

EFFECTS OF ZnO NANOPARTICLES AND GRAPHENE OXIDE ON PROPERTIES OF ACRYLIC POLYMER NANOCOMPOSITE COATING

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Abstract. In this study, effects of graphene oxide (GO) and ZnO nanoparticles on the properties of acrylic polymer (R4152) coating were investigated. SEM images indicated that ZnO nanoparticles distributed uniformly on GO sheets. Hence, GO/ZnO could be dispersed homogenously in the acrylic polymer matrix while ZnO nanoparticles were agglomerated in acrylic polymer matrix in the absence of GO. In addition, GO had effect on the reduction of band gap energy of ZnO nanoparticles, i.e. 3.26 eV for GO/ZnO and 3.3 eV for ZnO. As a result, the photocatalytic activity of the R4152/GO/ZnO nanocomposite coating was higher than that of the R4152/ZnO nanocomposite coating. After 14 hours under UV exposure, the R4152/GO/ZnO nanocomposite coating can degrade over 80 % methylene blue coated on its surface while only 60 % methylene blue was degraded by the R4152/ZnO coating. Besides, in the presence of 2 wt.% ZnO nanoparticle, the abrasion resistance of the R4152/GO/ZnO coating was increased by nearly 25 % (from 75 to 92.9 L/mil) in comparison with the abrasion resistance of R4152/GO coating. However, ZnO nanoparticles reduced the starting thermal decomposition temperature.

Keywords: acrylic polymer, graphene oxide, ZnO nanoparticle, photocatalytic activity, composite coating, abrasion resistance

Classification numbers: 2.5.3

1. INTRODUCTION

Recently, due to the increasing of environment awareness, waterborne polymers have been attracting a lot of interest from scientists and manufacturers. Among these, waterborne acrylic polymers are the most popular because of its superior properties. Waterborne acrylic polymers are usually used as adhesives and binders for finish coats of steel structure, wall paints, wood paints, etc. Like a coin, acrylic polymer emulsions have drawbacks. Hence, a lot of approaches have been applied to improve properties of coating based on waterborne acrylic resin [1 - 4].

Inorganic nanoparticles addition can bring a lot of advantages to organic coatings such as improving the weathering durability [3], physico-mechanical properties [4], thermal properties [4], self-cleaning [5] and bactericidal activities [6], etc. ZnO nanoparticles have been widely used because of their outstanding optical and electrical properties. ZnO nanoparticles combining

with acrylic polymer emulsion (AC261) produced UV-shielding coating [7]. UV-Vis spectra of nanocomposite containing 2 wt.% ZnO showed that the coating absorbed almost of UV radiation (> 95 %) but a large amount of visible light (> 60 %) transmitted through the coating. Obviously, ZnO nanoparticles, in this case, acted as a UV absorber in the nanocomposite coating. However, accelerated aging test of ZnO/AC261 nanocomposite coatings showed that the nanocomposite coating filled with 2 wt.% nanoZnO had degradation degree as neat coating. It was found that photo-stabilizing and photo-catalytic properties of ZnO nanoparticles were two parallel processes. Photo-stabilizing or photo-catalytic activities' priority of ZnO nanoparticles depend on morphology and surface of nanoparticles [8]. Besides, nanocomposite coating based on acrylic polymer emulsions and ZnO nanoparticles, which was transparent coating, is used as a topcoat for solar-heat reflective (SHR) paint [5]. The acrylic polymer emulsion coating filled with 1 wt.% ZnO nanoparticles showed highly efficient self-cleaning ability. After 96-hour UV irradiation, the ZnO nanocomposite coating recovered strongly the reflectance index of solar-heat reflective (SHR) paint covered by artificial dirt (from 56.45 to 80.78 %) [5]. It is caused by photo-catalytic properties of ZnO nanoparticles.

