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THE EFFECT OF NANOCARBON MATERIALS STRUCTURES ON THE PERFOMANCES OF EPOXY-BASED PAINT COATING FOR STEEL SURFACES

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ABSTRACT

This paper reports the effect of the nanocarbon materials addition on the physico-mechanical properties and corrosion protective ability of epoxy based paint coatings for the steel surfaces. In this work the nanotubes and nanosheets (layers) structures of nanocarbon materials were used for the investigation. The properties of received products were measured by the test techniques for paint coating characterization. The results showed that the addition of the nanocarbon materials (only ratio of 0.1 wt%) significantly improved the physico-mechanical performance and corrosion protection ability of epoxy coatings for steel surfaces. However improvement quantity depends on the structure of nanocarbon materials. The obtained results showed that the nanosheets structure of carbons coatings made the physico-mechanical properties of the epoxy coating increased better than those of nanotube structure.

Keywords: nanocarbon materials, graphene, carbon nanotubes, corrosion protection property, epoxy paint coatings.

1. INTRODUCTION

Metals are selected as construction material because of their mechanical properties and machine-ability at a low price but they are not resistant in the corrosion medium. The coatings of anti-corrosion paint always play essential role in this area. By applying an appropriate coating, a base metal with good mechanical properties can be utilized. Many alloys have been developed to resist corrosion. However, the use of these materials may not be practical from the standpoint of cost, based on the specific application. In addition, a coating can be applied for decorative purposes [1]. The majority of coatings are applied on external surfaces to protect the metal from natural atmospheric corrosion and pollution. Occasionally, it may also be necessary to provide protection from accidental spills and splashes [1]. Organic coatings provide protection either by a barrier action from the layer or from active corrosion inhibition provided by pigments in the coating [2]. Coating systems are defined by generic type of binder or resin, and are grouped according to the curing or hardening mechanism of that generic type. The organic binder or resin of the coating material is primarily responsible for determining the properties and resistances of the paint [3]. Epoxy resins are known for their excellent properties of anti-corrosion and of chemical resistance [2]. When properly co-polymerized with other resins (particularly those of the amine or polyamine family) or esterified with fatty acids, epoxy resins will form a durable protective coating [4]. The epoxy resin can react through pendant hydroxyl groups or the terminal ring. The properties of the final film will depend on the molecular weight of the epoxy used, the co-reacting resin, and modifiers such as phenolic resins or coal tar. However, the type and amount of pigments, solvents, and additives also have an influence on the application properties and protective properties of the applied film [4]. Moreover, organic materials alone cannot be used for high-performance applications because of their limited properties. Consequently, the addition of fillers that can withstand high temperatures, such as carbon black, silicone, and silica is frequently employed into the epoxy paint system to overcome restraint [5]. Multiple applications of nanocarbon materials are anticipated to follow from their unique properties. This specific band structure of nanocarbon leads to both the major advantages of these materials and the main challenges of their technology [6]. The addition in polymer binders as a pigment or a filler, that to improve physico-mechanical performances and corrosion protection for paint coatings, is very necessary and important in the paint technology. Therefore, this work dealt with using nanocarbon materials to fill in epoxy binder for protective coatings application for steel surfaces. The tube structure and sheet structure of nanocarbon materials were used to investigate the effect on the properties of the epoxy coating.

