

## EFFECT OF ZIRCONIA NANOPARTICLES MODIFIED BY SILANE COUPLING AGENT ON SOME PROPERTIES OF EPOXY COATING

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**Abstract.** Effect of zirconia nanoparticles (zirconia NPs/ZrO<sub>2</sub> NPs) modified by 3 wt.% (glycidylxypropyl) triethoxysilane – GPTES (m-ZrO<sub>2</sub> NPs) on some properties of epoxy coating such as mechanical properties, thermal stability and anti-corrosion performance was investigated. The obtained results indicated that the addition of zirconia nanoparticles to epoxy coating could enhance the properties of this coating. The addition of 2 wt.% of pure ZrO<sub>2</sub> NPs (u-ZrO<sub>2</sub> NPs) to the epoxy matrix could increase the mechanical properties (hardness and adhesion to the steel substrate) by approximately 10 %, the onset temperature of thermal degradation of the epoxy/u-ZrO<sub>2</sub> NPs coating was 4.4 °C higher, and the anti-corrosion performance of epoxy coating was improved in comparison with the neat epoxy coating. Organically modified ZrO<sub>2</sub> NPs had higher improvement for epoxy coating's properties than pure ZrO<sub>2</sub> NPs. The epoxy coating filled with m-ZrO<sub>2</sub> NPs had 19.7 % higher in relative hardness, 88.73 % more in adhesion to steel substrate, 25.6 °C higher in the onset temperature of thermal degradation, and higher anti-corrosion performance in comparison with the epoxy coating filled with 2 wt.% of pure zirconia nanoparticles. The cross-section FESEM images of the epoxy/m-ZrO<sub>2</sub> NPs coating showed that m-ZrO<sub>2</sub> NPs could regularly disperse in epoxy polymer matrix while unmodified zirconia nanoparticles (u-ZrO<sub>2</sub> NPs) were agglomerated to big cluster in the epoxy coating. This was the reason for the high performance of the epoxy coating filled with zirconia NPs modified by GPTES.

**Keywords:** epoxy coating, zirconia nanoparticles, modified nanoparticles, anti-corrosion, silane coupling agent.

**Classification numbers:** 2.5.3.

### 1. INTRODUCTION

Metals and alloys in general as well as steel in particular are unstable in ambient environment. They are always susceptible to corrosion. Metal corrosion has a significant impact on human society and economy. Metal corrosion is also a cause of environmental pollution. According to a report by the National Association of Corrosion Engineers (NACE), U.S.A metal corrosion costs \$ 276 billion that takes apart more than 3 % of the U.S Gross Domestic Product (GDP) [1]. Hence, protection of metal materials against corrosion is very necessary. Using organic coating is one of the best solutions for this purpose [2]. Because of their nature, epoxy resins are usually used as binders in anticorrosive coating formulas. Epoxy resins could work well on almost metal substrates with high adhesion and good coverage. They could be compatible with most of metal corrosion inhibitors [3].