Since being discovered in 2010 by Andrei Geim and Konstantin Sergeevich Novoselov, graphene and its derivatives have been studied and applied in various fields including organic coating technology due to their superior properties. Among graphene's derivatives, graphene oxide (GO) has attracted attention due to its low cost and simple synthesis. Furthermore, graphene can easily be prepared from graphene oxide. Liu Cao and his co-workers synthesized graphene aerogel from GO by hydrothermal synthesis and used it in combination with styrene-acrylic polymer emulsion to enhance the thermal conductivity of paraffin, accordingly the thermal conductivity of the composite increased by 265 % compared with that of pure paraffin, reaching 0.92 W/m.K [8]. GO was also used to enhance thermal and mechanical properties of acrylic coating. In comparison with neat coating, GO/acrylic composite coating had higher chemical resistance and better thermal properties [8]. Besides, the adhesion of the composite coating containing GO modified by γ -Methacryloxypropyltrimethoxysilane increased significantly compared with that of neat coating [9]. Effects of GO content on the acrylic emulsion coating were studied. The obtained results showed that GO could be dispersed uniformly in acrylic polymer matrix at a GO weight ratio of 0.5 %. As a result, thermal and mechanical properties of the composited coating filled by 0.5 wt.% GO were substantially higher than those of neat coating [10].

As above mentioned, using separately GO and ZnO nanoparticles can enhance various properties of composite materials. It is reported from the publications that combining GO and ZnO can create synergistic effects on composite materials. The GO/ZnO composite was simply prepared by a suspension mixing method [11] or a solution precipitation method [12]. GO can enhance photocatalytic properties of ZnO nanoparticles. [11]. Moreover, the GO/ZnO composite expressed superior antibacterial activity [12]. However, studies on GO/ZnO composite almost focused on properties and applications of alone GO/ZnO composite while GO/ZnO composite combined with organic coating in general and polymer acrylic coating in particular was of insignificant interest and thus limiting the application of GO/ZnO composite. Hence, a study on properties of GO/ZnO and organic binders, especially acrylic polymer emulsion, is necessary. This work will present the effects of the ZnO/GO composite on properties such as physico-mechanical properties, thermal properties and photocatalytic activity of coatings based on acrylic polymer emulsion.

2. MATERIALS AND METHODS

2.1. Materials

The acrylic polymer emulsion, Plextol R4152, obtained from Symthomer, had a solid content of 50 ± 1 % and pH of 7 - 8.5. A film-forming agent used was Texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) from Dow Chemical Company. Graphite (≤ 20 μm) and ZnO nanoparticles (having a diameter < 100 nm and a specific surface of 18 m^2/g) were purchased from Sigma. P grade H_2O_2 , NaNO_3 , H_2SO_4 were supplied by Xilong Scientific Co., Ltd. (China) and KMnO_4 (type P) was provided by DucGiang Chemical company.

GO was prepared by a modified Hummer method as follows. Firstly, 5 g of graphite and 2.5 g of NaNO_3 were combined with 115 mL of 98 % H_2SO_4 solution. The mixture was stirred at a speed of 350 - 400 rpm for 30 minutes in an ice bath. Then, 15g of KMnO_4 was added into the mixture, which was continuously stirred slowly for 4 hours at a temperature below 20 $^\circ\text{C}$. When the color of mixture turned to black-greenish, the mixture was warmed up and kept at 35 $^\circ\text{C}$ for 30 minutes, followed by adding a drop by drop of 230 mL of H_2O to the mixture. In this step, the temperature of the mixture was kept in a range of 44 - 48 $^\circ\text{C}$. Until the color of the mixture changed to dark-brown, the mixture was heated and maintained at 95 - 98 $^\circ\text{C}$ for 15 minutes. When the color of the mixture was brown, 50 mL of 30 % H_2O_2 was slowly added into the mixture, which was then stirred at 500 rpm for 20 minutes until the color of the mixture turned to light brown. After that, the mixture was rinsed by distilled water. The rinsed mixture was treated by ultrasound for 2 hours to extract graphite oxide to graphene oxide. Finally, GO was dried out at 70 $^\circ\text{C}$ in a vacuum oven for 24 hours.

2.2. Sample preparation

GO was dispersed in deionized water with a GO/water weight ratio of 1/10 by ultrasonic treatment with Branson Sonifier (model D450 with a power of 450 W and a frequency of 20 kHz) for an hour, forming mixture A. After that, ZnO nanoparticles were added into mixture A and then the mixture was continuously vibrated for 1 hour. A part of mixture A with a GO/ZnO weight ratio of 1/4 was dried out at 70 $^\circ\text{C}$ in a vacuum oven for UV-Vis and SEM measurements.