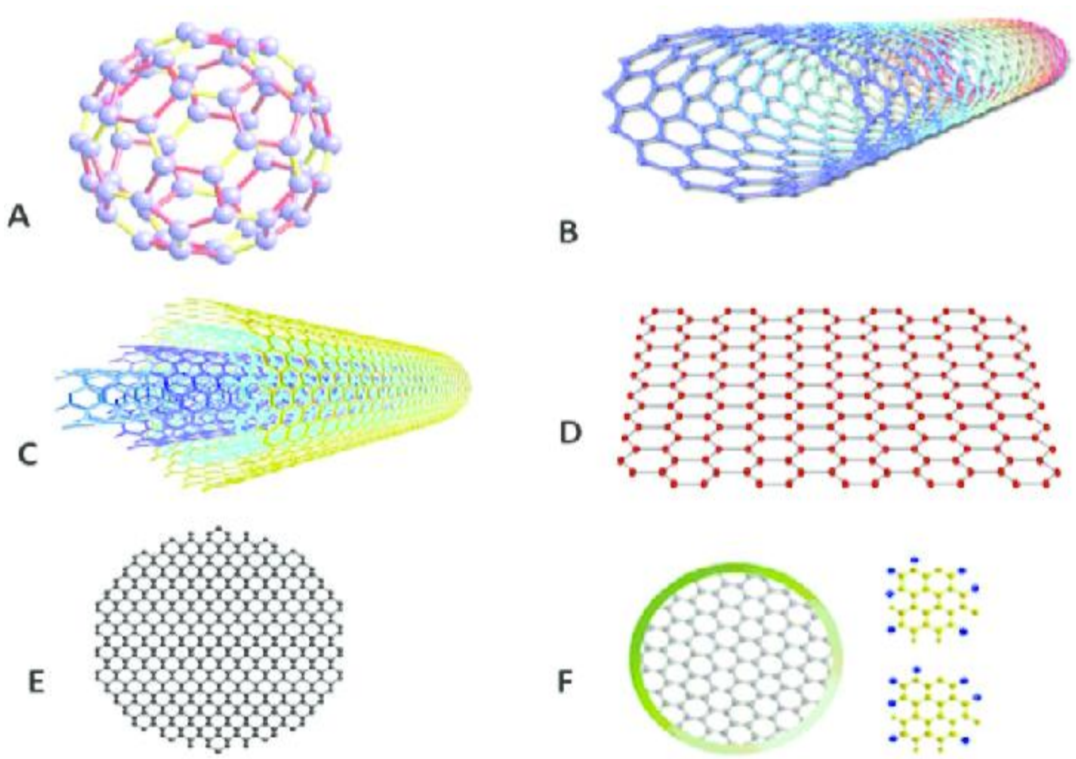


Figure 1. Structures of nanocarbon: (A) Fullerene (B) SWCNT (C) MWCNT (D) Graphene (E) nano-diamond (F) Graphene quantum dots [7].

2. MATERIALS AND METHODS

2.1. Materials

In this study, N008-N pristine graphene powder was supported by Angstrom Materials Company (USA); Multiwalled carbon nanotubes (MWCNTs) material was produced by Bao Lam Khoa company (Da Nang, Viet Nam). The dissolution of Epotec YD 011 in xylene facilitates handling was used as a binder for the paint coatings. Epotec TH 7515 is a high viscosity reactive polyamide used as a curing agent for epoxy resins. Organic solvents used include: aceton, etanol, n-butanol, xylene. They are produced by Xilong Chemical Factory and Guangdong Guanghua Sci-Tech Co.

2.2. Methods

2.2.1. Preparation of steel substrate surface

The adhesion of the coating and the corrosion protective property of the product depend on the preparation of the surface. The preparation is often referred to as pretreatment. The used metal samples are Q-Panel standard steel panels with their dimension depending on testing properties. The surface pretreatment was done according to three- stages procedure as follows:

Stage 1 - Abrading by mechanical method as a sanding to remove dirt, rust, oxides, etc.

Stage 2 - Cleaning by hand wiping with an organic solvent as acetone, ethanol, n-butanol for 5 minutes at ambient temperature to remove abrasion dust.

Stage 3 - Drying in the vacuum dryer for 10 minutes at 50 ^{o}C. They were kept in plastic bags at room temperature for coating of the paint.

2.2.2. Dispersion of the nanocarbon materials in the epoxy binder

The nanocarbon materials were used to disperse in epoxy resin with a content ratio of 0.1 wt% [7]. At first, the nanocarbon materials were dispersed in epoxy binder by a sonication bar (Sonic VC 750) for 1 h until becoming a homogeneous mixture.