To improve the performance of epoxy coatings, inorganic nanoparticles have been added to coating formulas [4, 5]. Zirconia nanoparticles were investigated to improve the physico-mechanical properties [6-8] as well as the anticorrosion ability of polymer nanocomposite coatings [9, 10]. In the study of Xiaoqian Ma *et al.*, zirconia nanoparticles synthesized by sol-gel technique having an average diameter of 11 nm were modified by silane coupling agent (KH-550). The modified zirconia nanoparticles were introduced into the epoxy resin. The optimal mechanical properties of the epoxy/zirconia nanocomposite were found using m-ZrO<sub>2</sub> NPs at 3 wt.%. The maximum critical strain energy release rate, fracture toughness, tensile strength, tensile modulus, and hardness of the nanocomposite increased by 122 %, 63 %, 44 %, 29 %, and 17 % compared with the neat epoxy resin, respectively [7]. A. Dorigato *et al.* also synthesized zirconia nanoparticles by sol-gel method. The synthesized zirconia nanoparticles were used as additives for epoxy adhesives. The nanocomposite had the highest tensile modulus with a zirconia nanoparticle content of 1 vol.% [8]. S. A. Haddadi *et al.* confirmed that zirconia nanoparticles modified by trimethoxy methyl silane not only improved the mechanical properties (i.e. tensile and hardness) but also enhanced the corrosion protection of epoxy nanocomposite coatings compared with untreated zirconia nanoparticles [9]. Wenhua Xu *et al.* studied the effect of zirconia nanoparticles on the anticorrosion of phenolic-epoxy coatings in hot acid solution. The obtained results indicated that the anticorrosion of the epoxy coating was enhanced by filling with 1 wt.% and 3 wt.% zirconia nanoparticles while the coating filled with 5 wt.% zirconia nanoparticles had lower anticorrosive ability than neat coating. The coating filled with 3 wt.% of zirconia nanoparticles (ZrO<sub>2</sub>NPs) had the lowest average roughness (5.94 nm), the highest C/O ratio (4.55) and coating resistance among the coatings investigated [10]. Xinding Lv *et al.* used zirconia nanoparticles combined with graphene microsheets to enhance anticorrosion performance of epoxy coatings. The obtained results indicated that the 0.5 wt.% ZrO<sub>2</sub> nanoparticles (ZrO<sub>2</sub> NPs) encapsulation of the graphene microsheets could enhance corrosion-protective ability of epoxy coating in 3.5 wt.% NaCl solution. The resistance of the nanocomposite coating immersed in the first day was 81.8 GΩ/cm<sup>2</sup>. The metal substrate was not corroded after 60 days of immersion in 3.5 wt.% NaCl solution [11].

In conclusion, ZrO<sub>2</sub> NPs could be used as additives to enhance the properties of the coatings (i.e. mechanical properties, corrosion-protective performance, etc.). Nevertheless, due to the difference in nature and structure, inorganic nanoparticles in general and ZrO<sub>2</sub> NPs in particular had low compatibility with polymers. Consequently, the properties of nanocomposite coatings based on ZrO<sub>2</sub> NPs were lower than those of neat coatings [12]. Hence, organic surface modification of ZrO<sub>2</sub> NPs has been used to improve the compatibility between ZrO<sub>2</sub> NPs and polymer matrix. Silane coupling agents are commonly used for surface modification of inorganic nanoparticles [12, 13]. However, the efficiency of silane-modified nanoparticles in the improvement of coating's properties depends on structure, nature and content of silane coupling agent. (3-glycidylxypropyl) triethoxysilane (GPTES) and its peers have three ethoxy groups

and a linear chain containing an epoxy group. These ethoxy groups can be easily hydrolyzed to silanol groups which are compatible with the nanoparticles while the epoxy ring opens and establish a stable bond with the polymer matrix. As a result, GPTES could improve the compatibility of polymers and nanoparticles, thereby enhancing the properties of the hybrid materials [13]. In our previous work, ZrO<sub>2</sub> NPs modified by GPTES were well dispersed in the acrylic polymer matrix, thereby enhancing some characteristics and weather stability of acrylic coatings [13]. The effect of ZrO<sub>2</sub> NPs modified by GPTES on the properties of epoxy coatings (physico-mechanical properties, thermal stability, morphology and anticorrosion performance) will be further studied and presented in this paper.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Epoxy resin (trade name of KEP 301X75) was supplied by Kumho P&B Chemical (South Korea). Hardener (trade name of G-700XB60) was purchased from Kukdo Chemical Co. LTD (South Korea). Organosilane (3-glycidyloxypropyl triethoxysilane) (GPTES, purity  $\geq 97\%$ ) and ZrO<sub>2</sub> nanoparticles (powder, particle size  $< 100$  nm, purity of 99 %) were obtained from Sigma (USA). Some other chemicals such as ethanol (99.7 %), ammonia solution 25 %, NaCl, xylene, etc. were provided from Duc Giang Chemical Company (Viet Nam).

