles, the degradation temperatures ( $T_d$ ) were enhanced. The most effective response of coatings with MAI addition was witnessed at  $T_d$  15%, where the prepared coatings showed significant improvement in withstanding the temperature of 334°C with 2% MAI addition as compared to 240°C for epoxy without modification. This improvement is approximately 39%, which suggests that adding Al particles alters the thermal decomposition of the modified coatings and can play a crucial role in the areas where the temperature is an important aspect. The other  $T_d$  values at various weight loss stages for modified epoxy coatings were also proved to be superior in withstanding temperature than epoxy alone. The  $T_d$  values at 25, 50, and 75% weight loss were found to be increased by 6.1, 3.1, and 3.4%, respectively, in comparison to unmodified epoxy coatings.

In order to understand more about the effect of MAI particles with different percentages on the final mechanical properties of the modified coatings, different characterizations were performed on the coating panels. Table 3 presents the obtained characterization values from the test performed on the samples, also the dry film thickness (DFT) was also measured for the result comparison.

The values obtained after testing are presented in Table 3. There is a minor improvement in the mechanical properties in all domains. The impact strength with different added percentages of MAI shows slight improvement, whereas the scratch

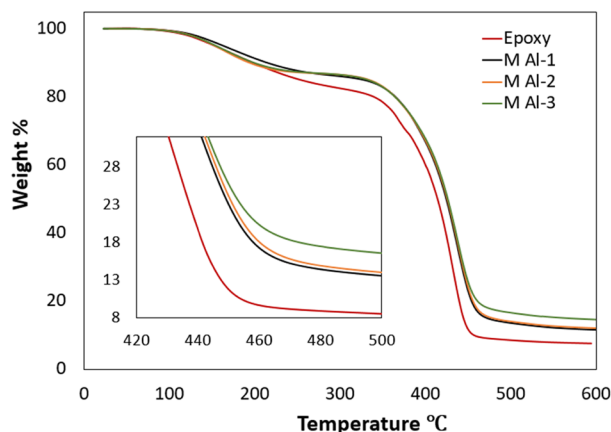
| S. code    | $T_d$    | $T_d$    | $T_d$    | $T_d$    | Residue (%) |
|------------|----------|----------|----------|----------|-------------|
|            | 15% (°C) | 25% (°C) | 50% (°C) | 75% (°C) |             |
| Epoxy [22] | 240.22   | 360.54   | 413.03   | 435.24   | 7.88        |
| MAI-1      | 327.28   | 381.65   | 424.57   | 447.88   | 10.41       |
| MAI-2      | 334.18   | 381.29   | 425.66   | 449.11   | 10.92       |
| MAI-3      | 332.33   | 382.07   | 426.41   | 451.05   | 13.35       |

**Table 2.** Recorded temperature at various percentages of weight loss.

resistance shows greater improvements, especially with 2 wt% addition. The pendulum hardness, which is the measure of surface hardness, was the highest in the coating with 3 wt% addition. Thus, this suggests a mild brittle nature in comparison to other coatings. This brittle nature was also exposed when the other two tests were performed on the coatings, which results in inferior values than the similar particles loaded in lesser quantity (with 2 wt%).

It has been observed from both Table 3 and Figure 4 that the mechanical behavior of the prepared coatings enhanced proportionally with increasing Al particle percentage up to 2%, beyond which the mechanical properties began to decline with the addition of 3% Al. This is due to the reduction in crystallinity of the epoxy, as witnessed by XRD, and also due to the filling of free volume spaces in the complex network structure of epoxy resin. The reduction of impact and scratch with 3 wt% addition suggests that 2 wt% is the optimum balanced percentage. As reported from the literature, by adding filler particles to the epoxy coatings, an increase in the coating's properties up to a certain limit will be achieved [26,27].

Nanoindentation was performed to evaluate both the hardness and modulus of elasticity of formulated coatings



**Figure 3.** Temperature vs weight loss TGA curves for neat epoxy and modified coatings containing various proportions of MAI powder.

| S. Code    | DFT ( $\mu\text{m}$ ) | Hardness<br>(MPa) | Scratch<br>test (kg) | Impact<br>resistance<br>(lb/in <sup>2</sup> ) |
|------------|-----------------------|-------------------|----------------------|-----------------------------------------------|
| Epoxy [22] | 100 $\pm$ 10          | 159               | 5.5                  | 48                                            |
| MAI-1      | 100 $\pm$ 10          | 162               | 6.5                  | 50                                            |
| MAI-2      | 100 $\pm$ 10          | 165               | 7                    | 53                                            |
| MAI-3      | 100 $\pm$ 10          | 171               | 6                    | 51                                            |

**Table 3.** Mechanical properties of produced epoxy coatings with different Al percentages.

embedded with various percentages of Al particles. A load-controlled testing program was implemented to produce indentations with the aid of a Berkovich-type indenter machine. Epoxy coatings were loaded up to the highest load of 250 mN, under the loading/unloading conditions of 10 mN/s. Once reaching the 250 mN load, the applied load was maintained for 60 s before commencing the unloading. Each coating sample was subjected to a minimum of six indentations at corresponding locations relative to the first indentation for consistency purposes, while the results are provided as an average of all the indentations performed.