2.2.3. Preparation of the nanocomposite coating samples on the steel surface for tests

Before coating the dispersed mixture on the steel surface, the curing agent (calculated weight ratio of 10:1 on the epoxy binder) was added into the mixture. Following this, incorporating them evenly was carried out by using a stirrer bar. Because of curing reaction of the mixture at room temperature, so that coatings on the prepared substrate surfaces was done by a spray gun immediately after mixing. Finally, the promotion was carried out for fully curing the epoxy coating at room temperature for 7 days. The test samples were formed for examination of physico-mechanical and anti-corrosion properties. Dry film thickness of the samples was about 20 - 30 µm.

2.2.4. Characterization methods of the nanocarbon materials

The crystal structure characterization of the nanocarbon materials was analyzed by X-ray diffraction (XRD), which was performed using a Siemens D5005 X-ray diffractometer.

Scanning electron microscope (SEM) was used to analyze morphology of the materials, using a machine S4800-NIHE, Jeol (Japan).

2.2.5. The physico-mechanical properties test of nanocomposite paint coatings

In the study, the physico-mechanical properties tests of the films which were chosen to investigate properties of nanocomposite coatings based on the epoxy resin and the nanocarbon materials are described below:

- Adhesion: The cross-cut test is a simple and easily practicable method for evaluating the adhesion of single- or multi-coat systems [2]. The standard ASTM D 3359-97 test was used; a numerical rating system from 1-mark for total failure to 5-marks scale may be used to evaluate tape adhesion test results [2]. The test was operated using aslicer's instrument of Sheen (England).

- Hardness: The hardness test was performed according to ASTM D3363 via a pencil method and using a Wolff-Wilborn Pencil Tester which includes 20 pens corresponding from 6B to 6H scale. It is usually used to measure resistance to indentation by a series of increasingly hard pencils that have been sharpened to a chisel point [2].

- Bending strength: The bending strength was determined according to ASTM D522, the data was collected using Sheen's 809 device.

- Impact resistance: A way to measure impact resistance is using ASTM D2794-93, a standard weight that is dropped from a height onto a coated panel. The indentation is inspected to detect if the coating has cracked. The weight can be dropped from different heights, and the results are then measured in kG.cm unit [2].

2.2.6. The corrosion protective test of nanocomposite coatings

Salt spray test was chosen to examine the corrosion protective property of the samples. This specification is related to ASTM B117 using a Q-FOG salt spray test machine.

