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Improving the anticorrosive performance of epoxy coatings by embedding various percentages of unmodified and imidazole modified CeO_2 nanoparticles

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ABSTRACT

The surface of CeO_2 nanoparticles was modified with imidazole as an effective corrosion inhibitive pigment via layer by layer method. At first, the surface of nanoparticles was coated by polyaniline via oxidative polymerization. Then, the imidazole layer was formed on polyaniline due to opposite electrostatic charges. The modification of nanoparticles by imidazole was investigated by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, thermogravimetric analysis (TGA), Dynamic light scattering (DLS) and Zeta potential (ZP) and Transmission electron microscopy (TEM). The anticorrosion performance of epoxy coating on mild steel in the presence of different concentrations of unmodified and imidazole modified CeO_2 nanoparticles (0.5, 1 and 2 wt%) was evaluated in NaCl 3.5 wt% solution by electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The optimum percentage of embedded CeO_2 nanoparticles in the epoxy coating (unmodified and imidazole modified) was 0.5 wt% in which the coating has minimum agglomeration and appropriate corrosion resistance. The coating resistance of epoxy/imidazole modified CeO_2 nanoparticles 0.5 wt% after 200 h immersion in NaCl 3.5 wt% solution was obtained $1.19 \times 10^7\ \Omega\,cm^2$ which is higher than epoxy/unmodified CeO_2 nanoparticles ($6.51 \times 10^6\ \Omega\,cm^2$). Also, the water uptake percentage of epoxy containing 0.5 wt% of imidazole modified CeO_2 nanoparticles at the end of immersion time was obtained 3.85% which was lower than unmodified CeO_2 nanoparticles (4.56%) due to inhibitive features and hydrophobicity of imidazole.

1. Introduction

Due to the extensive application of mild steel in industry, manufacturing and heavy constructions like marine and automotive, many researches have been done in corrosion protection of it such as inhibitors, cathodic and anodic protection and protective coatings [1–3]. Among various corrosion protection methods, application of the epoxy coatings is one of the most common ways to improve the corrosion resistance of metals [4]. During coating and curing processes, some defects and cavities created in the structure of the epoxy coatings. By exposing coatings in the aggressive medium, corrosive species such as dissolved oxygen and chloride ions in water interpenetrated through the coating's pathways. Consequently, corrosion resistance and adhesion of coating were decreased [5,6]. So, making a coating with the long-term corrosion resistance with high adhesion needed the use of additive material that reinforces of the coating. Recently the use of nanoparticles as inorganic nanofillers has been attracted a special attention because of their unique barrier properties [7,8]. Extensive studies have been done to improve the corrosion resistance of the epoxy coating using nanoparticles such as TiO_2 [9], ZnO [10], SiO_2 [11], Al_2O_3 [12] and nanoclays [13]. CeO_2 is one of these nanoparticles that enhance the mechanical abrasion, corrosion and wear resistances [14,15]. In spite of suitable properties of the nanoparticles, they interact with each other easily and agglomerate. Surface modification of nanoparticles with different organic-inorganic compounds such as corrosion inhibitors, surfactants, silanes and other materials enhances the features of nanoparticles [16,17]. Therefore, the agglomeration of nanoparticles decreased and a homogeneous dispersion of them in coating matrix obtained. Also, efficient filling of the coating pores prevented the penetration of aggressive species into the coating result in the improvement of the corrosion resistance [18]. Different types of corrosion inhibitors such as imidazole (IM), benzotriazole (BTA), phosphates, vanadates and borates can be readily embedded into the coating which can improve coating resistance against corrosion [19]. However, direct addition of inhibitors influences the activity of the coating that has many disadvantages such as degradation of coating,

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the interaction of inhibitor and coating, osmotic blistering and deactivation of inhibitor [20,21]. Different methods were reported in the litratures for surface modification of inorganic nanoparticles such as chemical treatment, grafting of synthetic polymer, ligand exchang techniqe [22] and layer by layer (LBL) assembly which is based on deposition of oppositely charged layered [23,24]. To the best of our knowledeg, there are limited researches about the modification of CeO_2 nanoparticles by corrosion inhibitors via layer by layer method. In this work, the surface of CeO_2 nanoparticles was modified with imidazole by LBL method. Also, the effect of imidazole modified and unmodified CeO_2 nanoparticles on the corrosion resistance of the epoxy coating was investigated in 3.5 wt% NaCl solution by electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Material

Chemical materials of imidazole (Merck, 99%), ethanol (Merck, 99.9%), NaCl and HCl were all used without further purification. The CeO_2 nanoparticles were purchased by US Research Nanomaterials, Inc (99.95%). The aniline monomer was purchased by Fluka (purity 99.5%) and distilled for three times. The ammonium persulphate (APS) as initiator, sodium dodecyl sulphate (SDS) as surfactant and polyvinyl pyrolidone (PVP, Mw = 30000 g mol^{-1}, extra pure 98%) were provided by DAEJUNG Co.,Ltd (Korea). The NANYA epoxy resin (NPEL-127) with ACR Hardner (H-3895: amine type) were used as received.