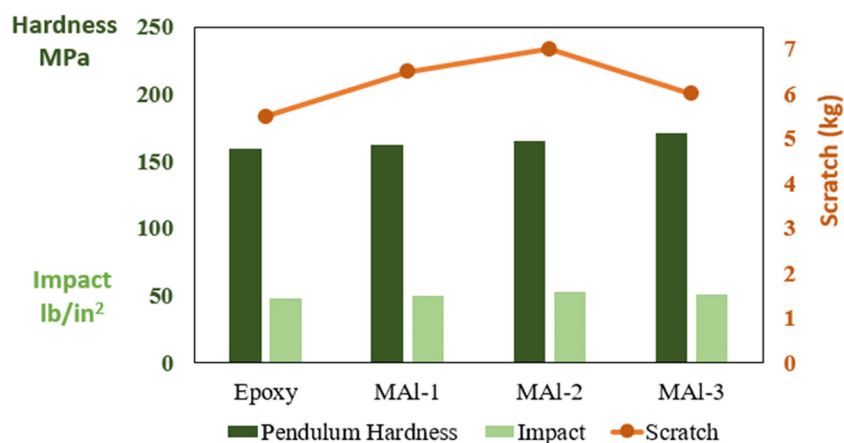
In Figure 5, load versus displacement curves of 250 mN load for all the coatings with different percentages of Al particles are shown. In the loading section of all the samples, a smooth loading behavior is witnessed without any abrupt discontinuation, suggesting a defect-free coating surface. The resistance to indentation force has been enhanced due to the presence of Al particles in the epoxy resin. The load vs displacement curves move to lower values, signifying that the load-bearing capability of the prepared epoxy coating has been strengthened.

The samples were indented by means of software offered by Micro Materials Inc. to assess their modulus and hardness. The software calculates the hardness and modulus of the coatings using the Oliver and Pharr [28] approach. Table 4 displays the acquired results.

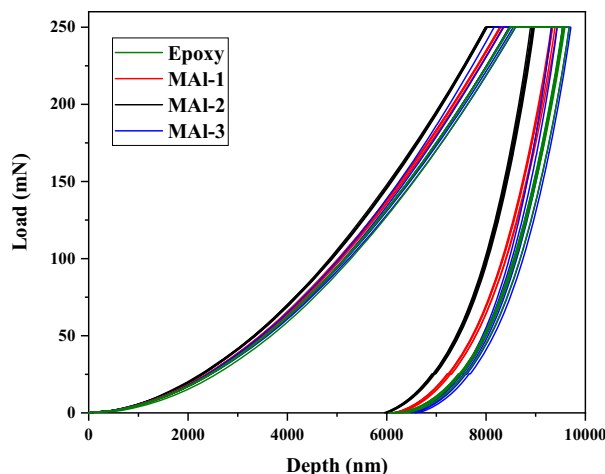
Figure 5 illustrates the effect of Al particles on the modulus of elasticity and hardness at 250 mN load. It is observed that both the modulus and hardness are increased due to addition of particles to the base epoxy coating [29]. Indentation hardness values have been recorded at the highest levels when 2 wt% Al particles are added. It is estimated that the hardness of the coating has increased by approximately 12% when compared to the base material, while the elastic modulus has decreased by approximately 4.3%.

The nanoindentation hardness results differ from the conventional hardness measurements due to the scale and method of testing. Nanoindentation assesses the hardness at a much smaller scale, which is influenced by the local microstructure and the distribution of Al particles within the epoxy matrix. While the conventional hardness shows an increase with Al content up to 2%, the nanoindentation results indicate a more complex interaction. The presence of Al particles enhances the cross-linking density and overall structural integrity of the epoxy, leading to increased hardness at lower loads. However, at 3% Al, the potential for particle agglomeration becomes more pronounced, which can create localized weak points in the coating. This agglomeration can lead to a reduction in the effective load-bearing capacity at the nano-scale, resulting in lower nanoindentation hardness values compared to the expected trend observed in conventional hardness tests (Figure 6).

Based on the results obtained, Al particles contribute to improving the hardness of coatings as a result of their incorporation in the epoxy resin and impact on cross-



**Figure 4.** Graphical representation of the pendulum hardness, impact strength, and scratch resistance of MAI filled epoxy coatings.



**Figure 5.** Indentation ( $L$  vs  $D$ ) curves obtained for fabricated coatings.

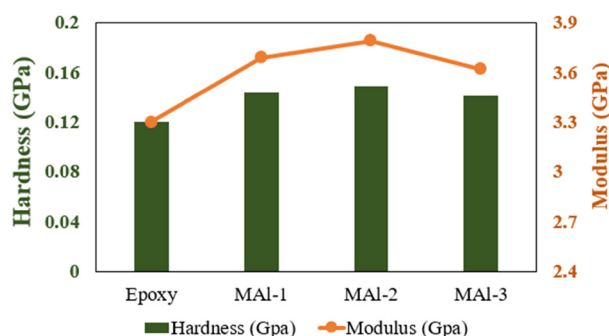
| Sample | Hardness (GPa) | Modulus (GPa) |
|--------|----------------|---------------|
| Epoxy  | 0.120          | 3.3           |
| MAI-1  | 0.144          | 3.69          |
| MAI-2  | 0.149          | 3.79          |
| MAI-3  | 0.141          | 3.62          |

