*Vietnam Journal of Science and Technology **55** (5B) (2017) 203-209*

CORROSION RESISTANCE AND MECHANICAL PROPERTIES OF TiO_2 NANOTUBES / EPOXY COATING ON STEEL SPCC-JISG 3141

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Received: 11 August 2017; Accepted for publication: 7 October 2017

ABSTRACT

Titanium dioxide nanotubes (TNTs) have been considered the promising nanostructures employed for many practical applications such as biomedical, photonic and optoelectronic devices. Coatings prepared from epoxy-nano-TiO_2 nanotubes synthesized by *in situ* polymerization were found to exhibit excellent corrosion resistance much superior to epoxy resin in aggressive environments. The corrosion studies were carried out on steel SPCC JISG 3141 plates coated with 5 wt % and without of TiO_2 nanotubes (TNTs). The synthesis of titanium dioxide nanotubes (TNTs) using hydrothermal method was investigated. The synthesized TNTs were characterized with Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) specific area surface test, X-ray diffraction (XRD) and Transmission Electron Microscope (TEM) imaging. The results demonstrated a unique tubular nanostructure of TNTs shape. The mechanical performance of the nanocomposites was examined to show that the 5 wt % TNTs/epoxy coating was more impact resistance, the film hardness behavior and bending resistance than epoxy coating. The effects of TNT particles on corrosion resistance of epoxy coating were studied by salt spray test (Model SAM Y90) and compared to that of non-filler. After 144 h exposure, the corrosion resistance of epoxy resin greatly improved by using reinforcing the white pigment of TNTs. The results indicated that the coating containing TNTs shows the best protection efficiency.

Keywords: salt spray, TiO_2 nanotubes, epoxy resin, nanocomposite, corrosion resistance.

1. INTRODUCTION

SPCC-JISG 3141, which represents a commercial quality cold rolled steel, offers high corrosion resistance compared to other steels. However, they display poor resistance to localized pitting corrosion in aqueous solutions containing complex agents such as chloride ions [1 - 3]. JISG 3141 has been widely used for structural components because of the low absolute strength and higher material cost of aluminum alloys. Therefore, the improvement of JISG 3141 corrosion resistance has been a topic of great importance.

Organic coatings have been widely used to protect metals against corrosion through playing as a physical barrier between the metal surface and the corrosive environment. However, the corrosive species such as oxygen, water and chloride ions can reach the metal/coating interface through diffusion into the coating porosities. In recent years, the researchers' attentions have been directed toward using nano size materials in the polymer coating to enhance its protection properties. Titanium dioxide (TiO_2) is a most important white pigment with the high potential for applications in coating industry [4 - 6]. For nanomaterials, titanium dioxide nanotubes (TNTs) are one of the promising nanostructured oxides because of being inexpensive, harmless and chemically stable. Many methods such as replica [7, 8], template [9] and anodizing of metal substrates [10, 11] have been investigated to synthesis in a nanotubular form. However, TNTs that is synthesized by so-called Kasuga method [12, 13], which using a simple and low temperature solution chemical processing. Recently, Ashraf M. ElSaeed *et al.* has reported that the TNT tubular, is an inert lamellar pigment, which orientate themselves parallelly to the substrate surface and inhibiting corrosion by acting as a barrier to water and oxygen from the environment [14].

In this paper, TNTs were successful synthesized by hydrothermal methods. In addition, the aim was to enhance mechanical properties and corrosion resistance of epoxy matrix adding the TNTs pigment.

2. MATERIAL AND METHODS

2.1. Materials

All of solvent chemical during hydrothermal and grafting treatments were sourced Merck (Germany), such as toluene (99.8 %), HCl, NaOH. Titanium dioxide powder (> 99 %) manufactured by Merck, with an average particle sizes of 21 nm.

D.E.R.331 (Dow, USA) liquid epoxy resin is a liquid reaction product of epichlorohydrin and bisphenol A, with a molecular mass of 182-192 according to the supplied. And epoxy curing agent was also purchased from Dow, USA (D.E.H.24).

Mild steel (Normal steel SPCC JISG 3141) panels were used as the base metal in this investigation.