### 2.2. Surface modification of ZrO<sub>2</sub> nanoparticles (ZrO<sub>2</sub> NPs)

ZrO<sub>2</sub> NPs surface was modified according to the procedure in our previous report [13]. In the first step, GPTES was mixed with 100 mL of ethanol and then 1 mL of ammonia solution was introduced to the solution. Next, the solution was stirred at a speed of 300 rpm and 50 °C for 180 min for transferring ethoxy groups to silanol groups. Then, ZrO<sub>2</sub> NPs were added to the solution at a ZrO<sub>2</sub> NPs/GPTES weight ratio of 100/3). The above suspension was continuously stirred for 24 h at 50 °C to perform surface modification reaction. Finally, the solid part was obtained by centrifugation at 6000 rpm. GPTES residue was removed by washing the solid part with ethanol and acetone. Modified ZrO<sub>2</sub> NPs were obtained by drying the solid part in a vacuum oven at 40 °C for 24 h.

### 2.3. Preparation of epoxy/ZrO<sub>2</sub> nanoparticles coating

Epoxy coatings filled with unmodified and modified ZrO<sub>2</sub> nanoparticles (u-ZrO<sub>2</sub> NPs and m-ZrO<sub>2</sub> NPs, respectively) were prepared according to the following procedure. In the first step, unmodified/modified ZrO<sub>2</sub> NPs were dispersed into xylene by a superspeed stirrer at 10000 rpm for 5 min and ultrasound treatment for 1 h. The weight ratio of nanoparticles and xylene was 1/10. In the next step, epoxy resin was introduced to the above suspension and the mixture was stirred on a magnetic stirrer for 15 min at room temperature at a speed of 300 rpm before ultrasonication for 1 h. After that, hardener was added to the mixture before continuous stirring at 300 rpm for 5 min and vibrating by ultrasound for 5 min. The investigated coatings were formed on the cleaned substrates (glass or steel) by a film applicator (Erichsen 360) with a wet thickness of 90  $\mu\text{m}$  (corresponding to a dried thickness of 30  $\mu\text{m} \pm 2 \mu\text{m}$ ). The coated plates were completely dried at ambient temperature for 7 days and then they were conditioned at 25  $\pm 2$  °C and a relative humidity of 50  $\pm 5$  % for at least 48 h prior to testing. A blank epoxy resin sample

was also prepared under the same conditions. The composition and abbreviation of the epoxy coating samples were presented in Table 1.

Table 1. Composition (wt.%) of epoxy/ZrO<sub>2</sub> NPs coatings and designation of samples.

No.	u-ZrO <sub>2</sub> NPs	m-ZrO <sub>2</sub> NPs	Xylene	Epoxy resin	Hardener	Sample
1	0.00	0.00	0.00	66.67	33.33	E0
2	0.00	0.47	4.74	63.19	31.60	EmZ-1.0
3	0.00	0.90	9.01	60.06	30.03	EmZ-2.0
4	0.00	1.96	19.61	52.29	26.14	EmZ-5.0
5	0.90	0.00	9.01	60.06	30.03	EuZ-2.0

## 2.4. Analysis

### 2.4.1. Physico-mechanical properties

Epoxy coatings were measured for relative hardness with a Pendulum Hardness Tester (Erichsen - Germany, model 299/300) according to ISO 1522, impact resistance with an Impact Tester (Erichsen - Germany, model 304) in accordance with ISO 6272-1:2011, and were pull-off tested for adhesion with an Adhesion Tester (DEFELSKO - USA, PosiTest AT-A Automatic Adhesion Tester model and S/N AT 08704 equipment) according to ISO 4624.

### 2.4.2. Thermal stability

Thermogravimetric analysis curves of investigated epoxy coatings were recorded by Labsys TG/DSC1600, TMA (Setaram, France) at a heating rate of 10 °C/min from ambient temperature to 600 °C in air atmosphere.

### 2.4.3. Morphology

FESEM images of investigated epoxy coatings were taken by FESEM S-4800 (Hitachi – Japan). An ultra-thin Pt layer was applied on the investigated coating surface to enhance electrical conductivity of the coating.

### 2.4.4. Potentiodynamic polarization curves

The recording of the polarization curves of the investigated epoxy coatings immersed in 3.5 wt.% NaCl solution was carried out using a Biologic VSP 300 (France) at a scan rate of 2 mV/s. This experiment used a three-electrode system, where Ag/AgCl acted as the reference electrode, C45 steel coated by the investigated coatings with an exposed area of 9.075 cm<sup>2</sup> acted as the working electrode and 316 stainless steel served as the auxiliary electrode.