**Table 4.** Modulus and hardness values obtained for the fabricated coatings.

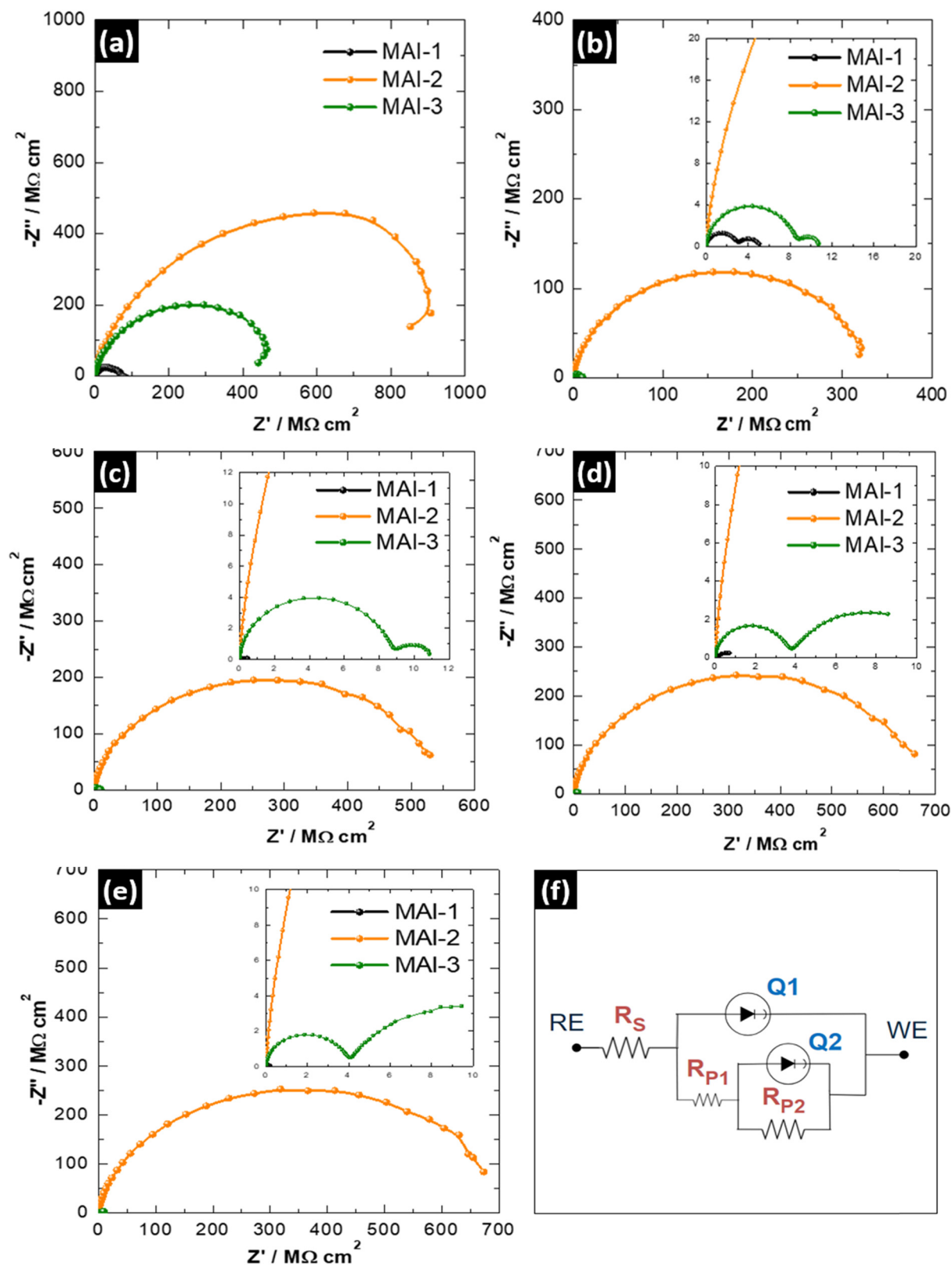
linking. Also, the value of elastic modulus increasing with particle addition indicates the increased toughening. The hardness of the coatings increases due to the adherence of Al particles to the epoxy matrix, which enhances the cross-linking density of coatings. Moreover, the chain mobility is restraining due to the inclusion of fillers throughout the curing process, thereby preventing disaggregation [7,30]. The mechanical properties obtained from nanoindentation are consistent with the results from other conventional studies where Al particle incorporation enhanced

the pendulum hardness and scratch resistance. Significantly, it has been seen from the conventional study that the impact strength increased with the increasing percentage of Al particles. Nanoindentation analysis suggests that the modulus increases very unlikely. This is because the incorporation of metal particles as a filler to the epoxy decreases the impact strength when the modulus increases [31,32]. Al powder in the base matrix acts as a strengthening agent since both the impact and modulus are increased concurrently [33].

The electrochemical characteristics of the developed coatings were measured by the EIS measurements. EIS technique was effectively employed to study the corrosion and corrosion mitigation [34–39] with a scan rate of  $\pm 5$  mV. The obtained Nyquist plots for the fabricated coatings after being ball-milled as previously described and as-prepared with the compositions shown in Table 1 for the different MAI samples are depicted in Figure 7, after exposure to a solution of 3.5 wt% NaCl for 1 h to 30 days. Those experiments were collected to report the effect of



**Figure 6.** Hardness and modulus for the prepared epoxy coatings.



**Figure 7.** Nyquist plots for the coatings with different Al wt% after exposure to NaCl solution for (a) 1 h, (b) 7 days, (c) 14 days, (d) 21 days, and (e) 30 days. (f) Circuit model used to fit the obtained EIS data.

