

A STUDY ON PHYSICO-MECHANICAL AND ANTICORROSIVE PROPERTIES OF CHEMICALLY MODIFIED GRAPHENE-BASED EPOXY NANOCOMPOSITE COATINGS

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ABSTRACT

The use of coatings of functionalized nanostructured carbon based composite to inhibit corrosion is an area getting much of attention among scientists and industrialists. Lately, Graphene has started to play an important role in many applications. Graphene possesses excellent mechanical and thermal stability, low chemical reactivity, impermeability to most of gases, and high transparency. Thanks to these properties, Graphene is so far finding some applications for protective coatings. However, Graphene is apolar and nanostructured, so that is difficult to be dispersed into polar polymers as epoxy resin. In this paper, results of using chemically modified Graphene to reinforce the physico-mechanical properties and corrosive resistance properties of the epoxy paint coating are presented. Graphene was modified by oxidative method with mixtures of H₂SO₄, H₃PO₄ and KmnO₄ solutions. The properties of obtained products were characterized by some physico-chemical methods such as Fourier transformed Infrared Spectroscopy (FTIR), X-ray diffraction (XRD). The physico-mechanical and anti-corrosion properties of paints based on chemically modified Graphene-epoxy nanocomposite have been exceptionally superior to that of paints based on epoxy and Graphene.

Keywords: epoxy paint, Graphene, chemically modified Graphene, anti-corrosion properties, paint based on chemically modified Graphene – epoxy nanocomposite.

1. INTRODUCTION

Construction metals are selected because of their mechanical properties and machineability 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]. Epoxy resins are known for their excellent properties of anti-corrosion and of chemical resistance. Because of their tendency to fade and chalk when exposed to sunlight, they are used for interior topcoat applications or as primer for exterior applications [2]. Organic coatings provide protection either by a barrier action from the layer or from active corrosion inhibition provided by pigments in the coating [1]. Since the historical observation of single layer Graphene by Andre Geim and Kostya Novoselov in 2004, this atomically thin carbon sheet has received ever-increasing attention and become a rapidly rising star on the horizon of materials science [3, 4]. Graphene is a two dimensional material made entirely of carbon atoms and it is only a single atom thick. Graphene is mechanically very strong it is also lightweight and flexible [3 - 5]. Due to the excellent properties of Graphene, it is believed that it could be used to enhance significantly the performance of coating. In addition, it can be used with nanoparticles to form Graphene nanoparticles composites coating and as a high quality coating materials solely [5]. However, graphene sheets are hard to be incorporated and distributed homogeneously into various matrices for applications [6]. Recently, research into Graphene-based materials, which includes Graphene, Graphene oxide (GO), reduced Graphene oxide (rGO), and Graphene embedded polymers, has demonstrated potential for applications in anti-corrosion coatings [4]. For composites based coating, the functionalization of graphene renders this latter to achieve good interfacial bonding between matrixes and graphene sheets. The functionalization of graphene can be performed via physical or chemical approaches. There are three major categories of functionalization: functionalization via organic species, functionalization via macromolecules and functionalization via nanoparticles [5]. The Graphene sheets are tightly attached to each other making them directly insoluble in any solvent while GO shows desirable dispersion behavior [6]. The reactive oxygenic groups, present on the edges (carbonyl and carboxyl groups) and planes (hydroxyl and epoxide groups) of GO sheets, can stabilize the dispersion of GO in aqueous media, enhance the interfacial bonding within the components, and facilitate the stress transfer in the composites, which render GO as attractive and promising nanoscale reinforcement fillers in polymer composites [7, 8]. Therefore, in this work we adopted improved Tour method [6] to chemically modifying commercial graphene and investigated the effects of pristine Graphene and modified Graphene on physico-mechanical and anticorrosion properties of epoxy primer paints. In 2010 year, a report of an improved Hummers method [3 - 5] for the preparation of GO which was studied by authors group of James M. Tour comes from Rice University (Texas, USA) was published on ACS Nano journal [9]. This improved Hummers method provides a greater amount of hydrophilic oxidized graphene materials as compared to Hummers method with additional KMnO_4 and excluding NaNO_3 , hence the reaction is kept away from toxic gases formation [6]. Hence, this method is considered as an environment-friendly approach.