## 3. RESULTS AND DISCUSSION

### 3.1. Physico-mechanical properties of investigated epoxycoatings

Theoretically, the addition of reinforced nanoparticles to polymer coatings can improve some properties of these coatings. However, due to the difference in structure and nature between nanoparticles and organic polymers, the nanoparticles have poor compatibility with

organic polymers. Consequently, the nanoparticles agglomerate into large clusters in the polymer matrix. Therefore, the properties of the nanocomposite coating will be reduced compared to the neat polymer coating [12]. To improve the compatibility of nanoparticles and organic polymers, the nanoparticles are often organically modified. Modified nanoparticles showed better compatibility with organic polymers, thereby improving the properties of nanocomposites [12, 13]. The properties of the nanocomposite coating depended on the content of the silane coupling agent used to modify the nanoparticles and the content of the modified nanoparticles. The results obtained from our previous study showed that the suitable content of silane coupling agent (GPTES) used to modify zirconia nanoparticles was 3 wt.% [13]. The zirconia nanoparticles modified by 3 wt.% GPTES (in comparison with ZrO<sub>2</sub> NPs weight) (m-ZrO<sub>2</sub> NPs) were chosen for this study. The effect of m-ZrO<sub>2</sub> NPs on epoxy coatings' properties was presented in Table 2.

Table 2. Mechanical properties of epoxy nanocomposite coatings filled with different m-ZrO<sub>2</sub> NPs content.

No	Samples	Relative hardness	Impact resistance (kG.cm)	Adhesion (MPa)
1	E0	0.65 ± 0.03	60 ± 4	0.63 ± 0.03
2	EmZ-1.0	0.78 ± 0.03	80 ± 4	1.01 ± 0.03
3	EmZ-2.0	0.85 ± 0.02	80 ± 8	1.34 ± 0.04
4	EmZ-5.0	0.77 ± 0.02	60 ± 8	0.93 ± 0.04
5	EuZ-2.0	0.71 ± 0.03	60 ± 8	0.71 ± 0.04

As can be seen from Table 2, the effect of nanoparticles on the properties of epoxy coatings can be clearly indicated for the relative hardness and adhesion while there was only a slight difference in impact resistance. Specifically, in terms of relative hardness, the addition of unmodified zirconia nanoparticles (u-ZrO<sub>2</sub> NPs) increased the relative hardness of epoxy coatings by about 10 % compared with neat epoxy coatings. This result was in agreement with the published literature [6-8] because zirconia nanoparticles acted as a reinforcing additive. However, the relative hardness of epoxy coatings filled with u-ZrO<sub>2</sub> NPs was lower than that of epoxy coatings filled with m-ZrO<sub>2</sub> NPs. This is explained by the organic modification of zirconia nanoparticles leading to improved compatibility of zirconia nanoparticles and epoxy macromolecules as well as dispensability enhancement of zirconia nanoparticles in the epoxy matrix [12, 13]. It is obvious that the hardness of nanocomposite coatings depends on m-ZrO<sub>2</sub> NPs content. The coating filled with 2 wt.% m-ZrO<sub>2</sub> NPs had the highest relative hardness. If increasing or reducing m-ZrO<sub>2</sub> NPs content to 5 wt.% or 1 wt. %, the relative hardness of nanocomposite coatings was also reduced.

In terms of adhesion, compared with the neat epoxy coating, the adhesion to the steel substrate of the epoxy coating filled with u-ZrO<sub>2</sub> NPs was slightly higher while it was 60 % higher and over doubled for the coatings filled with 1 wt.% and 2 wt.% m-ZrO<sub>2</sub> NPs, respectively. However, the adhesion to the steel substrate of the nanocomposite containing 5 wt.% m-ZrO<sub>2</sub> NPs was lower than that of the nanocomposite coating filled with 2 wt.% m-ZrO<sub>2</sub> NPs. Thus, the introduction of additives into polymer resins can enhance the adhesion of polymer coatings as reported in some literatures [14, 15].