| Sample code     | $R_s/\Omega$ (cm <sup>2</sup> ) | Q1                             |      | $R_{P1}$ (M $\Omega$ cm <sup>2</sup> ) | Q2                             |      | $R_{P2}$ (M $\Omega$ cm <sup>2</sup> ) |
|-----------------|---------------------------------|--------------------------------|------|----------------------------------------|--------------------------------|------|----------------------------------------|
|                 |                                 | $Y_{Q1}$ (F cm <sup>-2</sup> ) | $N$  |                                        | $Y_{Q2}$ (F cm <sup>-2</sup> ) | $n$  |                                        |
| MAI-1 (1 h)     | 157                             | 0.000546                       | 0.57 | 1,358                                  | 0.000668                       | 0.87 | 2,374                                  |
| MAI-2 (1 h)     | 162                             | 0.000142                       | 0.94 | 2,568                                  | 0.001874                       | 0.82 | 3,075                                  |
| MAI-3 (1 h)     | 151                             | 0.000152                       | 0.94 | 1,856                                  | 0.001246                       | 0.70 | 2,539                                  |
| MAI-1 (7 days)  | 144                             | 0.0006847                      | 0.93 | 2,048                                  | 0.004785                       | 0.63 | 4,480                                  |
| MAI-2 (7 days)  | 163                             | 0.000159                       | 0.93 | 2,998                                  | 0.001915                       | 0.78 | 1,010                                  |
| MAI-3 (7 days)  | 140                             | 0.001249                       | 0.97 | 2,135                                  | 0.004288                       | 0.53 | 2,339                                  |
| MAI-1 (14 days) | 95                              | 0.000792                       | 0.90 | 3,756                                  | 0.000576                       | 0.40 | 3,676                                  |
| MAI-2 (14 days) | 129                             | 0.000119                       | 0.56 | 2,555                                  | 0.000965                       | 0.99 | 3,916                                  |
| MAI-3 (14 days) | 101                             | 0.001220                       | 0.97 | 2,870                                  | 0.000709                       | 0.59 | 3,224                                  |
| MAI-1 (21 days) | 107                             | 0.000861                       | 0.94 | 1,206                                  | 0.003905                       | 0.68 | 2,202                                  |
| MAI-2 (21 days) | 131                             | 0.0001492                      | 0.94 | 5,936                                  | 0.000885                       | 0.14 | 2,702                                  |
| MAI-3 (21 days) | 110                             | 0.0001710                      | 0.93 | 5,321                                  | 0.002593                       | 0.81 | 2,450                                  |
| MAI-1 (30 days) | 113                             | 0.002131                       | 0.91 | 1,051                                  | 0.006147                       | 0.65 | 1,622                                  |
| MAI-2 (30 days) | 121                             | 0.000972                       | 0.99 | 3,143                                  | 0.001098                       | 0.56 | 2,716                                  |
| MAI-3 (30 days) | 98                              | 0.0001236                      | 0.97 | 3,161                                  | 0.005593                       | 0.67 | 1,916                                  |

**Table 5.** Fitted parameters from the impedance data.

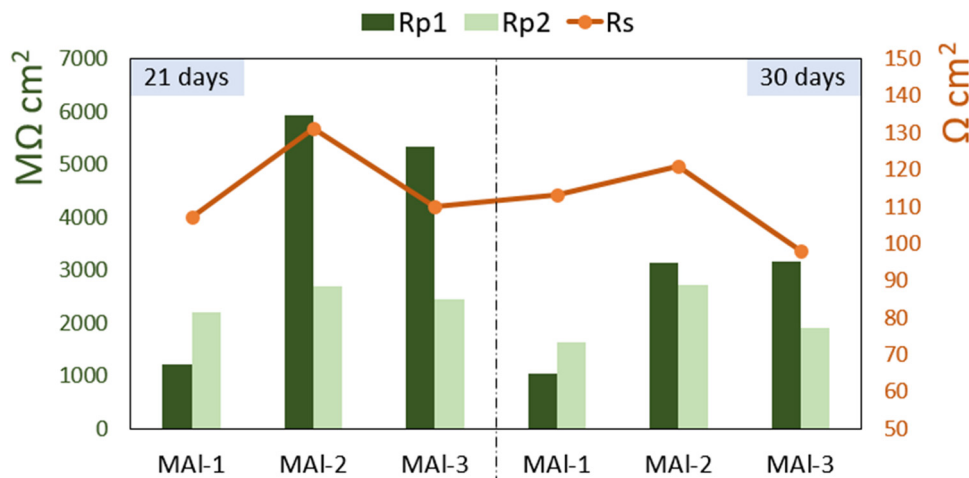
changing the composition of the MAI as well as the effect of different times of exposure from 1 h to 30 days on the corrosion and degradation of the fabricated sample coated in 3.5% NaCl solution. The parameters obtained from circuit fitting the impedance data are given in Table 5. The Nyquist plot of 1, 2, and 3 wt% in all EIS diagrams refers to the different concentrations of Al as shown in Table 1 by MAI-1, MAI-2, and MAI-3, for the developed coatings.

Figure 7a shows the Nyquist plots for the coatings after 1 h immersion in the chloride test solution, and only one semicircle is seen. It is obvious from the figure that the widest diameter of the semicircles is obtained for the coating that contains 2 wt% Al. On the other hand, the semicircle of the coating containing 1 wt% MAI has the smallest diameter. Increasing the percentage of Al to 3 wt% again decreased the diameter of the semicircle obtained, as compared to 2 wt% Al addition but still much wider than that of coating with 1 wt% Al. This confirms that 2 wt% Al is the optimum concentration to be added to the coating to maintain a higher performance after 1 h immersion in the chloride test solution.

The Nyquist plots depicted in Figure 7b were obtained for the coatings that contain different percentages of MAI after being immersed for 7 days in 3.5 wt% NaCl solution. It is clear that the Nyquist plots obtained for 1 wt% MAI and 3 wt% MAI show two semicircles, a wide semicircle followed by a small one, while the 3 wt% MAI is as this

obtained for the different coatings shown in Figure 7a but at lower diameters for the obtained semicircle. The plot obtained for 1 wt% MAI coating has the smallest diameter which greatly increased for the coating added with 2 wt% Al. Increasing the content of Al to 3 wt% in the coating shows a smaller diameter than that obtained for the coating with 2% Al but still wider than the coating with 1 wt% MAI. This indicates that the corrosion resistance for the fabricated coatings increases as per its MAI content in the following order: 2 wt% MAI > 3 wt% MAI > 1 wt% MAI. It is also worth mentioning that the increase of immersion time from 1 h (Figure 7a) to 7 days (Figure 7b) decreases the corrosion resistance for all coatings. This was indicated by the smaller diameters for the obtained semicircles for the different coatings after 7 days of immersion in the chloride solution. Here, the decrease of corrosion resistance of the coatings with the increase of the time of immersion from 1 h to 7 days is due to the corrosion and/or the degradation of the surface of the coatings as a result of the chloride ion attack [40].