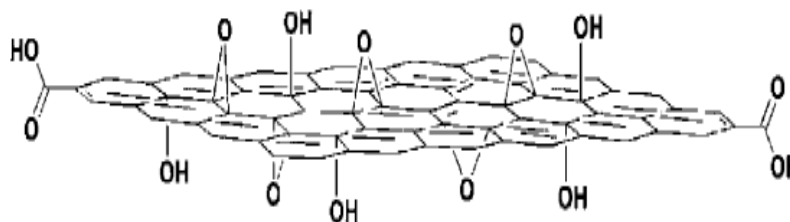


Figure 1. Schematic model of a sheet of Graphene oxide showing possible oxygen-containing functionalities [3].

2. MATERIALS AND METHODS

2.1. Materials

In this study, N008-N pristine Graphene powder was supported by Angstrom Materials Company; Epotec YD 011X-75 is a solution of unmodified low molecular weight solid diglycidyl ether of bisphenol-A resin in xylene. The dissolution of Epotec YD 011 in xylene facilitates handling. Epotec TH 7515 is a high viscosity reactive polyamide used as a curing agent for liquid or solution grade epoxy resins such as Epotec YD 515 or Epotec YD 011X75 to produce thermoset adhesives and coatings. They are received by Aditya Birla Chemicals Ltd, Rolling; The another chemicals are required such as potassium permanganate (KMnO_4 99 %), phosphoric acid (H_3PO_4 63 %), sulphuric acid (H_2SO_4 98 %), hydrochloric acid (HCl 36,5 %), organic solvents including: acetone, ethanol, n-butanol, xylene. They are produced by Xilong Chemical Factory and Guangdong GuanghuaSci-Tech Co.

2.2. Methods

2.2.1. Preparation of chemically modified Graphene

In this work, modified Tour's method [3] was used for chemical modification of commercial Graphene materials. The modification of this method is that only HCl acid was used to remove oxidative agent (KMnO_4) and unused hydroperoxide (H_2O_2). The detailed synthesis procedure is shown as follow:

The synthesis procedure was carried out in a reaction system consisting of a glass three-necked reactor, a welding tube, a heating magnetic stirrer. At first, both H_2SO_4 acid and H_3PO_4 acid (volume ratio of mixture of acids is 9:1) were mixed together in the reactor. The reactor was putted in an ice bath to refrigerate down below 5 °C for about 30 minutes and kept on stirring the mixture at the same time. The next step, Graphene materials were incorporated into the acids mixture and following to stir at a suitable speed for about 30 minutes. After that, KMnO_4 oxidative agent (weight ratio of 6: 1 on Graphene) was divided into three parts and loaded into the reaction mixture three times for 45 minutes. The mixture was followed stirring for 15 minutes more, then the ice bath was removed from the reaction system. Controlling of the magnetic stirrer was done to heat upto 35 °C temperature and kept for 30 minutes. Follow that, the reaction was increased until 60 °C and maintained for 3 hours. After that, HCl acid solution was added to the reactor and stirred with a higher speed for 5 minutes then stop stirring. The reaction mixture was washed with deionized water several times to completely remove the reactants such as acids, KMnO_4Then, solid products were recovered by a vacuum filter-paper hopper system. The products were dried at 60 °C for 12 hours in vacuum dry machine. The finally, they were milled by a stone mortar and packed in plastic bag for using in further experiments. The formed products were called as Graphene oxide and symbolized of GO in this paper.

2.2.2. Preparation procedure of test samples

Preparation of steel substrate surface: The adhesion of the coating and the anti-corrosion 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 depends 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...

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 °C. They were kept in plastic bags at room temperature for coating of the paint.