The effect of nanoparticles on the impact resistance of the coatings was not as clear as that on the hardness and adhesion of the investigated coatings. Compared with the neat epoxy coating, the impact resistance of coatings filled with 1 wt.% or 2 wt.% m-ZrO<sub>2</sub> NPs was higher while that of coatings filled with u-ZrO<sub>2</sub> NPs or 5 wt.% m-ZrO<sub>2</sub> NPs was the same.

Theoretically, if the filler or additive has good interaction with the organic polymer, the load can be transferred from the matrix to the filler and thus improves the impact resistance. In contrast, fillers or additives have poor compatibility with organic polymers. Consequently, the fillers or additives tend to agglomerate to form large clusters which limit the load transfer from the matrix to ZrO<sub>2</sub> NPs, leading to crack initiation and easy propagation [14].

### 3.2. Thermal stability

The thermal stability of the coating was evaluated by thermogravimetric analysis (TGA). TGA diagrams of epoxy coating and epoxy nanocomposites filled with u-ZrO<sub>2</sub> NPs and m-ZrO<sub>2</sub> NPs in the air atmosphere are presented on Fig.1. TGA parameters such T<sub>5</sub>, T<sub>50</sub>, and T<sub>90</sub> corresponding to coating weight loss of 5 %, 50 % and 90 %, respectively, are listed in Table 3.

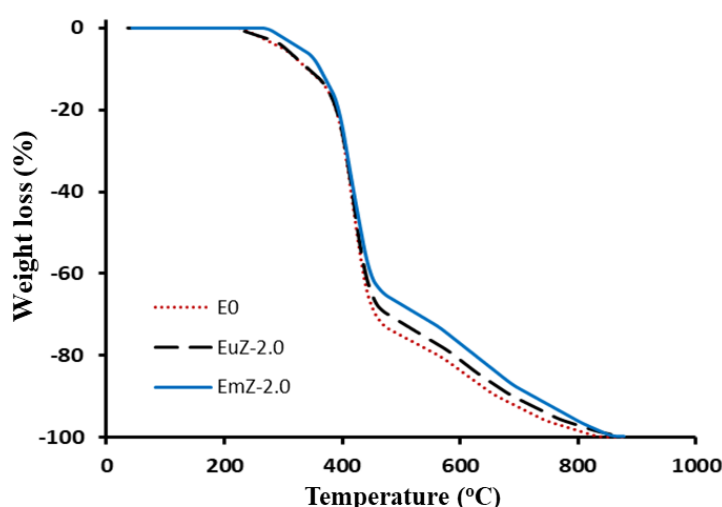


Figure 1. TGA diagrams of neat epoxy coating and epoxy nanocomposite coatings filled with u-ZrO<sub>2</sub> NPs and m-ZrO<sub>2</sub> NPs.

As can be seen from Fig. 1, the shape of investigated epoxy coatings' TGA diagrams was similar. The weight of coatings lost through three periods. In this first period from ambient temperature to over 200 °C, the weight of coatings was unchanged before rapidly reducing. From 400 °C, the weight loss of coatings was slower than that of the previous period. The thermal degradation of epoxy coating completed at over 800 °C. The residue weight of epoxy coating after thermal degradation was small.

Table 3. TGA parameters of epoxy coatings filled with u-ZrO<sub>2</sub> NPs and m-ZrO<sub>2</sub> NPs.

No	Samples	T <sub>5</sub> (°C)	T <sub>50</sub> (°C)	T <sub>90</sub> (°C)
1	E0	299.4	425.0	663.2
2	EmZ-2.0	329.4	432.4	724.6
3	EuZ-2.0	303.8	426.9	690.3

Typically, the temperature corresponding to a 5 % weight loss of the material is often considered as the onset of thermal degradation. Table 3 indicated that the onset of thermal

degradation of epoxy coating filled with u-ZrO<sub>2</sub> NPs was 4.4 °C higher than that of neat epoxy coating. This result was in agreement with the published literature [16]. The onset of thermal degradation of epoxy filled with 2 wt.% m-ZrO<sub>2</sub> NPs was the highest, leveling off 329.4 °C, which was 30 °C higher than that of neat epoxy coating. The thermal stability of a material often depends on its nature and structure. If the material has a tight structure and few defects, the oxygen permeation into the material will be restricted. As a result, the material becomes more stable under thermal effect.