The Nyquist plots displayed in Figure 7c were obtained for the coatings that contain different percentages of MAI after immersion for 14 days in the solution of 3.5 wt% NaCl. It is clear that the Nyquist plots show almost similar behavior for different coatings, as shown in Figure 7b, but with a slightly wider diameter for the obtained semi-circles for all coatings. The plot obtained for 2 wt% MAI coating has

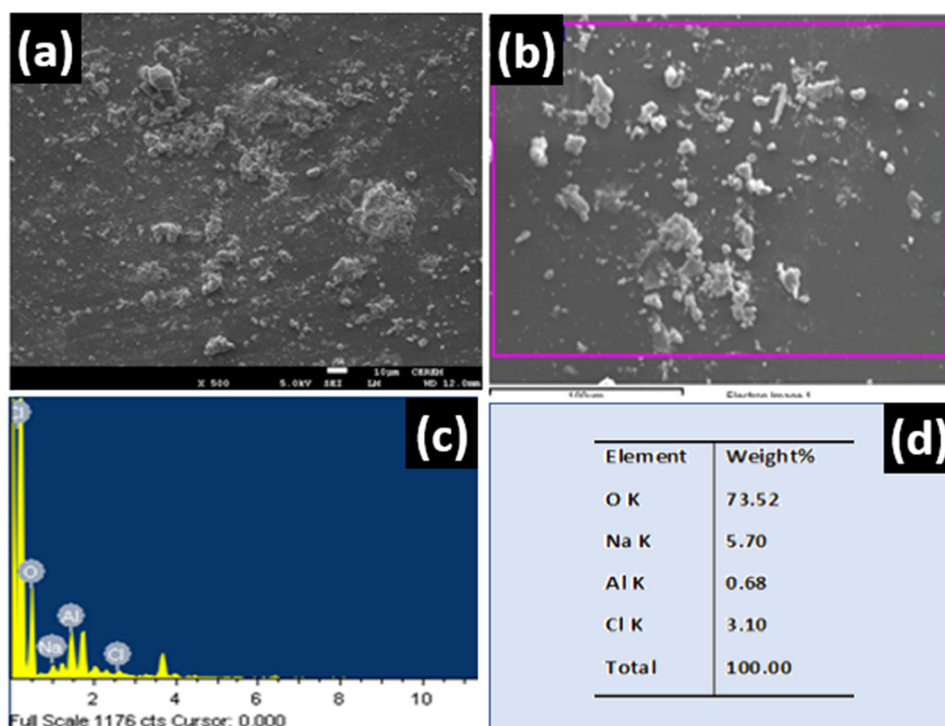


**Figure 8.** Resistance values ( $R_s$ ,  $R_{p1}$ , and  $R_{p2}$ ) of epoxy coatings with varying concentrations of MAL nanoparticles (1, 2, and 3 wt%) after 21 and 30 days of immersion in 3.5 wt% NaCl solution.

the widest diameter as compared to the ones obtained for 1 wt% MAL and 3 wt% MAL coatings. According to the obtained diameter of the semicircles, the corrosion resistance increases as per its MAL content in the following order: 2 wt% Al > 3 wt% Al > 1 wt% Al. The increase of the corrosion resistance of the coating panels is because

of the formation of a corrosion product layer that partially protects the surface from degradation or corrosion with time [41,42].

The Nyquist plots in Figure 7d and e indicate the impact of adjusting the proportion of MAL on the corrosion behavior of the developed coatings after extending the



**Figure 9.** SEM images of 2 wt% Al coated samples (a) after 30 days of immersion along with (b–d) EDX elemental analysis.

exposure period of time to 21 and 30 days, respectively. It is clearly concluded that the spectra show almost a similar behavior and almost the same real resistance ( $Z'$ ) and imaginary resistance ( $Z''$ ). Both figures show a little higher value of both  $Z'$  and  $Z''$  when compared to the values recorded for the coatings after 7 days (Figure 7b) and also after 14 days (Figure 7c). This increase of the plotted values of  $Z'$  and  $Z''$  was reflected as the increase in the diameters of the semicircle for the coatings immersed for 21 and 30 days. This behavior indicates that the prolonging of the immersion time decreases the corrosion of the surface of the coatings, which can be explained by the formation of thicker layers of corrosion products on the surface of the coatings. The formed layer has the ability to reduce or even prevent the degradation as well as the corrosion of the fabricated coatings by preventing the chloride ions present in the test solution from reaching the surface and thus preventing the corrosion of those coatings [43–45]. The EIS results for the milled coatings confirmed that the presence of 2 wt% Al within the fabricated coating leads to the increase of the corrosion resistance to its maximum because it is the optimum concentration that exhibits the best resistance against corrosion in the tested chloride solution. Addition of nanoparticles increases the cathodic protection of fillers by preventing the corrosive media from penetrating and increases the binding power of the interface by cross-linking with amino radicals [46,47].

The impedance data listed in Table 5 reveal that the highest resistance values, solution resistance ( $R_s$ ), first polarization resistance ( $R_{p1}$ ), and second polarization resistance ( $R_{p2}$ ) are observed for the 2 wt% MAL coating. Additionally, the constant phase element values ( $Y_{Q1}$  and  $Y_{Q2}$ ) are the lowest for this sample, indicating fewer defects and enhanced barrier properties. The  $n$ -values close to unity suggest the formation of a stable double-layer capacitor with minimal porosity. These results confirm that the 2 wt% MAL coating provides optimal corrosion resistance among the tested formulations, especially during extended immersion in 3.5 wt% NaCl solution.