Texanol was mixed with R4152 acrylic emulsion polymer (mixture B) by stirring at aspeed of 300 rpm for 30 minutes. The weight ratio of Texanol in comparison with the solid in acrylic polymer emulsion (R4152) was 3 wt.%. Finally, mixture A and mixture B were mixed together by stirring at a speed of 300 rpm for 15 minutes, followed by ultrasound treatment for an hour. The weight ratios of components of the investigated coatings were displayed on Table 1.

Table 1. Compositions weight ratio of formula coatings.

No	GO (g)	Nano ZnO	Water (g)	R4152 (g)	Texanol (g)
1	0.02	0	0.8	8	0.12
2	0.02	0.01	0.8	8	0.12
3	0.02	0.02	0.8	8	0.12
4	0.02	0.04	0.8	8	0.12
5	0.02	0.08	0.8	8	0.12
6	0.02	0.20	2	8	0.12
7	0	0.08	0.8	8	0.12

Formula coatings with various ZnO nanoparticle contents were prepared on steel for abrasion resistance test, on mortar sheet substrate for adhesion test and on glass for thermal gravimetric analysis and morphology measurements.

All samples were naturally dried out for 7 days and then conditioned at 25 °C and 60 % relative humidity for 24 hours before each test.

2.3. Analysis

2.3.1. Morphology

SEM images of formula coatings were recorded by SEM S-4800 (Hitachi, Japan) at Institute of Materials Science, Vietnam Academy of Science and Technology.

SEM images of GO/ZnO were captured by Nova NanoSEM 450 (FEI, Netherland) at Faculty of Physics, VNU University of Science.

2.3.2. Thermal analysis

Thermal gravimetric analysis (TGA) diagrams were taken by DTG-60H (Shimadzu) at Department of Physical Chemistry, Faculty of Chemistry, Hanoi National University of Education. The sample was heated from ambient temperature to 600 °C at a heating rate of 10 °C/min in air atmosphere.

2.3.3. Physico-mechanical properties

- Adhesion: Adhesion of coatings to mortar sheet substrate was determined by a cutting test method in accordance with ISO 2409:2013.

- Abrasion resistance: Abrasion resistance of formula coatings was measured in accordance with ASTM D968-15. The abrasion resistance value was determined by the following formula: $AR = V/d$ (L/mil), where V was the volume of sand (L) and d was the thickness of coatings (mil; 1 mil = 25 μm).

2.3.4. Photo-catalytic activity

The photo-catalytic property was tested by methylene blue degradation. Formula coatings were prepared on a glass plate with a wet thickness of 60 μm. After 7 days, the formula coatings were coated by methylene blue (2 mL/cm²) and then dried out in air for 7 days. After that, they were removed from the plate and amounted onto an aluminum window exposed to UV radiation. UV-Vis spectra of formula coatings coated by methylene blue were captured by GBC Cintra 400 - USA before and after UV exposure. Methylene blue content was determined through the optical density of absorbance in UV-Vis spectra at 665 nm. The coating containing 2 wt.% ZnO nanoparticles was used as reference coating.

2.3.5. UV-Vis diffuse reflectance spectroscopy

UV-Vis diffuse reflectance spectra of ZnO nanoparticles and GO/ZnO nanocomposite were recorded by UV-2600 spectroscopy at Institute of Physics, Vietnam Academy of Science and Technology.

2.3.6. X-ray diffraction

X-ray diffraction patterns of graphite and graphene oxide were recorded by D8 Advance (Bruker) at Faculty of Chemistry, VNU University of Science.

3. RESULTS AND DISCUSSION

3.1. Properties of GO/ZnO nanocomposite

3.1.1. Graphene oxide's X-ray diffraction patterns

The X-ray diffraction (XRD) patterns of graphite and graphene oxide were presented in Fig. 1.