### 3.4. Morphology

The dispersibility of the nanoparticles significantly affects the properties of the nanocomposite materials. The dispersibility of epoxy nanocomposite coatings were evaluated by cross-section FESEM images. The cross-section FESEM images of epoxy nanocomposite coatings filled with 2 wt.% m-ZrO<sub>2</sub> NPs, 2 wt.% u-ZrO<sub>2</sub> NPs, and 5 wt.% m-ZrO<sub>2</sub> NPs are displayed in Fig. 2. It is clear that organically modified ZrO<sub>2</sub> NPs can regularly be dispersed in an epoxy polymer matrix. The average diameter of the m-ZrO<sub>2</sub> NPs dispersed in the epoxy polymer matrix was approximately 100 nm, while the u-ZrO<sub>2</sub> NPs tended to agglomerate into large clusters in the epoxy polymer matrix due to the different nature and structure between ZrO<sub>2</sub> NPs and epoxy.

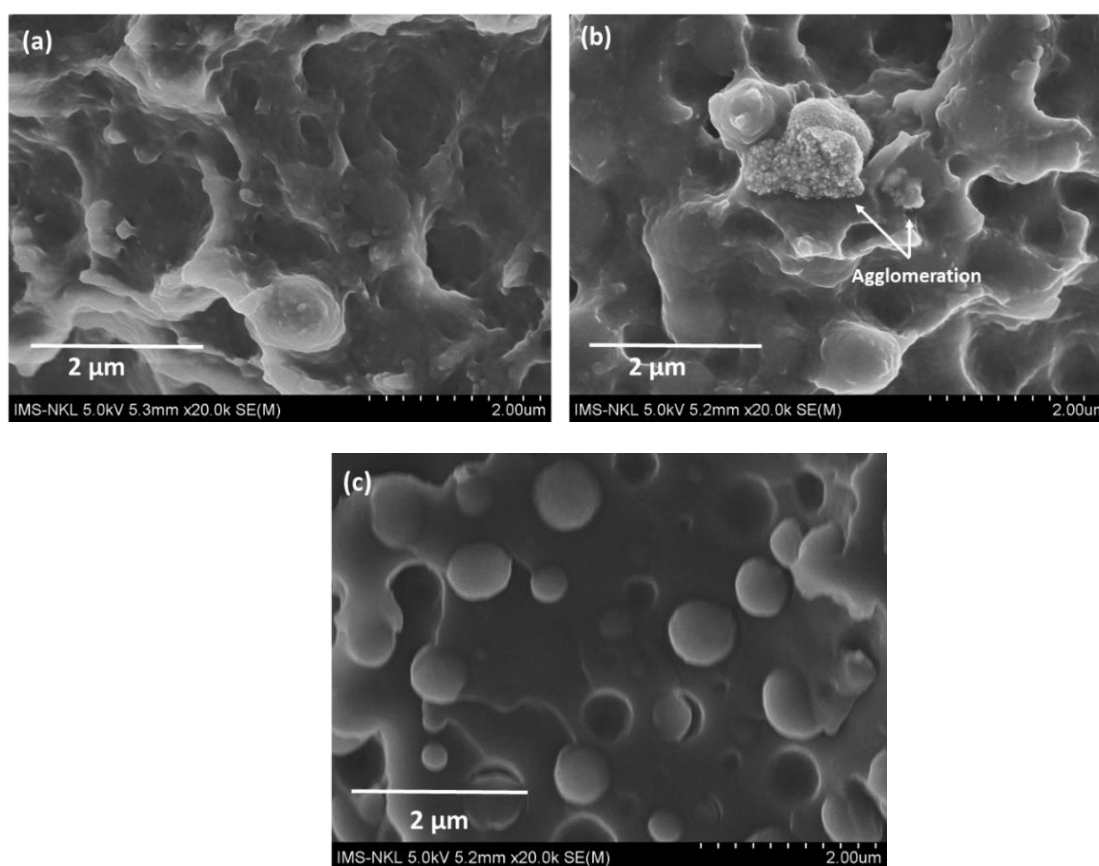


Figure 2. Cross-section FESEM images of epoxy coatings Filled with 2 wt.% m-ZrO<sub>2</sub> NPs (a), 2wt.% u-ZrO<sub>2</sub> NPs (b), and 5 wt.% m-ZrO<sub>2</sub> NPs (c).