Preparation of thenanocompositepaint systems: Graphene and GO materials were used to produce nanocomposite paint with a content of 0,1 wt% on epoxy resin [3]. At first, measured Graphene/GO was dispersed in n-butanol solvent with 1mg/1ml rate using sonication bath for 1h. After that, they were mixed in the epoxy binder by a stirrer bar until becoming a homogeneous mixture.

Coating of the paint on the surface for test samples: Before applying paint on the surface, the curing agent (calculated weight ratio of 10:1 on the epoxy binder) was added to the paint system which has a primarily formula including: epoxy resin (as a binder), GO/Graphene (as a pigment), organic solvents. Following this, incorporating them evenly was carried by the stirrer bar. Because of curing reaction of the mixture at room temperature, so that coating the paint on the prepared substrate surfaces was done by spray gun immediately after mixing. The finally, the promotion was carried for fully curing the epoxy binder to creating the paint films at room temperature for 7 days. The test samples were formed for examination of physico-mechanical and anti-corrosion properties. Dry paint film thickness of the samples was about 20-30 μm .

2.2.3. Characterization techniques

In this work, Fourier Transform Infrared spectroscopy (FTIR) was employed to evaluate results of chemical modification of Graphene. A Thermo Nicolet 6700 spectrometer was used to collect the FTIR data for chemical structure analysis of Graphene and modified Graphene. The crystal structure characterization of Graphene and chemically modified Graphene (GO) were analyzed by X-ray diffraction (XRD) and performed using a Siemens D5005 X-ray diffractometer.

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

In the study, the physico-mechanical properties tests of the films were chosen to investigate properties of nanocomposite coatings based on the epoxy resin and are listed 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 is 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 is operated using aslicer's instrument of Sheen (England).

- Hardness: 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: Determined according to ASTM D522, the data was collected using Sheen's 809 device.

- Impact resistance: A way to measure impact resistance is ASTM D2794-93 was used, a standard weight 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].

2.2.5. The corrosion resistance test of nanocomposite paint coatings

Salt spray test was chosen to examine for the corrosion resistance 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. The result of chemical modification of Graphene

3.1.1. The results of FTIR analysis

Figure 2A and 2B show the FTIR spectrum for the obtained Graphene and GO in full range of wave numbers (400 - 4000 cm^{-1}).

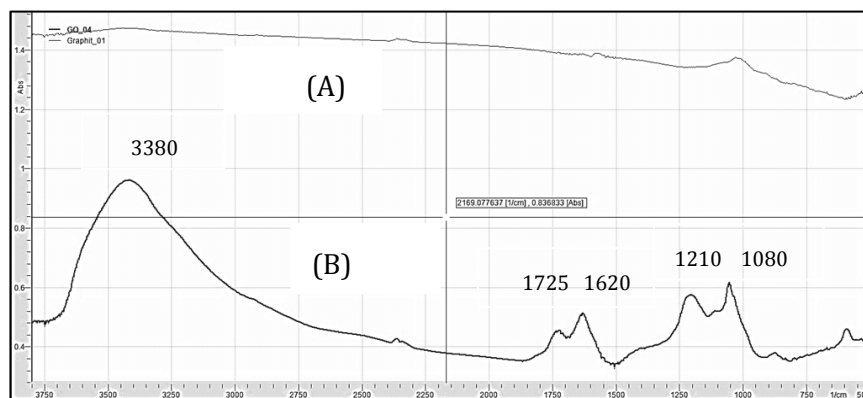


Figure 2. FTIR spectrum of Graphene (A) and chemically modified Graphene-GO (B).

The presence of different types of oxygen functionalities in GO was confirmed at 3380 cm^{-1} due to O-H stretching vibrations, at peak 1725 cm^{-1} observed stretching vibrations from C=O and at 1080 cm^{-1} stretching vibrations of O-H group. Two strong peaks were observed in GO, the one at 3380 cm^{-1} were due to O-H stretching vibrations of absorbed water molecules and structural OH groups and C-O-C of epoxy groups centered at 1210 cm^{-1} . Also, the peak at 1620 cm^{-1} is attributed to the vibrations of unoxidized graphitic domains, in these samples. These results are same the reported in references [5 - 10]. The presence of these functional groups on Graphene sheets demonstrated that chemical modification of Graphene was successful by carrying out via a modified Tour's method.