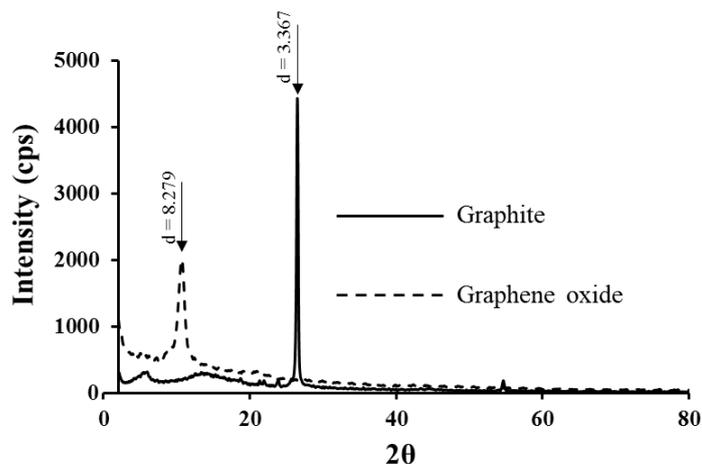


Figure 1. The X-ray diffraction patterns of graphite and graphene oxide

As can be seen from Fig.1., graphite had a diffraction peak at $2\theta = 26.5^\circ$, while diffraction peak of graphene oxide located at $2\theta = 10.61^\circ$. Moreover, spacing of crystal plane of graphene oxide was significantly higher than that of graphite, 8.279 Å for the former and 3.367 Å for the later. The interlayer distance of 8.279 Å is a typical interlayer space for graphene oxide [13]. It was suggested that some functional groups containing oxygen in graphene oxide such as hydroxyl, carbonyl, etc. cause the interlayer distance of graphene oxide to be greater than that in graphite [13].

3.1.2. Morphology of GO/ZnO nanocomposite

SEM images of GO/ZnO nanocomposite at various magnifications were displayed in Fig. 2. As can be seen from Fig. 2, GO was exploited to thin sheets and decorated by ZnO nanoparticles, showing fairly uniform distribution on GO sheets. It was observed that there was no agglomeration of ZnO nanoparticles.

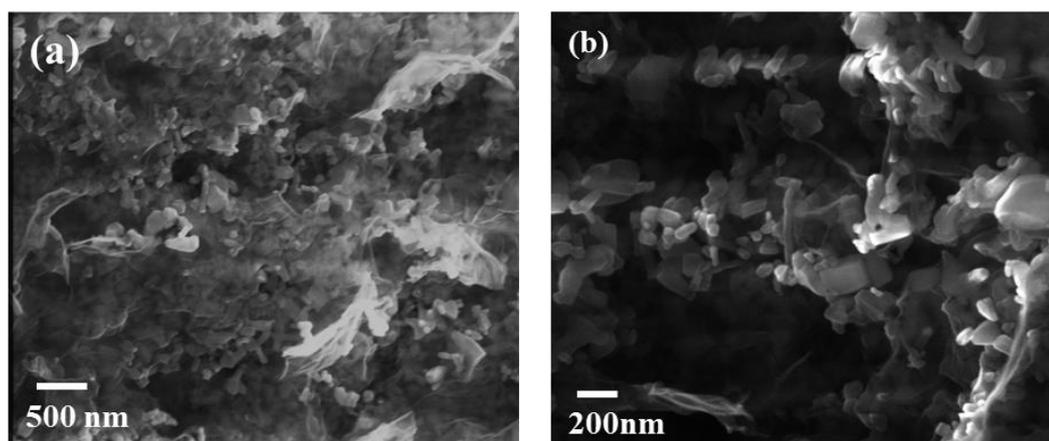


Figure 2. SEM images of GO/ZnO nanocomposite at 25 k and 50 k magnifications.

3.1.3. UV-Vis diffuse reflectance spectra and band gap

To determine direct band gap energies of ZnO nanoparticles and GO/ZnO nanocomposite, their UV-Vis diffuse reflectance spectra were recorded and then a Kubelka-Munk model was used to calculate direct band gap energies [14]. UV-Vis diffuse reflectance spectra of ZnO nanoparticles and GO/ZnO nanocomposite and their band gap energies were illustrated in Fig. 3.

