The Effect of 2-Mercaptobenzimidazole-Polyaniline-CeO₂ Ternary Nanocomposite Addition as a Superior Pigment for Improvement of Corrosion Resistance in Epoxy Coatings

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Abstract

The 2-mercaptobenzimidazole-polyaniline-ceria (MBI-PANI-CeO₂) ternary nanocomposite synthesized and used as pigment into epoxy (EP) to improve protection properties of coating on mild steel. The MBI-PANI-CeO₂ nanocomposite was prepared using layer by layer assembly. Initially, the PANI layer was polymerized on the surface of CeO₂ nanoparticles. Then, the MBI inhibitor was adsorbed on PANI with opposite electrostatic charges. The anticorrosive performance of EP coatings was investigated using electrochemical impedance spectroscopy, salt spray test, and scanning electron microscopy by incorporating various amounts (0.5, 1, and 2 wt. %) of the MBI-PANI-CeO₂ nanocomposite. The EP coating containing 1 wt. % of nanocomposite showed the highest corrosion resistance and minimum agglomeration. This coating indicated the coating resistance of 19.1 MΩ cm², which is greater than EP and EP/CeO₂ coatings. The EP/MBI-PANI-CeO₂ (1 wt. %) coating showed water uptake percentage (2.09 %) about two times lower than EP/CeO₂ coatings (4.56 wt. %), indicating appropriate barrier performance of inhibitor incorporated EP.

1. Introduction

Anodic protection, cathodic protection, and organic coating are well known as practical ways for protecting metallic substrates from corrosion. Over time, researchers considerably focused on organic coatings as a financial protection technique [1–7]. Among organic coatings, the epoxy (EP) has been used extensively due to the superior features like good barrier properties against corrosive species, suitable adhesion, appropriate chemical, and mechanical resistances [8–14]. However, the lifetime of these coatings was decreased during immersion in corrosive media, which resulted in a diffusion of corrosive species at the metal/coating interface, initiating corrosion of the substrate beneath coating [15–17]. Therefore, improving the quality of the EP coating by organic and inorganic pigments has been attracting a lot of attention [13, 18–22]. In this regard, many kinds of research have been conducted to enhance the anticorrosive resistance of EP coatings by various compounds [23–26]. Embedding inorganic metal oxide nanoparticles (NPs) into EP resin improves the resistance of coating against corrosion and degradation due to decreasing of electrolyte diffusion pathways [27–31]. To uniform dispersion of nanoparticles without much agglomeration in EP and reduce the permeability of EP based coatings against oxygen, water, and ion transfer, the surface of nanoparticles was modified with a variety of organic and inorganic compounds [32–35]. Corrosion inhibitors can provide more corrosion protection, especially in active corrosion areas of coating. Direct embedding of inhibitors in the EP coating can decrease the interactions between the resin and inhibitor molecules, causing the reduction of inhibition performance [36–38]. One of the strategies for overcoming this problem is using the corrosion inhibitors to modify the metal oxides NPs [39, 40]. Layer by layer electrostatic deposition is reported as an effective method for treatment of metal oxide nanoparticles, which is based on adsorption of layers with opposite electrostatic charges. In our previous work, the surface of cerium (IV) oxide NPs was successfully modified with imidazole [41]. It was found out that EP coating with modified CeO₂ NPs displayed higher coating resistance with 5.4 orders of magnitude compared to unmodified CeO₂ NPs.

In this research, 2-mercaptobenzimidazole (MBI) was used to modify the ceria (CeO₂) NPs. For electrostatic adsorption of MBI on the surface of CeO₂ NPs, oxidative polymerization of polyaniline (PANI) was first

performed to obtain a positive layer. The impact of MBI-PANI-CeO₂ nanocomposite on the barrier performance of the EP coating was investigated.

2. Experimental

2.1 Synthesis of MBI-PANI-CeO₂ nanocomposite

0.3 g sodium dodecyl sulfate (SDS, DAEJUNG Co., Ltd Korea) and 0.5 g cerium (IV) oxide NPs (US Research Nanomaterials, Inc (99.95 %)) were mixed. Ammonium persulfate 0.3 M (APS, DAEJUNG Co., Ltd Korea) was added as the initiator, stirring for 10 min. Then, 5 cc aniline (Fluka, purity 99.5%) was added slowly, stirring for two h in an ice bath. The precipitates were dispersed in sodium chloride solution including 1 wt% of polyvinyl pyrrolidone (DAEJUNG Co., Ltd Korea, Mw=30000 g mol⁻¹) in ethanol for 20 min. The synthesized PANI - CeO₂ was poured in sodium chloride 0.1 M and 1 g of MBI was added, stirring for 20 min. Finally, the MBI-PANI-CeO₂ nanocomposite was centrifuged and dried.