As can be seen from Fig. 2c, the epoxy coating filled with 5 wt.% m-ZrO<sub>2</sub> NPs had particles which were regularly dispersed in the polymer matrix. The average size of the particles was 400 - 500 nm. These particles were assigned to m-ZrO<sub>2</sub> NPs. However, the size of the particles dispersed in the epoxy polymer matrix was much larger than that of the pristine ZrO<sub>2</sub> NPs. It was explained that m-ZrO<sub>2</sub> NPs at high content tended to agglomerate into large clusters. That may be the reason that the properties of epoxy coatings filled with 5 wt.% m-ZrO<sub>2</sub> NPs were lower than those of epoxy coatings filled with 2 wt.% m-ZrO<sub>2</sub> NPs.

If ZrO<sub>2</sub> NPs are modified by silane coupling agent at a suitable content, m-ZrO<sub>2</sub> NPs can be well compatible with the epoxy matrix, leading to enhanced properties of epoxy nanocomposite coatings compared with neat epoxy coatings. Hence, the properties of epoxy nanocomposite coatings filled with 2 wt.% m-ZrO<sub>2</sub> NPs are the best among the epoxy coatings investigated.

### 3.3. Polarization curve

The polarization curves of epoxy coatings filled with u-ZrO<sub>2</sub> NPs or different m-ZrO<sub>2</sub> NPs contents after 28-day immersion in 3.5 wt.% NaCl solution were recorded (Fig. 3). The corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $i_{\text{corr}}$ ) are illustrated in Table 4.

As can be seen from Table 4, the corrosion potential of epoxy coatings filled with u-ZrO<sub>2</sub> NPs and different m-ZrO<sub>2</sub> NPs contents was not much different while the corrosion current density ( $i_{\text{corr}}$ ) had a significant difference. Specifically, the corrosion potential of investigated coatings was approximately -190 mV. The epoxy coating filled with 5 wt.% m-ZrO<sub>2</sub> NPs was an exception. The corrosion potential of EmZ-5.0 was -213 mV, which was 20 mV more negative than that of the other epoxy coatings investigated. The corrosion potential movement could indicate cathodic effect (for negative movement) or anodic effect (for positive movement). However, the cathodic current density of EmZ-5.0 was not much different from that of the other coatings examined. In addition, the corrosion potential of investigated coatings was similar. Hence, the difference in the EmZ-5.0 corrosion potential was just a measurement error. In terms of corrosion current density, the E0 coating had the highest corrosion current density, leveling off 1.153 nA/cm<sup>2</sup>. The addition of u-ZrO<sub>2</sub> NPs to the epoxy coatings reduced the corrosion current density. The  $i_{\text{corr}}$  value of the epoxy coating filled with u-ZrO<sub>2</sub> NPs was nearly 40 % lower than that of the neat epoxy coating. The  $i_{\text{corr}}$  of the epoxy coating filled with 2 wt.% m-ZrO<sub>2</sub> NPs was the lowest, stable at 0.155 nA/cm<sup>2</sup>.

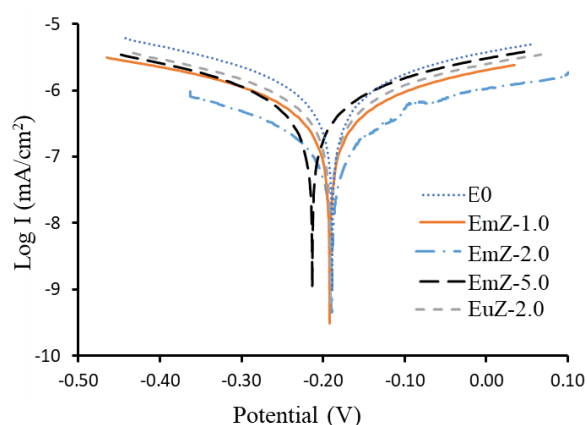


Figure 3. Polarization curve of epoxy coating filled with u-ZrO<sub>2</sub> NPs or different m-ZrO<sub>2</sub> NPs contents after 28-day immersion in 3.5 % NaCl solution.