The graphical representation of  $R_s$ ,  $R_{p1}$ , and  $R_{p2}$  values over 21 and 30 days of immersion (Figure 8) further supports the trend observed in Table 5. The coating with 2 wt% MAL consistently shows the highest resistance across both immersion periods, confirming its superior long-term corrosion resistance. In contrast, the 1 and 3 wt% MAL coatings exhibit lower resistance values, with the latter likely affected by particle agglomeration that reduces coating integrity. These trends suggest that 2 wt% MAL is the optimal filler concentration for achieving a balance between mechanical stability and corrosion protection.

Figure 9 displays the SEM and EDX profiles obtained after 30 days of immersion in a 3.5% NaCl solution. According to the EDX examination of the corrosion products that developed on the surface, the percentage of Al was lower than it was before immersion. This suggests that the dissolution of Al under the attack of chloride ions may have been the cause of the coating's corrosion. Moreover, the high oxygen content results from the surface-formed layer of Al oxide ( $Al_2O_3$ ), which reduces the corrosion on the coated surface. The presence of NaCl salt on the composite surface was due to its deposition during immersion in the test solution, as shown by the low concentration of NaCl.

## 4. Conclusions

Three different coating formulations were fabricated by incorporating varying percentages of ball-MAL powder, designated as MAL-1 (1 wt% Al), MAL-2 (2 wt% Al), and MAL-3 (3 wt% Al). Characterization of these coatings was performed using several methods, including nanoindentation, scratch resistance testing, TGA, SEM, and pendulum hardness testing.

- The mechanical properties improved with the addition of Al up to 2 wt%, while increasing the Al content to 3 wt % led to a decrease in mechanical properties, as demonstrated by all mechanical tests conducted.
- EIS measurements revealed the effect of MAL powder on the corrosion behavior of the fabricated coatings in a 3.5 wt% NaCl solution.
- The impact of immersion time on corrosion resistance and degradation of the prepared coatings was analyzed through EIS data collected after various immersion periods in the chloride solution.
- Coatings with 2 wt% Al exhibited the highest resistance to corrosion across all immersion durations.
- Prolonged immersion initially resulted in a decline in corrosion resistance after 7 days, followed by an increase due to the formation of protective oxide products on the coating surface.
- Both mechanical and electrochemical testing confirmed that the coating formulated with 2 wt% Al displayed superior mechanical properties and higher corrosion resistance compared to coatings containing 1 and 3 wt% Al.

## Acknowledgements

This work was funded by the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdul-Aziz City for Science and Technology, Kingdom of Saudi Arabia, grant number (2-17-02-001-0023).

## Funding information

This work was funded by the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdul-Aziz City for Science and Technology, Kingdom of Saudi Arabia, grant number (2-17-02-001-0023).

## Author contributions

Conceptualization, U.A.S., M.A.A., S.M.A.-Z., E.M.S. and A.H.S.; Methodology, U.A.S. and H.S.A.; Software H.S.A.; Validation, U.A.S., J.A.M., M.A.A., S.M.A.-Z., E.M.S. and A.H.S.; Formal analysis, U.A.S., J.A.M., M.A.A., S.M.A.-Z., and A.H.S.; Investigation, U.A.S., M.A.A., S.M.A.-Z., E.M.S. and A.H.S.; Resources, A.H.S., and S.M.A.-Z.; Data curation, M.A.A.; Writing—original draft, U.A.S., M.A.A., S.M.A.-Z., E.M.S., A.H.S., and H.S.A.; Writing—review & editing, H.S.A.; Visualization, H.S.A.; Supervision, S.M.A.-Z.; Project administration, A.H.S.; Funding acquisition, A.H.S. All authors have read and agreed to the published version of the manuscript.

## Conflict of interest statement

Authors state no conflict of interest.

## Data availability statement

The data that support the findings of this study are available within the article.

## References

- [1] Tjong, S.C., Chen, H., Nanocrystalline materials and coatings, *Mat. Sci. Eng. R.*, 2004, 45: 1–88. doi: 10.1016/j.mser.2004.07.001
- [2] Andrievski, R.A., Films as nanostructured materials with characteristic mechanical properties, *Mater. Trans.*, 2001, 42: 1471–1473. doi: 10.2320/matertrans.42.1471
- [3] Zhou, F.L., Gong, R.H., Porat, I., Mass production of nanofibre assemblies by electrostatic spinning, *Polym. Int.*, 2009, 58: 331–342. doi: 10.1002/pi.2521
- [4] Galliano, F., Landolt, D., Evaluation of corrosion protection properties of additives for waterborne epoxy coatings on steel, *Prog. Org. Coat.*, 2002, 44: 217–225. doi: 10.1016/S0300-9440(02)00016-4
- [5] Rajagopalan, N., Khanna, A.S., Effect of size and morphology on UV-blocking property of nanoZnO in epoxy coating, *Int. J. Sci. Res. Publ.*, 2013, 3: 1–14
- [6] hang, M.Q., Rong, M.Z., Yu, S.L., Wetzel, B., Friedrich, K., Improvement of tribological performance of epoxy by the addition of irradiation grafted nano-inorganic particles, *Macromol. Mater. Eng.*, 2002, 287: 111–115. doi: 10.1002/1439-2054(20020201)287:2<111::AID-MAME111>3.0.CO;2-I
- [7] Shi, X.M., Nguyen, T.A., Suo, Z.Y., Liu, Y.J., Avci, R., Effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coating, *Surf. Coat. Technol.*, 2009, 204: 237–245. doi: 10.1016/j.surfcoat.2009.06.048
- [8] Chattopadhyay, D.K., Raju, K.V.S.N., Structural engineering of polyurethane coatings for high performance applications, *Prog. Polym. Sci.*, 2007, 32: 352–418. doi: 10.1016/j.progpolymsci.2006.05.003
- [9] Hare, C.H., Corrosion control of steel by organic coatings, *Uhlig's corrosion handbook*, Ed. Revie, R.W., 2011, pp. 971–983. doi: 10.1002/9780470872864.ch67pp
- [10] Compere, C., Frechette, E., Ghali, E., The corrosion evaluation of painted and artificially damaged painted steel panels by Ac-impedance measurements, *Corros. Sci.*, 1993, 34: 1259–1274. doi: 10.1016/0010-938x(93)90086-V
- [11] Fedullo, N., Sorlier, E., Sclavons, M., Bailly, C., Lefebvre, J.M., Devaux, J., Polymer-based nanocomposites: Overview, applications and perspectives, *Prog. Org. Coat.*, 2007, 58: 87–95. doi: 10.1016/j.porgcoat.2006.09.028
- [12] Yang, L.H., Liu, F.C., Han, E.H., Effects of P/B on the properties of anticorrosive coatings with different particle size, *Prog. Org. Coat.*, 2005, 53: 91–98. doi: 10.1016/j.porgcoat.2005.01.003
- [13] González, S., Cáceres, F., Fox, V., Souto, R.M., Resistance of metallic substrates protected by an organic coating containing aluminum powder, *Prog. Org. Coat.*, 2003, 46: 317–323. doi: 10.1016/S0300-9440(03)00021-3
- [14] Becker, O., Varley, R., Simon, G., Morphology, thermal relaxations and mechanical properties of