2.2 Preparation of coatings

The mild steel panels (1×1 cm²) were polished and degreased with EtOH. Different amounts of MBI-PANI-CeO₂ nanocomposite were poured in 1g epoxy (NANYA EP resin, NPEL-127). Then, the 0.5 g ACR Hardener (H-3892, amine type) was added. The application of coatings on mild steel were carried out by brushing.

2.3 EIS measurements

The potentiostat-galvanostat (Orignalys, 01A) was used for EIS test in the 3.5 wt. % NaCl at OCP. The frequency range was 10⁵ Hz - 10⁻² Hz with an AC voltage of ± 5 mV. The saturated calomel electrode, platinum plate, and mild steel coated samples were used as the reference, counter, and working electrodes, respectively.

2.4 Salt spray test

The salt spray evaluation was carried out as reported by the ASTM B117 standard using GT7004-M chamber. The EP, EP/CeO₂ and EP/MBI-PANI-CeO₂ (1 wt. %) coated substrates were put in the room and encountered to the sodium chloride 5 wt. % (1.5 ± 0.5 ml h⁻¹) for 200 h at 35 °C.

2.5 Pull-off test

The ASTM D4541 procedure was used for pull-off test. The analysis was done using Digital Tester BGD500 for coated substrates (EP, EP/CeO₂ and EP/MBI-PANI-CeO₂ (1 wt. %)).

2.6 Characterization

The TENSOR27 spectrometer was used for FTIR analysis. The Raman spectroscopy was carried out by Teksan, Takram P50C0R10 spectrophotometer. The thermogravimetric evaluation (TGA) was done with Linseis STA PT-1000 analyzer (heating rate: 10°Cmin⁻¹). The DLS and Zeta potential measurements were carried out with Microtrace, Nanotrace Wave. The morphology was investigated by field emission scanning electron microscopy (FE-SEM, MIRA3).

3. Results And Discussions

3.1 Characterization of MBI-PANI-CeO₂ nanocomposite

The FTIR spectra of CeO₂, PANI-CeO₂, and MBI-PANI-CeO₂ nanocomposite were depicted in Fig. 1. The peaks at 545 cm⁻¹ and 722 cm⁻¹ are related to the vibrations of Ce-O, which are seen at all spectra [42, 43]. Fig. 1 (pattern b) approves the synthesis of PANI on the CeO₂ NPs. The characteristic peaks of PANI were observed at 3258 cm⁻¹ for the N-H of aromatic amines, 1579 cm⁻¹ for the C=N, 1503 cm⁻¹ for C=C, and 1336, 1290 cm⁻¹ for C-N stretching. The N-H stretching and bending vibrations of MBI can be observed at 3155 and 1456, respectively (Fig. 1 pattern c). Also, the stretching vibrations of C-H, C=N, C=C, C-N and C-S were perceived at 2800-3000 cm⁻¹, 1697 cm⁻¹, 1510 cm⁻¹, 1350 cm⁻¹ and 1167 cm⁻¹, respectively [44].

The Raman spectra were illustrated in Fig. 2. The peak at 459 cm⁻¹ is related to the F_{2g} mode of CeO₂ NPs [45]. The C-H bending of the quinoid ring, C-N, and C=N stretching vibrations for PANI can be seen at 1241 cm⁻¹, 1399 cm⁻¹, and 1547 cm⁻¹, respectively [46]. According to Fig. 2 (c), the C=S, CSN-H, and C-N peaks appear in 416, 1198, and 1280 cm⁻¹, respectively which are confirmed the formation of MBI layer.

The average nanoparticle size gradually increases with the formation of each layer. This approves the layer by layer building of the nanoparticles. Initially, the particle size of CeO₂ NPs was 262 nm. After forming the PANI, the size reached to 351 nm. By the addition of the MBI, size of the particles reached to 845 nm. An increase in the size with an increase in layer thickness illustrates the synthesis of MBI-PANI-CeO₂ nanocomposites.