3.1.2. The results of XRD analysis

XRD spectrum was conducted in order to clarify the change in the crystal structure of Graphene sheets before and after chemical modification. The XRD patterns of commercial Graphene material and GO products are indicated in Figure 3.

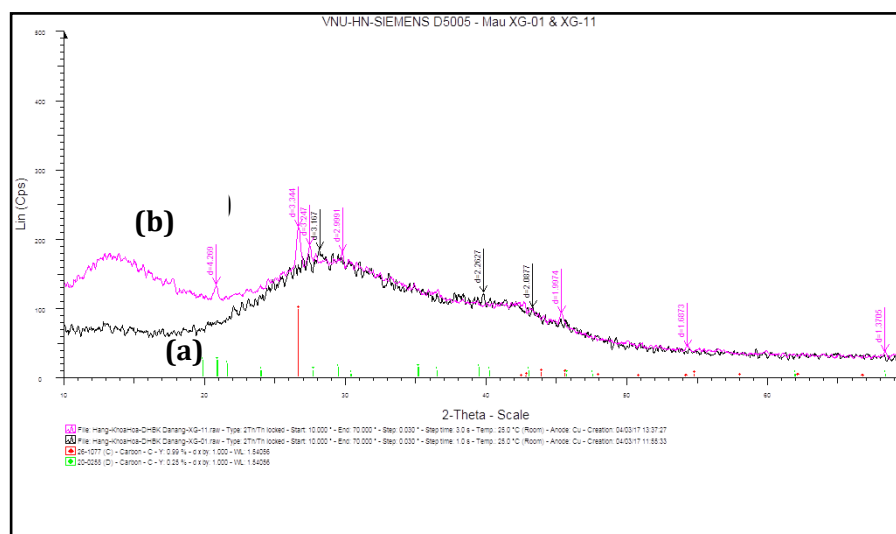


Figure 3. XRD spectrum of unmodified Graphene (a) and modified Graphene-GO (b).

The XRD spectrum of commercial Graphene material, which is shown in Fig. 3a, is a smooth hill sharp curve with diffraction peaks ranging at about $2\theta = 23 - 30^\circ$, which are peaks specific to graphene sheets as presented in the references [6 - 10]. The strong diffraction peak at $2\theta = 26^\circ$ is a characteristic peak of graphite powders as reported in many works [6 - 10]. The results of XRD spectrum evident also the mono-layer or few-layer structure of Graphene sheets. As shown in Fig. 3b the height of the hill top of the XRD patterns of Graphene at peak $2\theta = 23 - 30^\circ$ decreased while that the height of peak range at about $2\theta = 7 - 15^\circ$ increased. The strong diffraction peak at $2\theta = 11^\circ$ is a characteristic peak of Graphite oxide. While Graphene oxide is formed via a exfoliation of the Graphite oxide, hence the characteristic peak of GO is a lower diffraction peak range at $2\theta = 7 - 15^\circ$ as shown in almost XRD data of the references [6 - 10]. Therefore, almost XRD spectrums of Graphene and GO are often smooth hill sharp curves as shown in Fig. 3. These results suggest the Graphene sheets have been oxidized to form Graphene oxide sheets, which were not flocculated and settled together.

These results were expected that chemical modification of commercial Graphene material, which only decorated functional groups on the Graphene surfaces that still unchanged the crystal structure of Graphene. It is mean that the chemical modification procedure of Graphene by modified Tour method is useful to synthesis GO.

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

Testing is an important part of the operation of a paint system. Testing is done to monitor the system and to confirm that the paint coatings meets 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. The used particular tests depend on the properties that the coating has to provide and to respect the established quality standards [2]. The results of testing physico-mechanical properties of the samples are shown in Table 1 and illustrated graphically in Figure 4.