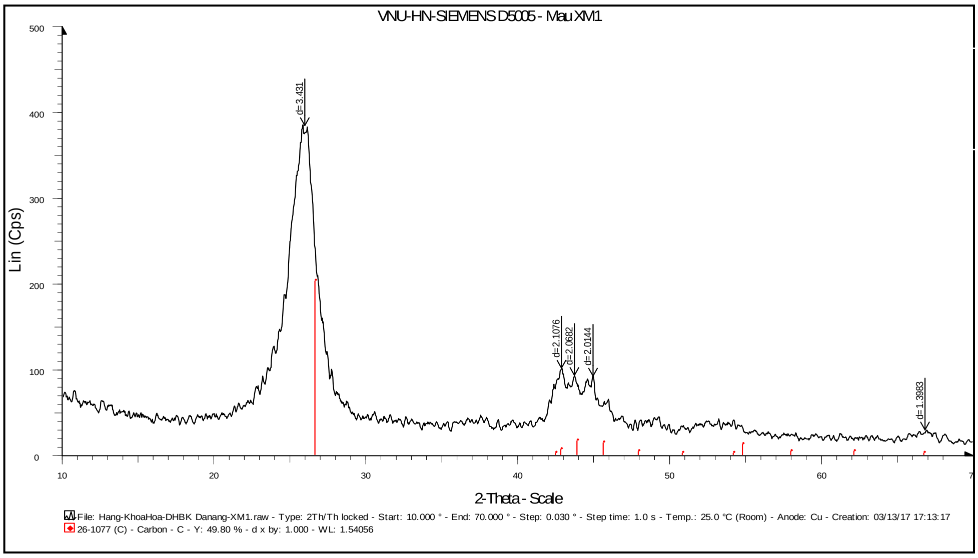
3. RESULTS AND DISCUSSION

3.1. Characterization of the nanocarbon materials

3.1.1. The results of XRD analysis

XRD diagram was analyzed according to the crystal structure of graphene nanosheets and multiwalled carbon nanotubes (MWCNTs). The XRD patterns of them are indicated in Figure 2A and 2B.

As shown in Fig. 2A the strongest and sharpest diffraction peak at around $2\theta = 26.5°$, could be indexed as the reflection of graphite. The sharpness of this peak indicates that the graphite structure of MWCNTs [8 - 10]. XRD was used to estimate the crystal size and interlayer spacing. Due to the CNT's intrinsic nature, the main features of the X-ray diffraction pattern of CNTs are close to those of graphite. This result is similar to the structure of CNTs described by XRD in the references [9 - 11]. While the XRD pattern of the graphene nanosheets material, which is shown in Fig. 2B, is a smooth hill sharp curve with dirraction peaks ranging at about $2\theta = 23 \div 30^o$, which are peaks specific to graphene nanosheets as presented in the references [13]. The results of XRD patterns evidence also the mono-layer or few-layer structure of carbon nanosheets (graphene)



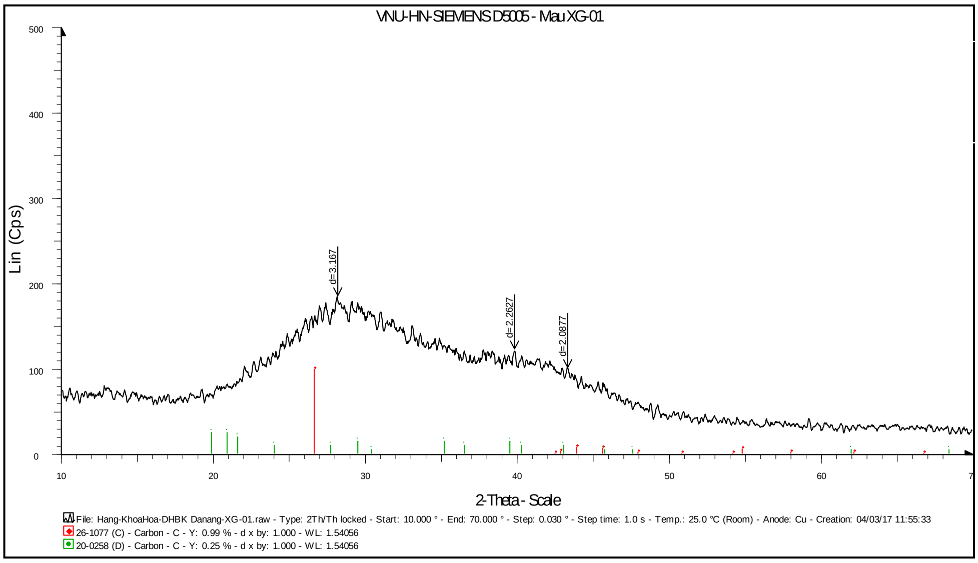
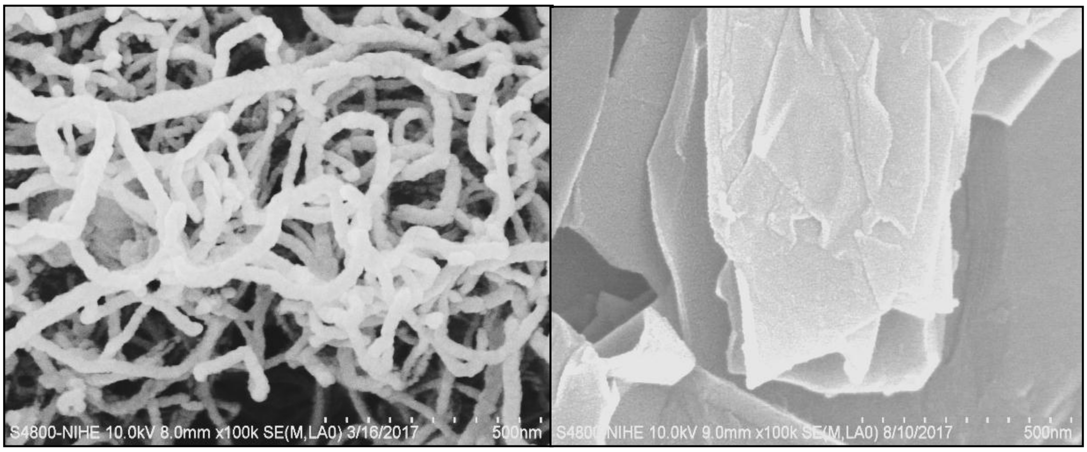