The zeta potential values were changed by the addition of each layer, which is indicating the electrostatic adsorption of PANI and the MBI layers. The charge of CeO₂ NPs was -11.3 mV. The negative charge of this layer was due to the existence of C₁₂H₂₅SO₄⁻ in SDS. After oxidative polymerization of PANI, the zeta potential value enhanced to 33.2 mV, confirming that the CeO₂ NPs covered with PANI. The zeta potential value decreased to -16.9 mV by loading of the MBI. According to the MBI structure, the presence of nonbonding electron pairs facilitates the adsorption of MBI molecules on the previous layer causing the negative charges on the particles.

The TGA results of PANI-CeO₂ and MBI-PANI-CeO₂ nanocomposite were shown in Fig. 3.

In both curves, the weight loss at 50-200°C was obtained from removing adsorbed water. Removing of water molecules in MBI-PANI-CeO₂ nanocomposite is gentle than the PANI-CeO₂. The hydrophobicity of the MBI decreased the amount of adsorbed water. The weight loss at 200 - 600°C is due to the deterioration of PANI in Fig. 3 (a). The sharp weight loss at 200-600°C is due to the degradation of MBI and PANI [47].

3.2 Morphological studies of coatings

The morphological properties of the EP coatings containing CeO₂ and MBI-PANI-CeO₂ nanocomposite were investigated by SEM (Fig. 4). Incorporating of the MBI-PANI-CeO₂ nanocomposite in the EP matrix causes uniform and homogeneous coating. The consistency of NPs with EP can be promoted in the presence of MBI-PANI-CeO₂ nanocomposite. The amount of aggregation was low in the presence of 1wt. % of MBI-PANI-CeO₂

nanocomposite compared to other percentages. With increasing the loaded percentage of MBI-PANI-CeO₂ nanocomposite from 1 wt. % to 2 wt. %, the amount of aggregation increased, indicating the decrease of the anticorrosive performance of the coating.

3.3 EIS test

The barrier properties of EP coatings containing CeO₂ and MBI- PANI-CeO₂ nanocomposite were evaluated by EIS in NaCl 3.5 wt. % at 65 °C. The Bode-phase curves of the EP, EP/CeO₂, and EP/MBI-PANI-CeO₂ coatings at 2, 24, 72, and 200 hours were depicted in Fig. 5. The EIS data were fitted with a more complex equivalent circuit as shown in Fig. 6.

The R_s , R_{coat} , and R_{ct} are related to solution resistance, coating resistance, and charge transfer resistance. The CPE_{coat} is a constant phase element of coating and CPE_{dl} is a constant phase element of the electrical double layer [48]. The fitted EIS parameters were given in Table 1.

The R_{coat} values of the EP, EP/CeO₂, EP/MBI-PANI-CeO₂ (0.5 wt. %), EP/MBI-PANI-CeO₂ (1 wt. %), and EP/MBI-PANI-CeO₂ (2 wt. %) were obtained 9.11 k Ωcm², 6.51, 16.6, 19.1, and 15.6 MΩcm², respectively.

It was seen that the R_{coat} value of EP coating was enhanced by the incorporation of CeO₂ NPs. The presence of metal oxide nanoparticles as effective fillers enhanced protection performance of epoxy coating with decreasing corrosive electrolyte diffusion pathways. The remarkable improvement in the anticorrosive properties was obtained for the EP/MBI-PANI-CeO₂ coatings. This was due to the hydrophobic feature of the EP/MBI-PANI-CeO₂ coatings.

Table 1
The extracted EIS results for the EP, EP/CeO₂, and EP/MBI-PANI-CeO₂ coatings.