2.2. Experimental

2.2.1. TiO_2 nanotubes synthesis

TiO_2 nanotubes were synthesized by Kasuga-hydrothermal methods. 10 M NaOH aqueous solution (100 ml, in D.I. water) was placed in 4 g TiO_2 powder covered Teflon lined stainless steel vessel subsequent to stir for 1 h at room temperature. Following this, the mixture in vessel was heated at 140 ^oC under autogenously pressure for 24 h. Then, the mixture was cooled to room temperature. The precipitates were neutralized by 0.1 M HCl for 1 hour, washed three times with distilled water through centrifugation process until the pH value reached a value of approximately 7. After washing, the obtained precipitates were dried at 100 ^oC overnight in the oven. Finally, the dried powder was annealed at 400 ^oC for 1 h

The structure of the obtained materials was evaluated using transmission electron microscope (TEM, JEM1010-JEOL). X-ray diffraction (XRD, Siemens D5005) using the diffractometer with a CuKα radiation in reflection mode and a step scan mode in a range of 20 -

80° to identify the crystal phases of the TNTs. The BET analysis (Micromeritics ASAP2020) and Fourier transform infrared spectroscopy (FTIR) were also performed to estimate the surface areas and surface structures of formed TNTs, respectively.

2.2.2. Preparation of TiO_2-epoxy coatings

5 wt.% of TNTs were separately mixed with D.E.R. 331 epoxy resin through the ultrasonic oscillation (Sonics, VC-505) and mechanical stirring process. Mixing the formulated epoxy resin with the D.E.H. 24 curing agent was done on the basis of stoichiometric ratio provided by the material suppliers.

Mild steel (Normal steel SPCC JISG 3141) panels were abraded using sand paper 400, 800, 1000 grades. Then, they were degreased with acetone prior to be spray by processed mixtures (Epoxy coatings and TNTs/ Epoxy coatings).

Panels used were of a dimension of 200 mm × 70 mm × 1 mm for all characterization mechanical methods, such as tape adhesion, impact resistance, and film hardness, bending resistance following ASTM D3359-97, D2794 and D3363, D522, respectively.

The same size panels were used for salt spray test (Model SAM Y90). In this case, salt spray was following ASTM B117.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of TiO_2 nanotubes

The morphologies and dimensions of the TNTs were determined through TEM investigations, as shown in Figure 1. TEM images of TNTs revealed the presence of tubular structures with narrow size distributions (Figure 1a). High-magnification TEM observations demonstrated the uniform diameters of the materials (10 - 20 nm) and the length of 100 - 150 nm, as shown in Figure 1b.

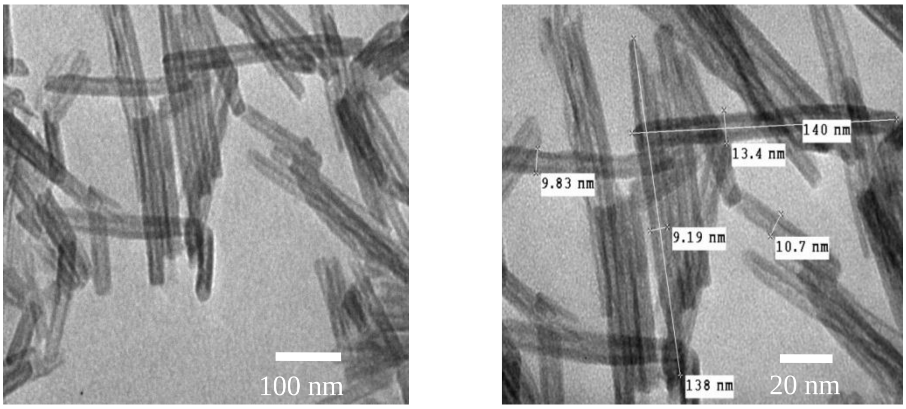

Figure 1. (a) Representative TEM image and (b) high-magnification TEM image with measured widths and lengths of as-prepared TNTs.

As can be seen in Fig. 2 the transmission FTIR spectra of TNTs were shown. The peaks below 700 cm^{-1} in Fig. 2, which were indicated the presence of Ti-O-Ti groups of TiO_2 nanotubes [15].