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

Physico-mechanical properties	Unit	Epoxy paint samples		
		<i>Original (no pigment)</i>	<i>Graphene</i>	<i>GO</i>
Hardness	-	HB	1H	1H
Adhesion	mark	2	2	1
Bending strength	cm	3	2	1
Impact resistance	kG.cm	20	900	110
Salt spray test	hours	96	336	600

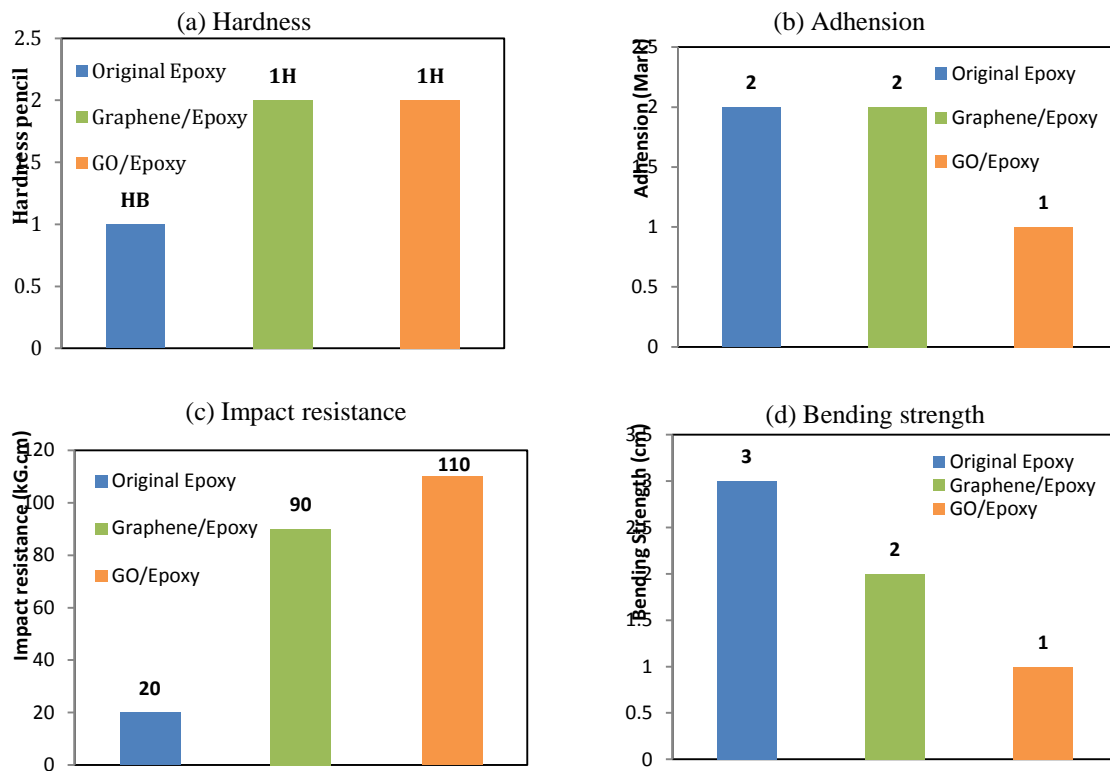


Figure 4. Charts of testing of physico-mechanical properties of the samples: (a)Hardness; (b) Adhesion; (c) Impact resistance; (d) Bending strength.

As can be seen from Fig. 4, with the concentration of Graphene or GO as low as 0,1wt%, the physico-mechanical properties of epoxy paint system have been significantly improved. Fig. 4a presented the hardness of both Graphene/Epoxy and GO/Epoxy nanocomposite paint coatings (~ 1H) is higher than that of original epoxy paint (~ HB). The results are shown in the Fig. 4b, that the adhesion of GO/Epoxy sample is the highest in all. It means that using GO to

improve the hardness and adhesion of Epoxy paint coating is better than using Graphene. The impact resistance is increased 4.5 times and 3.5 times compared to original epoxy samples, respectively, which is presented in Fig 4c. The Fig 4d shows that the bending strength of GO/Epoxy samples are increased upto ~200 % compared to one of original epoxy samples, and ~100 % for Graphene/Epoxy samples.