Figure 2. XRD spectrum of MWCNTs (A) and graphene (B).

3.1.2. SEM of the nanocarbon materials

The morphology of nanocarbon materials was analyzed by the scanning electron microscope method. The results are shown in Fig. 3a (CNTs) and Fig. 3b (Graphene).

SEM of MWCNTs material (Fig. 3A) shows that the morphology of MWCNTs is shaped as a cylinder. This is accordant with description of CNTs structure as nanoscale graphene cylinders that are closed at each end by half a fullerene. Structures comprising only one cylinder are termed SWNTs, whereas multiwalled nanotubes (MWNTs) contain two or more concentric graphene cylinders [9, 10, 14]. The Fig. 4B indicates that the morphology of graphene is of nanosheets or nanoplates. It is well known that graphite consists of hexagonal carbon sheets and graphene is a carbon sheet, which is exfoliated from graphite.



(a) (b)

Figure 3. SEM of MWCNTs (a) and graphene (b).

3.2. The results of physico-mechanical properties of nanocomposite paint coatings

Testing is an important part of the operation of a paint coating. Testing is done to monitor the system and to confirm that the paint coatings meet quality standards and the expectations of the customer. Testing of paint coating is used to confirm physico-mechanical properties of the coating after being applied and cured [12]. The results of testing physico-mechanical properties of the samples are shown in Table 1 and illustrated graphically in Fig. 4.

As can be seen from Fig. 4 only with the concentration of the nanocarbon materials as low as 0.1 wt%, the physico-mechanical properties of epoxy paint coatings have been improved significantly. The properties of nanocomposite samples were better very much than the epoxy coatings samples. This suggested that the addition of carbon nanostructure materials played as a pigment or filler for purposes of a paint coatings.

Table 1. The results of physico-mechanical properties testing of nanocomposite paint samples based on the epoxy binder.

Physico-mechanical properties	Unit	Epoxy nanocomposite paint samples		
		Original (no pigment)	*MWCNTs*	*Graphene*
Hardness	-	HB	1H	1H
Adhesion	mark	2	1	2
Bending strength	cm	3	2	2
Impact resistance	kG.cm	20	70	90
Salt spray test	hours	96	288	336