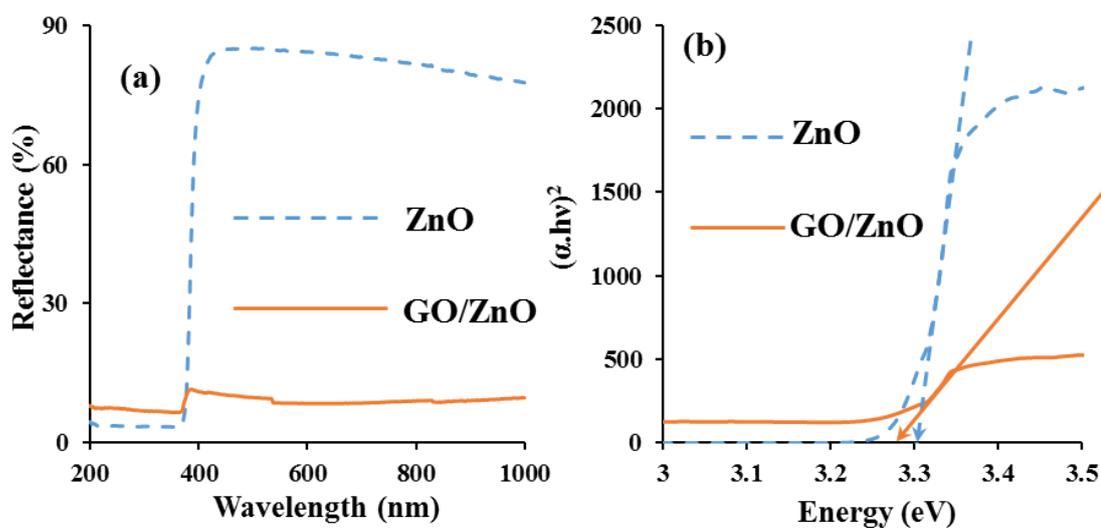


Figure 3. Diffuse reflectance spectra (a), and band gap energies (b) of ZnO nanoparticles and GO/ZnO nanocomposite.

As can be seen from Fig. 3a, increasing ZnO nanoparticles' and GO/ZnO composite's reflectance at a wavelength of nearly 400 nm, to some extent, related to direct band gap energy of ZnO (electron transition from valence band to conduction band) [14]. In order to determine direct band gap of ZnO nanoparticles and GO/ZnO composite, Kubelka-Munk function was used for transforming reflectance values to absorbance values, consequently, direct band gap energies

of ZnO nanoparticles and GO/ZnO composite were estimated from a plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) [14]. The direct band gap energies of ZnO and GO/ZnO were 3.3 and 3.26 eV, respectively. In addition, it was reported in the literature that band gap energy of ZnO semiconductor depended on structure and surface modification [15]. Hence, GO reduced ZnO nanoparticles' band gap energy since functional groups of GO, more or less, interacted with ZnO nanoparticles and thus modifying ZnO nanoparticles surface. As a result, ZnO nanoparticles' band gap energy was reduced.

3.2. Properties of GO/ZnO nanocomposite coating

3.2.1. Physico-mechanical properties of formula coatings

Physico-mechanical properties such as adhesion and abrasion resistance of formula coatings based on acrylic polymer emulsion R4152, graphene oxide at different contents of ZnO nanoparticles were shown in Table 2.

Table 2. Physico-mechanical properties of R4152/GO/ZnO nanocomposite coating

	0 % ZnO	0.25 % ZnO	0.5 % ZnO	1 % ZnO	2 % ZnO	5 % ZnO
Adhesion (Point)	1	1	1	1	1	1
Abrasion resistance (L/mil)	75.0	81.25	83.33	87.5	92.9	91.52

It is clear from Table 2 that, adhesion values of formula coatings on mortar sheet substrate were fairly unchanged with increasing the content of ZnO nanoparticles. It is possible that ZnO nanoparticles did not significantly affect the adhesion of formula coatings on mortar sheets. However, the value of abrasion resistance grew up with increasing ZnO nanoparticles content in formula coatings. ZnO nanoparticles, up to a point, played a role of a reinforced component. Moreover, if ZnO nanoparticles disperse widely and homogeneously in an acrylic polymer matrix, the addition of ZnO nanoparticles will improve the abrasion resistance of formula coatings, which increased from 75 L/mil for coating without ZnO nanoparticles to 92.9 L/mil with 2 wt.% ZnO nanoparticles. However, when ZnO content in nanocomposite coating increased to 5 %, the abrasion resistance of formula coating was fairly maintained in comparison with the coating filled by 2 wt.% nanoZnO, hovering around 91.5 L/mil.