These results verified that the incorporation of Graphene/GO based materials into epoxy binder not only improve properties such as hardness, adhesion of the paint coatings but also enhance significantly mechanical properties such as bending strength, impact resistance. It can be considered that Graphene and GO play role as pigments or fillers for the paint coatings [8, 12].

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 [2]. In order to achieve the desired results, pigments have to possess certain properties. Pigments (or fillers) have to be uniformly dispersed in the binder to provide a consistent appearance [2]. Therefore, this result could be explained by the presence of the oxygen containing functional groups of GO nanosheets which may form covalent bonding with epoxy binder creating the interfacial bonding of Graphene with epoxy resin leading to further great distribution and dispersion of GO into the resin compared to Graphene in epoxy resin [8, 12]. Hence, the improvement of GO in physico-mechanical properties of paint coatings is better than pristine Graphene.

3.3. The results of testing anticorrosive properties of nanocomposite paint coatings

The Graphene/Epoxy and GO/Epoxy nanocomposite paint coatings were examined for their applications in anti-corrosion. In the work, salt spray test method was used for investigating anti-corrosion property of the samples. The tested results are presented in Table 1 and illustrated graphically on Figure 5.

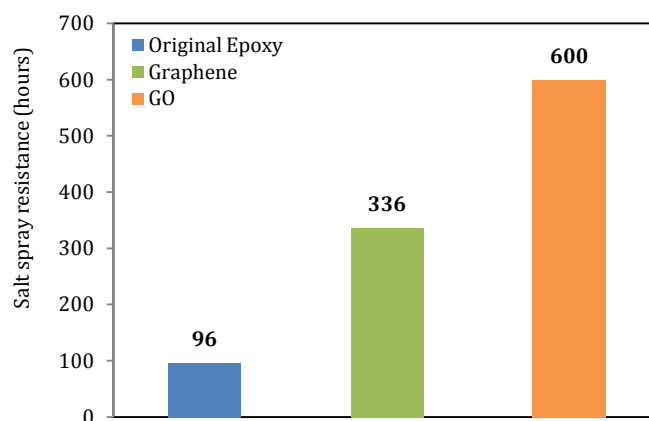


Figure 5. Charts of testing of salt spray resistance of the samples.

As shown in Fig. 5, the time necessary to rust appearance at the cross cut on test coatings of GO/Epoxy samples is 6.25 times and approximately 2 times longer than the original Epoxy samples, Graphene/Epoxy samples, respectively. It is mean the salt spray resistance of GO/Epoxy samples was the greatest in all. The results demonstrate that addition of Graphene and GO enhance anti-corrosion property of epoxy paint coatings. Likewise, GO offered

efficiency better than that of Graphene. It is well known that the attachment of O-containing functional groups to Graphene sheets aids in dispersion in a hydrophilic media, as well as in the polar organic polymer. Hence, an efficient approach to the production of surface-functionalized Graphene sheets may form covalent bonding with epoxy binder so that could promote stronger interfacial bonding between GO sheets and epoxy resin and leading to the fully curing paint films that become tighter and stronger than Graphene/Epoxy films and original Epoxy films [8, 12]. Therefore barrier ability and corrosion protection of GO/Epoxy coatings for the substrate surface are the greatest in all.

4. CONCLUSIONS

- The pristine Graphene material was successfully chemically modified via modified Tour's method. The formed products are Graphene Oxide (GO), which are only decorated oxygen containing functional groups on the Graphene sheet surfaces but unchanged the crystal structure of Graphene.

- The physico-mechanical properties of the epoxy paint coatings have been significantly improved by adding only 0,1 weight% of Graphene/GO in the epoxy binder notably, the anti-corrosion ability of the nanocomposite paint coatings for the metal surfaces is also greatly enhanced. Regarding to this application, the anti-corrosion performance of GO/Epoxy nanocomposite paint is 6.25 times and 2 times higher than the original epoxy paint and the unmodified Graphene/Epoxy nanocomposite paint, respectively. The chemically modified Graphene is greatly promised candidate in primer paints application for metal surfaces.

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