Table 4. Polarization curve parameters ( $E_{\text{corr}}$ ,  $i_{\text{corr}}$ ) of epoxy coating filled with u-ZrO<sub>2</sub> NPs and different m-ZrO<sub>2</sub> NPs contents after 28-day immersion in 3.5 % NaCl solution.

No	Samples	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ (nA/cm <sup>2</sup> )
1	E0	-189.0	1.153
2	EmZ-1.0	-192.1	0.628
3	EmZ-2.0	-189.5	0.155
4	EmZ-5.0	-213.4	0.731
5	EuZ-2.0	-191.0	0.678

As the m-ZrO<sub>2</sub> NPs content increased/decreased to 5 wt.% or 1 wt.%, respectively, the  $i_{\text{corr}}$  of the nanocomposite coating also grew up. Theoretically, a lower corrosion current density indicates better anti-corrosion performance of epoxy coatings. The anti-corrosion performance of epoxy coatings could be arranged as follows: E0 < EmZ-5.0 < EuZ-2.0 < EmZ-1.0 < EmZ-2.0. However, there was insignificant difference in corrosion potential among the epoxy coatings investigated. Consequently, the epoxy coatings can protect the steel substrate from corrosion by NaCl solution because the coatings acted as a barrier to prevent the steel substrate from corrosive agents (Cl<sup>-</sup> ions). The nanocomposite coating had better anti-corrosion ability than the neat epoxy coating because u-ZrO<sub>2</sub> NPs and m-ZrO<sub>2</sub> NPs with small diameters could fill the defects of the epoxy chains leading to a tight coating's structure. Especially, m-ZrO<sub>2</sub> NPs have good compatibility with organic polymers. In addition, the suitable content of organically modified m-ZrO<sub>2</sub> NPs incorporated into the epoxy coating can minimize the agglomeration of nanoparticles. As a result, the structure of the nanocomposite coating becomes the tightest, which enhances the anti-corrosion and protective properties of the steel substrate.

#### 4. CONCLUSIONS

The effect of unmodified and organically modified zirconia nanoparticles (u-ZrO<sub>2</sub> NPs and m-ZrO<sub>2</sub> NPs, respectively) on some properties and morphology of epoxy coatings was studied. The obtained results showed that ZrO<sub>2</sub> NPs could enhance the properties of epoxy coatings such as mechanical properties, thermal stability, and anti-corrosion ability. The performance of the epoxy nanocomposite coating filled with u-ZrO<sub>2</sub> NPs was slightly better than that of the neat epoxy coating. ZrO<sub>2</sub> NPs modified by 3 wt. % GPTES improved much better properties of epoxy coating than u-ZrO<sub>2</sub> NPs. The epoxy nanocomposite coating filled with 2 wt.% m-ZrO<sub>2</sub> NPs indicated the best performance. The properties of this coating were a hardness of 0.85, impact resistance of 80 kG.cm, adhesion to steel substrate of 1.34 MPa, initiation of thermal degradation at 329.4 °C, and corrosion current density of 0.155 nA/cm<sup>2</sup> (after 28-day immersion in 3.5 wt.% NaCl solution). The cross-section FESEM images showed that m-ZrO<sub>2</sub> NPs could be regularly dispersed in the epoxy matrix while u-ZrO<sub>2</sub> NPs agglomerated in the epoxy coating. This could be the reason for the best performance of the epoxy nanocomposite coating filled with 2 wt.% m-ZrO<sub>2</sub> NPs.

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**CRedit authorship contribution statement.** Dao Phi Hung: Writing the original draft; Nguyen Thuy Chinh: Revision, administration; Nguyen Anh Hiep: Methodology; Nguyen Xuan Thai: Formal analysis, investigation; Ly Thi Ngoc Lien: Formal analysis, investigation; Dao Huu Toan: Investigation; Hoang Thi

Huong Giang: Data administration; Thai Hoang: Setting up scientific idea, funding acquisition, supervision, and revision.

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