The Figure 4a performs the hardness of both epoxy/MWCNTs and epoxy/graphene nanocomposite paint coatings (~1H) is higher than that of original epoxy paint (~HB). While the adhesion of epoxy coating samples is the lowest in all that are shown on the Fig.4b. It means that using nanocarbon materials improved the hardness and adhesion of epoxy paint coatings. It is important for features of paint coatings. The impact resistance is increased 4.5 times for epoxy/graphene samples and 3.5 times for epoxy/MWCNTs samples compared to original epoxy coating samples, respectively, which is presented in Fig 4c. Also the Fig. 4d showed that the bending strength of both epoxy/MWCNTs and epoxy/graphene samples are increased upto ~200 % compared to the one of original epoxy samples. It is known pigments or fillers are particulate solids that are dispersed in paints to provide certain characteristics to them, including color, opacity, durability, mechanical strength, and corrosion protection for metallic substrates [12-14]. These results demonstrated that the effect of carbon nanotubes structure materials on physico-mechanical properties of epoxy coatings is dissimilar to that of carbon nanosheets structure. The properties of epoxy/graphene nanosheets coatings samples were better than epoxy/carbon nanotubes samples. This can be explained that as known thank to nanosheets structure so that surface area of graphene is higher many times than carbon nanotubes [8,15]. Hence, the interaction of graphene with epoxy resin may be stronger than CNTs, this normally will lead to enhance the physico-mechanical properties of epoxy nanocomposite paint coatings. Therefore, the physico-mechanical properties of epoxy/graphene coatings is better than epoxy/CNTs coatings.

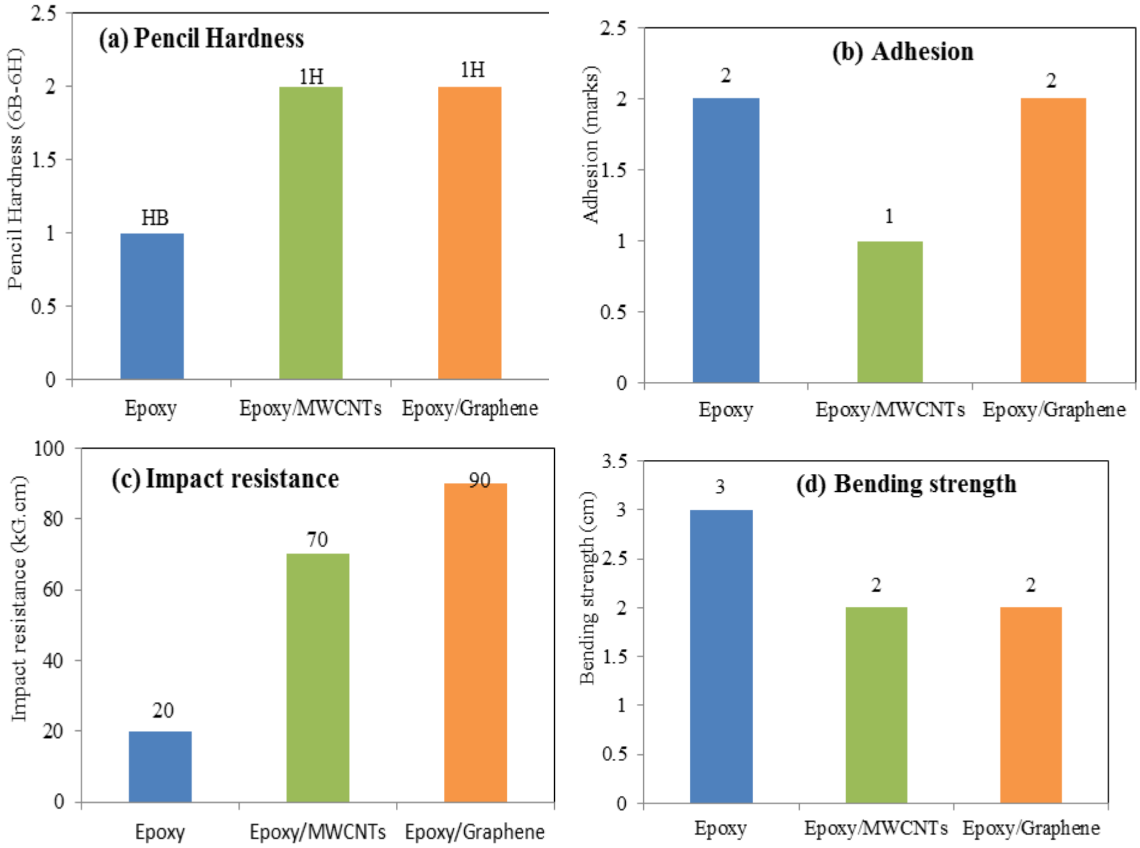


Figure 4. Charts of testing of physico-mechanical properties of the samples: (a) Hardness; (b) Adhesion; (c) Impact resistance; (d) Bending strength.