2.2. Modification of nanoparticles

The surface modification of CeO_2 nanoparticles was done by LBL method during two steps. At first step, 0.3 g SDS and 0.5 g CeO_2 nanoparticles were dispersed in 50 mL distilled water. Then, 0.7 g APS in 10 mL distilled water was added to previous solution and stirred for 10 min in ice bath (~4 °C). After that, 5 mL distilled aniline monomer was added dropwisely in order to chemical oxidative polymerization of polyaniline on CeO_2 surface and stirred for 2 h. Finally, the precipitates were centrifuged at 4000 rpm and washed with distilled water. At the end of first step, the synthesized polyaniline coated CeO_2 was incubated in 0.5 M NaCl containing 1 wt% of PVP in ethanol for 20 min. Then, the mixture was centrifuged and washed with distilled water. At the second step, prepared polyaniline coated CeO_2 was dispersed in 100 mL NaCl 0.1 mol/L and 1 g imidazole was added at pH = 3 followed by stirring for 20 min. Imidazole modified CeO_2 nanoparticles were centrifuged, washed with distilled water and dried for 48 h at ambient temperature.

2.3. Substrate pretreatments and coating preparation

The $1 \times 1\ cm^2$ steel specimens polished by 500–2000 grade SiC papers then washed by distilled water and degreased with ethanol then dried by air flow. The composition of the steel substrate was analyzed by quantmetry technique and presented Table 1.

Modified and unmodified nanoparticles with different weight percentages (0.5, 1 and 2 wt%) dispersed in 3 g epoxy resin during 2 days by a magnetic stirrer. After that, the hardener was added to the mixture with 1:2 wt ratio (1: Hardener, 2: epoxy resin). The mixture was stirred for 20 min and was applied on the pretreated sheets by brushing method. The samples were cured and dried at room temperature. The thickness of coatings were measured with eXacto FN elcometer and were obtained 200 ± 5 µm after drying.

Table 1
The chemical composition of the steel substrate.

Fe	Si	C	S	P	Cu	Mn	Others
99.4%	0.022%	0.070%	0.007%	0.008%	0.027%	0.283%	0.183%

2.4. Electrochemical corrosion test

Electrochemical corrosion tests were carried out in 3.5 wt% NaCl aqueous solution using an Origa Flex-OGF01A/potentiostat-galvanostat (Origalys, France) in the frequency range of 10 kHz to 0.01 Hz with an AC voltage of ± 5 mV at room temperature in three electrode cell by electrochemical impedance spectroscopy (EIS). Reference, working and counter electrodes were saturated calomel electrode (SCE), the coated specimens and platinum sheet, respectively.

2.5. Characterization test

The FTIR analysis was done by Fourier transform infrared TENSOR27 spectrometer (Brucker) in the range of 400–4000 cm^{-1} using the KBr pellets. The Raman spectroscopy was done by Teksan, Takram P50C0R10 Raman spectrophotometer. The spectra were recorded in the 100–4400 cm^{-1} range and the excitation wavenumber was 532 nm.

The thermogravimetric analysis (TGA) were carried out with Linseis STA PT-1000 (Germany) Thermal analyzer in the N_2 atmosphere at the heating rate of 10 °C/min. The DLS and Zeta potential tests were performed with Microtrace, Nanotrace Wave. The Transmission electron microscopy (TEM) images were taken by LEO 906 E (100 kV).

The surface morphology of samples was studied by field emission scanning electron microscopy (FE-SEM, MIRA3).

3. Result and discussion

3.1. Characterization of imidazole modified CeO_2 nanoparticles

Fig. 1 shows the FTIR spectra of unmodified CeO_2 nanoparticles (1-a), CeO_2 loaded with polyaniline (1-b) and CeO_2 loaded with polyaniline and imidazole (1-c). According to Fig. 1(a), the Ce-O stretching vibrations can be observed at 545 cm^{-1} and 722 cm^{-1}. Furthermore, the stretching Ce-O at 722 cm^{-1} leads to the peaks in the range of 1000–1500 and 2850–2950 cm^{-1} [25]. The observed peaks at 3258 cm^{-1} (N—H stretching mode of aromatic amines), 1579 cm^{-1}

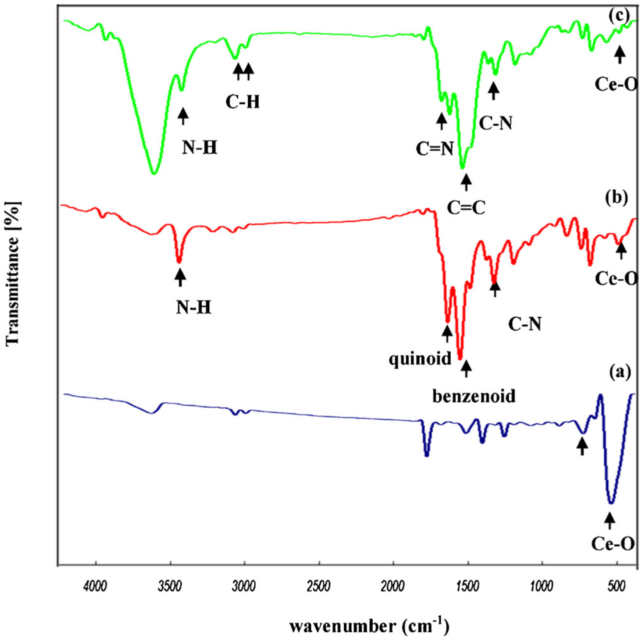

Fig. 1. The FTIR spectra of (a) CeO_2 nanoparticles (b) CeO_2 loaded with polyaniline and (c) CeO_2 loaded with polyaniline and imidazole.