3.2.2. Thermal properties

TGA diagrams of composite coating filled and unfilled with ZnO nanoparticles were displayed in Fig. 2.

As can be seen from Fig. 4., TGA diagram of nanocomposite coating based on acrylic polymer emulsion (R4152) and 0.5 wt.% GO showed that the thermal decomposition of nanocomposite included three stages. Firstly, the weight of nanocomposite coating was fairly stable until 300 °C. Nanocomposite coating began to decompose (T_{onset}) at 290 °C and then, the weight of coating lost rapidly (nearly 97 % wt.) from 300 to 400 °C.

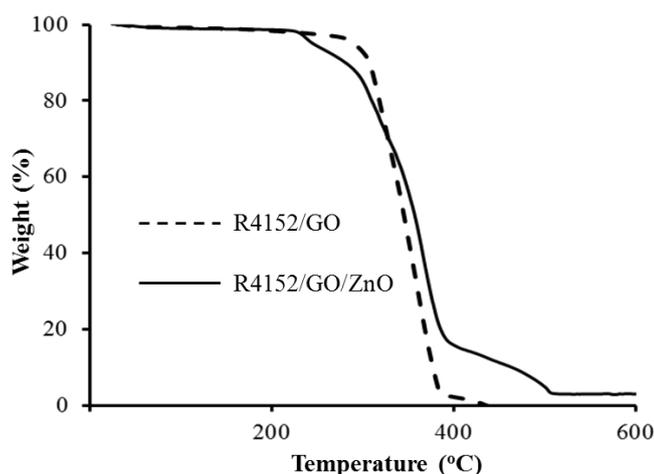
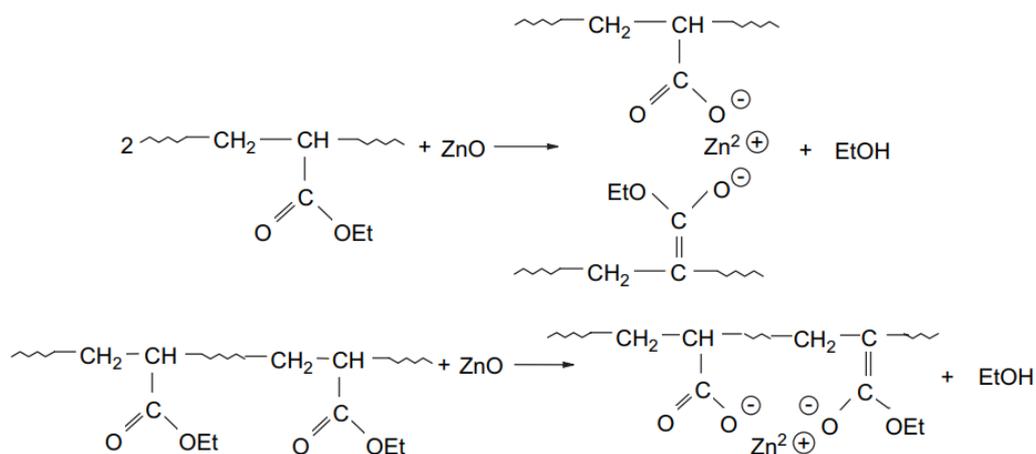


Figure 4. TGA diagrams of nanocomposite coating.