3.3. The results of testing corrosion protective properties of nanocomposite paint coatings

The epoxy/MWCNTs and epoxy/ graphene nanocomposite paint coatings were examined for their applications in anti-corrosion. The tested results are presented in Table 1 and illustrated graphically in Figure 5.

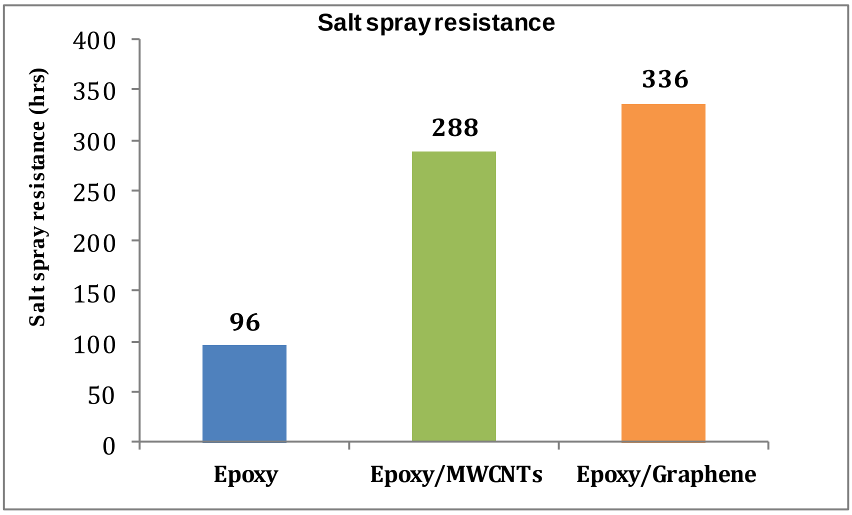


Figure 5. Charts of testing of salt spray resistance of the samples.

As shown in Fig. 5, the time necessary to rust appearance at the cross cut on test coatings of epoxy/MWCNTs coatings samples is longer 3 times and 3.5 times for epoxy/graphene samples than the original epoxy samples, respectively. It means the salt fog resistance of epoxy/ graphene coating samples was the greatest in all. The results demonstrated that the addition of both graphene and MWCNTs enhanced corrosion protective property of epoxy paint coatings. Likewise, graphene offered efficiency better than that of MWCNTs. It is well known that the nanosheets structure of graphene can made epoxy coatings become better than the nanotubes structure of MWCNTs, so that can lead to increase barrier ability and protective ability of the paint coatings. Moreover, the nanocarbon materials addition in epoxy paint coating can make the fully cured coatings become tighter and stronger than original epoxy films [13,15]. Therefore barrier ability and corrosion protection of epoxy nanocomposite paint coatings for the substrate surface are improved significantly.

4. CONCLUSIONS

The physico-mechanical properties and corrosion protective ability of the epoxy paint coatings have been significantly improved by adding only 0.1 wt% of nanocarbon materials in the epoxy binder notably. In there the corrosion protective property for steel was enhanced greatly, which is higher over three times than original epoxy paint coatings (without pigments).

The structure of nanocarbons have affected positively on physico-mechanical properties and corrosion protective ability of epoxy paint coatings for steel surfaces. Their addition improved the performances of epoxy paint coatings,

The nanosheets structure of graphene, which were dispersed in epoxy paint coatings, made the physico-mechanical properties and corrosion protective ability of the epoxy based nanocomposite paint coatings for the metal surfaces to become significantly better than the nanotubes structure of MWCNTs.

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