The broad absorption band between 3400 - 3200 cm^{-1} and the low intensity peak at 1640 cm^{-1} confirm the stretching vibration of absorption water as well as surface hydroxyl group (-OH) on the TNTs.

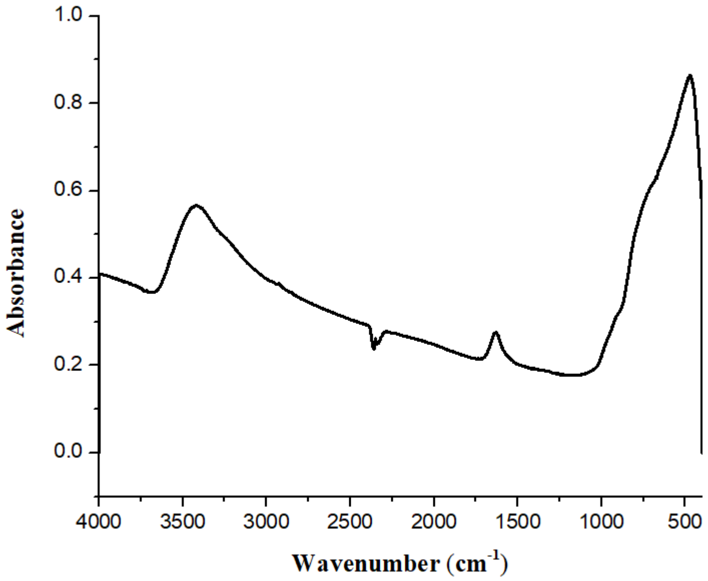

Figure 2. FTIR spectra of TiO_2 nanotubes.

BET experiment results showed that the surface area of TNTs is 188 m^2/g at 140 ^oC and then decrease with further temperature increase (119 m^2/g at 400 ^oC).

The crystal structure of TiO_2 nanotubes was monitored with XRD analysis. Figure 3 shows the XRD patterns of the TNTs after experiencing the 400 ^oC of calcinations. The as-synthesized nanotubes showed the formation of pure TNTs in anatase crystalline phases, which corresponded to the representative peaks are the anatase (101) diffraction at a scattering angle (2θ) of 25.35 ^{o} and the anatase (200) diffraction at 48.10 ^{o}.

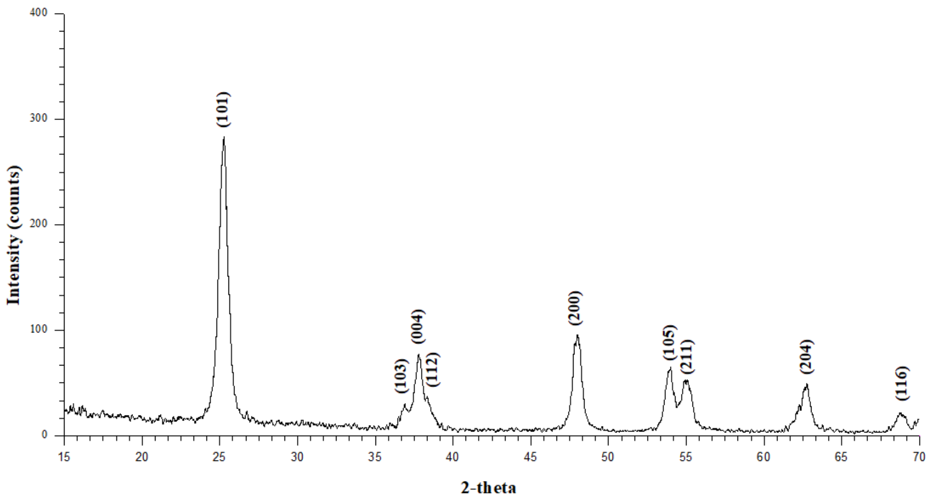

Figure 3. XRD patterns of obtained TNTs aggregates calcined at 400 ^oC.

3.2. Mechanical behavior of epoxy and TNTs/epoxy composite coatings

The mechanical properties of epoxy with and without TNTs composite coatings were evaluated using the American Society for Testing Materials (ASTM) standard test method. Table 1 presents the resulting of the epoxy coating and the TNTs/ Epoxy composite coatings.