Sample	time (h)	R _{coat} (Ω cm ²)	CPE _{coat}		R _{ct} (Ω cm ²)	CPE _{dl}	
			n	Y ₀ (Ω ⁻¹ cm ⁻² S ⁿ)		n	Y ₀ (Ω ⁻¹ cm ⁻² S ⁿ)
EP	3.21×10 ⁴	0.61	2.13×10 ⁻⁸	1.45×10 ⁶	0.48	5.42×10 ⁻⁹	
	24	1.36×10 ⁴	0.99	3.02×10 ⁻¹⁰	6.56×10 ⁴	0.61	5.69×10 ⁻⁹
	72	1.31×10 ⁴	0.99	3.18×10 ⁻¹⁰	4.38×10 ⁵	0.72	8.41×10 ⁻¹⁰
	200	9.11×10 ³	0.99	3.33×10 ⁻¹⁰	3.94×10 ⁵	0.64	2.16×10 ⁻⁹
EP/CeO ₂	2	7.54×10 ⁶	0.97	1.37×10 ⁻¹⁰	2.57×10 ⁷	0.78	1.06×10 ⁻¹⁰
	24	6.38×10 ⁶	0.97	1.52×10 ⁻¹⁰	8.86×10 ⁶	0.61	6.21×10 ⁻¹⁰
	72	3.41×10 ⁶	0.99	1.38×10 ⁻¹⁰	4.78×10 ⁶	0.58	1.07×10 ⁻⁹
	200	6.51×10 ⁶	0.97	1.69×10 ⁻¹⁰	1.41×10 ⁷	0.57	7.65×10 ⁻¹⁰
EP/MBI-PANI-CeO ₂ (0.5%)	2	6.86×10 ⁸	0.98	1.09×10 ⁻¹⁰	9.39×10 ⁸	0.99	1.97×10 ⁻¹¹
	24	2.67×10 ⁷	0.99	1.18×10 ⁻¹⁰	1.76×10 ⁸	0.99	2.13×10 ⁻¹¹
	72	1.53×10 ⁷	0.99	1.21×10 ⁻¹⁰	5.31×10 ⁸	0.62	1.15×10 ⁻¹⁰
	200	1.66×10 ⁷	0.99	1.29×10 ⁻¹⁰	1.58×10 ⁸	0.83	5.74×10 ⁻¹¹
EP/MBI-PANI-CeO ₂ (1%)	2	9.49×10 ⁸	0.99	1.29×10 ⁻¹¹	8.09×10 ⁸	0.99	1.65×10 ⁻¹¹
	24	2.81×10 ⁷	0.99	1.39×10 ⁻¹¹	4.93×10 ⁸	0.99	1.74×10 ⁻¹¹
	72	1.59×10 ⁷	0.99	1.43×10 ⁻¹¹	6.29×10 ⁸	0.68	7.18×10 ⁻¹¹
	200	1.91×10 ⁷	0.99	1.47×10 ⁻¹¹	2.11×10 ⁸	0.85	4.03×10 ⁻¹¹
EP/MBI-PANI-CeO ₂ (2%)	2	1.34×10 ⁷	0.99	1.16×10 ⁻¹⁰	1.06×10 ⁸	0.76	8.53×10 ⁻¹¹
	24	1.68×10 ⁷	0.99	1.23×10 ⁻¹⁰	5.82×10 ⁸	0.61	1.16×10 ⁻¹⁰
	72	1.72×10 ⁶	0.95	1.85×10 ⁻¹⁰	3.01×10 ⁶	0.65	6.27×10 ⁻¹⁰
	200	1.56×10 ⁷	0.99	1.33×10 ⁻¹⁰	6.16×10 ⁷	0.99	2.38×10 ⁻¹¹

The protection properties of EP/MBI-PANI-CeO₂ coatings depend on the MBI-PANI-CeO₂ content. By increasing MBI-PANI-CeO₂ content to 1%, R_{coat} enhanced by three orders of magnitude and afterward, a significant

decrease was observed. A similar trend was also observed in the R_{ct} values of coatings, confirming less surface corrosion of these coatings.

CPE is one of the essential parameters which was calculated according to Eq. 1 for the coating and electrical double layer.

$$CPE = \frac{(R \times Y_0)^{\frac{1}{n}}}{R} \quad (1)$$

Where R is the resistance (Ωcm^2), Y_0 is the admittance ($\Omega^{-1} \text{cm}^{-2} \text{s}^n$), and n is the CPE exponent, which is between 0 and 1. The CPE_{coat} values of all samples were increased with diffusion of aqueous electrolyte into the coating (Fig. 7). A smaller increase of CPE_{coat} was observed for EP/MBI-PANI-CeO₂. The CPE_{coat} of EP coating was higher than that of EP/CeO₂ and EP/MBI-PANI-CeO₂ coatings, respectively. These results indicate that incorporating CeO₂ nanoparticles in the EP coating had a positive effect on the corrosion protection, while the tremendous improvement was observed in the case of MBI-PANI-CeO₂ nanoparticles. The same behavior was also observed for CPE of double layer (Fig. 7(b)).

The amount of water uptake was calculated by Eq. 2 [49] and shown in Fig. 7 (c) for all samples.

$$\text{Water uptake (\%)} = \{[\log(CPE_{coat,t}) / \log(CPE_{coat,0})] / \log(86)\} \times 100 \quad (2)$$

The water uptake values for EP are 1.86 and 4.05 times higher than that of EP/CeO₂ and EP/MBI-PANI-CeO₂ (1 wt. %), respectively. This was due to the promotion of the protective behavior of the EP coating in the presence of the MBI modified NPs.