- layered silicate nanocomposites based upon high-functionality epoxy resins, *Polymer*, 2002, 43: 4365–4373. doi: 10.1016/S0032-3861(02)00269-0
- [15] González, S., Mirza Rosca, I.C., Souto, R.M., Investigation of the corrosion resistance characteristics of pigments in alkyd coatings on steel, *Prog. Org. Coat.*, 2001, 43: 282–285. doi: 10.1016/S0300-9440(01)00210-7
- [16] Supplit, R., Schubert, U., Corrosion protection of aluminum pigments by sol–gel coatings, *Corros. Sci.*, 2007, 49: 3325–3332. doi: 10.1016/j.corsci.2007.03.014
- [17] Zhang, Y.C., Ye, H.Q., Liu, H., Han, K., Preparation and characterisation of aluminium pigments coated with silica for corrosion protection, *Corros. Sci.*, 2011, 53: 1694–1699. doi: 10.1016/j.corsci.2011.01.027
- [18] Karbasi, A., Moradian, S., Tahmassebi, N., Ghodsi, P., Achievement of optimal aluminum flake orientation by the use of special cubic experimental design, *Prog. Org. Coat.*, 2006, 57: 175–182. doi: 10.1016/j.porgcoat.2006.06.008
- [19] Jalili, M., Rostami, M., Ramezanzadeh, B., An investigation of the electrochemical action of the epoxy zinc-rich coatings containing surface modified aluminum nanoparticle, *Appl. Surf. Sci.*, 2015, 328: 95–108. doi: 10.1016/j.apsusc.2014.12.034
- [20] Madhankumar, A., Nagarajan, S., Rajendran, N., Nishimura, T., EIS evaluation of protective performance and surface characterization of epoxy coating with aluminum nanoparticles after wet and dry corrosion test, *J. Solid. State. Electr.*, 2012, 16: 2085–2093. doi: 10.1007/s10008-011-1623-1
- [21] Liang, Y., Liu, F.C., Nie, M., Zhao, S.Y., Lin, J.D., Han, E.H., Influence of nano-Al concentrates on the corrosion resistance of epoxy coatings, *J. Mater. Sci. Technol.*, 2013, 29: 353–358. doi: 10.1016/j.jmst.2013.01.014
- [22] Alam, M.A., Samad, U.A., Seikh, A., Mohammed, J.A., Al-Zahrani, S.M., Sherif, E.S.M., Development and characterization of PA 450 and PA 3282 epoxy coatings as anti-corrosion materials for offshore applications, *Materials*, 2022, 15: 2562. doi: ARTN 256210.3390/ma15072562
- [23] Abdus Samad, U., Alam, M.A., Seikh, A.H., Mohammed, J.A., Al-Zahrani, S.M., Sherif, E.S.M., Corrosion resistance performance of epoxy coatings incorporated with unmilled micro aluminium pigments, *Crystals*, 2023, 13: 558. doi: 10.3390/cryst13040558
- [24] Rijesh, M., Sreekanth, M.S., Deepak, A., Dev, K., Surendranathan, A.O., Effect of milling time on production of aluminium nanoparticle by high energy ball milling, *Int. J. Mech. Eng. Technol.*, 2018 9(8): 646–652
- [25] Deka, S., Mozafari, F., Mallick, A., Thamburaja, P., Gupta, M., Development of high-performance nanostructured aluminum and its constitutive modeling, *Mech. Adv. Mater. Struct.*, 2023, 31: 1–20. doi: 10.1080/15376494.2023.2262733
- [26] Azani, N.F.S.M., Hussin, M.H., Comparison of cellulose nanocrystal (CNC) filler on chemical, mechanical, and corrosion properties of epoxy-Zn protective coatings for mild steel in 3.5% NaCl solution, *Cellulose*, 2021, 28: 6523–6543. doi: 10.1007/s10570-021-03910-x
- [27] Kim, H.J., Jung, D.H., Jung, I.H., Cifuentes, J.I., Rhee, K.Y., Hui, D., Enhancement of mechanical properties of aluminium/epoxy composites with silane functionalization of aluminium powder, *Compos. Part. B-Eng.*, 2012, 43: 1743–1748. doi: 10.1016/j.compositesb.2011.12.010
- [28] Oliver, W.C., Pharr, G.M., An improved technique for determining hardness and elastic-modulus using load and displacement sensing indentation experiments, *J. Mater. Res.*, 1992, 7: 1564–1583. doi: 10.1557/Jmr.1992.1564
- [29] Samad, U.A., Alam, M.A., Chafidz, A., Al-Zahrani, S.M., Alharthi, N.H., Enhancing mechanical properties of epoxy/polyaniline coating with addition of ZnO nanoparticles: Nanoindentation characterization, *Prog. Org. Coat.*, 2018, 119: 109–115. doi: 10.1016/j.porgcoat.2018.02.018
- [30] Vyazovkin, S., Modification of the integral isoconversional method to account for variation in the activation energy, *J. Comput. Chem.*, 2001, 22: 178–183. doi: 10.1002/1096-987x(20010130)22:2<178:Aid-Jcc5>3.0.Co;2-#
- [31] Nicodemo, L., Nicolais, L., Mechanical-properties of metal polymer composites, *J. Mater. Sci. Lett.*, 1983, 2: 201–203. doi: 10.1007/Bf00725619
- [32] Taşdemir, M., Gülsoy, H.Ö., Mechanical properties of polymers filled with iron powder, *Int. J. Polym. Mater.*, 2008, 57: 258–265. doi: 10.1080/00914030701473656
- [33] Anis, A., Elnour, A.Y., Alam, M.A., Al-Zahrani, S.M., AlFayez, F., Bashir, Z., Aluminum-filled amorphous-PET, a composite showing simultaneous increase in modulus and impact resistance, *Polymers (Basel)*, 2020, 12: 2038. doi: 10.3390/polym12092038
- [34] Qin, J., Shi, X.T., Li, H.Y., Zhao, R.F., Li, G.Q., Zhang, S.F., et al., Performance and failure process of green recycling solutions for preparing high degradation resistance coating on biomedical magnesium alloys, *Green. Chem.*, 2022, 24: 8113–8130. doi: 10.1039/d2gc02638d