(a) Tape adhesion test (ASTM D3359-97): Inspect the grid area for removal of coating from the both substrate. Two samples were obtained 0 % percent area removed (5B classification): the edges of the cuts are completely smooth; none of the squares of the lattice is detached.

(b) Impact resistance test (ASTM D2794): Drop heights in cm are noted on the panels. 5 wt% TNTs/Epoxy coating shows much higher impact resistance (up to 55 cm) than the epoxy coating (up to 10 cm).

(c) Film hardness by Pencil test (ASTM D3363): the pencil hardness is observed to vary between 6B and 6H. It is clear from Table 1, 5 wt% TNTs/ epoxy film showed better hardness than the epoxy coating film. It was increasing in hardness of epoxy resin when TiO_2 nanotube was added to ones.

(d) Bending resistance (ASTM D522): using a cylindrical mandrel tester. The 5 wt% TNTs/ epoxy coating samples were obtained the bending resistance at 10 mm of axis. And for the epoxy coating, the bending resistance achieved at 30 mm of axis.

Table 1. Mechanical resistance performance of the epoxy and TNTs/ epoxy composite coated panels (200 mm × 70 mm × 1 mm).

Mechanical Properties	Epoxy Coating	5wt.% TNTs/ Epoxy coating
Tape adhesion	No peel-off/100 %	No peel-off/100 %
Impact resistance (cm)	Paint film was broken at 10 cm	Paint film was broken at 55 cm
Film hardness	HB	1H
Bending resistance (mm)	30 mm/ OK	10 m/OK

3.3. Corrosion resistance of Epoxy coating and TNTs/ Epoxy coating

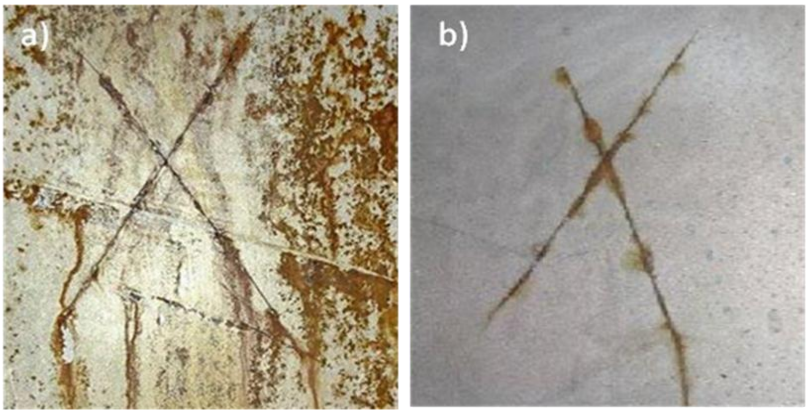

Figure 4. Salt spray corrosion test after 144 h exposure: a) Epoxy coating, b) 5 wt% TNTs/ epoxy coating.

Visual observation of the samples loaded without and with TNTs (5 wt %) after about 144 h of exposure in the salt spray chamber showed the corrosion behavior of both was not similar (Fig. 4).

The Epoxy coating' appearance after about 144 h (6 days) of exposure to salt spray medium was shown in Fig.4a, it can be seen that numerous blisters were observed near scribes. Visually, no blister was found near scribes and at the coating/steel interface of the epoxy matrix loaded with 5 wt% TNTs (Fig. 4b).

4. CONCLUSION

Titanium dioxide nanotubes (TNTs) with the diameters of about 10-20 nm were successfully synthesized via the hydrothermal method. Characterization results were confirmed by TEM, XRD analysis, BET and FTIR spectroscopes. The SPCC-JISG 3141 was coated successfully by TiO_2 nanotube/ epoxy systems.

Additionally, mechanical characterization including tape adhesion, impact resistance, film hardness and bending resistance for TNTs/epoxy and epoxy coating were conducted. The 5 wt % TNTs/epoxy coating was more impact resistance, the film hardness behavior and bending resistance than epoxy coating.

From the results of salt spray tests, TNTs/epoxy coating could significantly improve the corrosion protection properties of the Epoxy coating even at long immersion times.

Acknowledges. Authors are thankful to P.I.G.O Vietnam for supplying the materials, Mr. Le Anh Vu for carrying out part of the experiment.

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