3.4 Salt spray tests

The visual perspective of the neat EP, EP/CeO₂, and EP/MBI-PANI-CeO₂ (1 wt. %) coatings were illustrated in Fig. 8 after 200 h test.

According to Fig. 8 (a), the corrosion products were produced due to the inappropriate barrier feature of EP coating. Existing micropores in the EP facilitated the anodic and cathodic reactions and produced the corrosion products. The amount of produced rusts were significantly decreased in the presence of CeO₂ nanoparticles in comparison with EP. The CeO₂ nanoparticles can dramatically fill the coating's pores and reduce the diffusion pathways. The highest coating resistance of EP/MBI-PANI-CeO₂ provided the lowest corrosion products among all coatings.

3.5 Pull-off test

Adhesion strength is one of the crucial factors which influence the coating's barrier performance. The results of pull-off analysis for the EP, EP/CeO₂, and EP/MBI-PANI-CeO₂ (1 wt. %) coatings are presented in Fig. 9. It can be seen that the adhesion strength of EP/MBI-PANI-CeO₂ (1 wt. %) was 1.328 MPa which is higher than

EP/CeO₂ (1.223 MPa) and EP (0.985 MPa), respectively. It is concluded that the adhesion of EP coating increased with embedding pure CeO₂ and MBI-PANI-CeO₂ pigments, which results in appropriate protective performance during the lifetime of coating.

4. Conclusion

The effect of MBI-PANI-CeO₂ nanocomposite (various contents) on the anticorrosive property of EP coating was evaluated using EIS, salt spray measurements. SEM analysis showed that the incorporation of MBI-PANI-CeO₂ nanocomposite in epoxy resin resulted in the formation of EP/MBI-PANI-CeO₂ coatings with good surface coverage. The surface morphology of EP/MBI-PANI-CeO₂ coatings was found to be dependent on the wt. % of MBI-PANI-CeO₂ nanocomposite. The highest compact EP/MBI-PANI-CeO₂ coatings were formed in 1 wt. % of MBI-PANI-CeO₂, leading to the lowest water uptake and the highest R_{coat} (19.1 MΩ cm²). The low water uptake and high R_{coat} of EP/MBI-PANI-CeO₂ coatings delayed the electrolyte diffusion, resulting in remarkable improvements in the protective performance of these coatings compared to the EP and EP/CeO₂ coatings. Moreover, the deterioration of the EP coating was decreased in the presence of MBI-PANI-CeO₂ nanocomposite during the salt spray test.

Declarations

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Statements and Declarations

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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50. **The effect of 2-mercaptobenzimidazole-polyaniline-CeO₂ ternary nanocomposite addition as a superior pigment for improvement of corrosion resistance in epoxy coatings**

Figures

Figure 1

FTIR results of (a) CeO₂ (b) PANI-CeO₂ and (c) MBI-PANI-CeO₂ nanocomposite.

Figure 2

Raman result of (a) CeO₂ (b) PANI-CeO₂ and (c) MBI-PANI-CeO₂ nanocomposite.

Figure 3

TGA results of (a) PANI-CeO₂ (b) MBI-PANI-CeO₂ nanocomposite.

Figure 4

SEM results of EP coating in the presence of (a) CeO₂, (b) MBI-PANI-CeO₂ (0.5 wt. %), (c) MBI-PANI-CeO₂ (1 wt. %) and (d) MBI-PANI-CeO₂ (2 wt. %) nanocomposites.

Figure 5

Bode-phase diagrams of the EP, EP/CeO₂, and EP/MBI-PANI-CeO₂ coatings in a saline electrolyte at (a) 2h (b) 24 h (c) 72 h (d) 200 h.

Figure 6

The equivalent circuit model for fitting EIS data.

Figure 7

The variation of (a) CPE_{coat} (b) CPE_{dl} and (c) water uptake versus time for EP, EP/CeO₂ and EP/MBI-PANI-CeO₂.

Figure 8

Salt spray results of (a) EP (b) EP/CeO₂ and (c) EP/ MBI-PANI-CeO₂ (1wt. %).

Figure 9

The pull-off results for the EP, EP/CeO₂, and EP/MBI-PANI-CeO₂ (1 wt. %).

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