- [35] Zhang, W., Feng, B., Huang, L., Liang, Y., Chen, J., Li, X., et al., Fe/Cu diatomic sites dispersed on nitrogen-doped mesoporous carbon for the boosted oxygen reduction reaction in Mg-air and Zn-air batteries, *App. Catal. B Environ. Energy*, 2024, 358: 124450. doi: 10.1016/j.apcatb.2024.124450
- [36] Liang, Y., Ding, W., Liu, G., Traub, J., Gu, Z., Interlaced stacked hollow Cu<sub>2</sub>O dendrite for stable lithium metal anode, *Solid State Ionics*, 2024, 410: 116530. doi: 10.1016/j.ssi.2024.116530
- [37] Li, J.Y., Shi, H.W., Liu, F.C., Han, E.H., Self-healing epoxy coating based on tung oil-containing microcapsules for corrosion protection, *Prog. Org. Coat.*, 2021, 156: 106236. doi: 10.1016/j.porgcoat.2021.106236
- [38] Alam, M.A., Samad, U.A., Abdo, H.S., Anis, A., Alnaser, I.A., Hassan, A., et al., Fabrication of hybrid epoxy composites (Joint compound adhesive) for aluminum substrate applications and their evaluation for mechanical properties, *ACS Omega*, 2024 9(38): 39452–39463. doi: 10.1021/acsomega.4c02971
- [39] Samad, U.A., Alam, M.A., Abdo, H.S., Anis, A., Al-Zahrani, S.M., 2023. Synergistic effect of nanoparticles: enhanced mechanical and corrosion protection properties of epoxy coatings incorporated with SiO<sub>2</sub> and ZrO<sub>2</sub>, *Polymers*, 15(14): 3100. doi: 10.3390/polym15143100
- [40] Samad, U.A., Alam, M.A., Anis, A., Abdo, H.S., Shaikh, H., Al-Zahrani, S.M., 2022. Nanomechanical and electrochemical properties of ZnO-nanoparticle-filled epoxy coatings, *Coatings*, 12(2): 282. doi: 10.3390/coatings12020282
- [41] Alam, M.A., Samad, U.A., Anis, A., Sherif, E.-S.M., Abdo, H.S., Al-Zahrani, S.M., 2023. The effect of zirconia nanoparticles on thermal, mechanical, and corrosion behavior of nanocomposite epoxy coatings on steel substrates, *Materials*, 16(13): 4813. doi: 10.3390/ma16134813
- [42] Fan, L., Tang, F.J., Reis, S.T., Chen, G.D., Koenigstein, M.L., Corrosion resistances of steel pipe internally coated with enamel, *Corrosion*, 2017, 73: 1335–1345. doi: 10.5006/2497
- [43] Fan, L., Reis, S.T., Chen, G.D., Koenigstein, M.L., Corrosion resistance of pipeline steel with damaged enamel coating and cathodic protection, *Coatings*, 2018, 8: 185. doi: 10.3390/coatings8050185
- [44] Mayne J.E.O., The mechanism of the inhibition of the corrosion of iron and steel by means of paint, *Official Digest*, 1952, 24: 127
- [45] Davis, G.D., Krebs, L.A., Dacres, C.M., Coating evaluation and validation of accelerated test conditions using an in-situ corrosion sensor, *J. Coating Technol.*, 2002, 74: 69–74. doi: 10.1007/Bf02697959
- [46] Zhang, T.Y., Zhang, T., He, Y.T., Wang, Y.C., Bi, Y.P., Corrosion and aging of organic aviation coatings: A review, *Chin. J. Aeronaut.*, 2023, 36: 1–35. doi: 10.1016/j.cja.2022.12.003
- [47] Changkai, W., Tianyu, Z., Teng, Z., Yuting, H., Yuchen, W., Guoming, C., Deterioration behavior of graphene-modified epoxy-primer-coated aluminum alloy in a UVA acidic alternation immersion environment, *J. Alloy. Compd.*, 2023, 968: 171853. doi: 10.1016/j.jallcom.2023.171853