Scheme 1. Interaction between ZnO nanoparticles and acrylic polymers [18]

For R4132/GO/ZnO nanocomposite coating, TGA diagram can be divided into four stages. Firstly, the nanocomposite weight was maintained until 200 °C. The weight of the composite coating began losing (T_{onset}) at 244 °C. After that, the weight sharply reduced in a temperature range of 300 - 400 °C, which was followed by less sharply decreasing and remaining unchanged from 500 °C. In comparison with nanocomposite unfilled by ZnO nanoparticles, T_{onset} of coating filled by ZnO nanoparticles was lower. Some authors claimed that the addition of ZnO nanoparticles can accelerate composite decomposition by increasing the thermal transport during heating process [16]. Luifu and his co-workers also asserted that ZnO nanoparticles reduced T_{onset} of acrylic polymer coating [18]. The interaction between acrylic polymer and ZnO nanoparticles was illustrated in Scheme 1 upon heating process.

As from Scheme 1, hydroxyl groups on ZnO surface reacted with ester groups of acrylic polymer at over 200 °C to produce ester exchange reaction and release ethanol. As a result, the weight of coating filled by 2 wt.% ZnO nanoparticles started losing at 244 °C.

3.2.3. Photocatalytic activity

The photocatalytic activity of the nanocomposite coating was assessed through the methylene blue decomposition when exposed to ultraviolet rays of the nanocomposite coating coated with methylene blue.

The amount of methylene blue degradation was measured by reduction of UV-Vis absorbance at 665 nm which was assigned to methylene blue. UV-Vis spectra of methylene blue coated nanocomposite coatings were presented in Fig. 5.

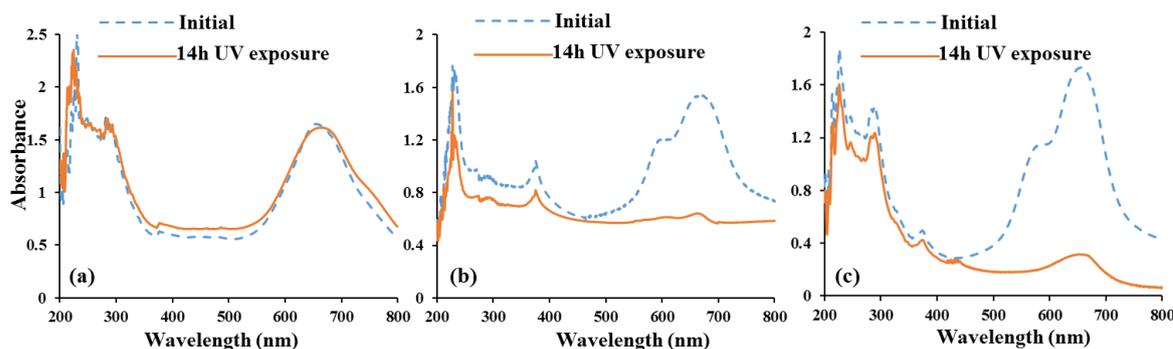


Figure 5. UV-Vis spectra of methylene blue coated GO (a), ZnO (b) and GO/ZnO (c) nanocomposite coating before and after 14 hours of UV exposure

As can be seen from Fig. 5, in comparison with initial coatings, the absorbance intensity of the peak at 665 nm in UV-Vis spectra of nanocomposite coatings after 14 hours of UV exposure had a different reduction rate. For R4152/GO nanocomposite, the absorbance of methylene blue remained fairly unchanged after UV exposure process. It was investigated that GO had no photocatalytic activity. In the meantime, the intensity of absorbance at 665 nm of methylene blue coated R4152/ZnO and R4152/GO/ZnO nanocomposite coatings' UV-Vis spectrum significantly decreased. For R4152/ZnO nanocomposite coating, after 14-hour UV irradiation the intensity of absorbance at 665 nm went down to 0.64, which was equivalent to nearly 40 % in comparison with its initial. The reduction rate of the absorbance intensity at 665 nm for R4152/GO/ZnO coating was higher than that of the absorbance intensity for R4152/ZnO coating. After 14-hour UV exposure, the reduction percentage of the absorbance intensity reached well over 80 % for R4152/GO/ZnO coatings. Studies have shown that the photocatalytic activity of nanocomposite coatings is produced by ZnO nanoparticles, whose photocatalytic property is improved by GO. To explain this result, some hypothesizes were proposed. Due to the uniform distribution of the ZnO nanoparticles on the GO sheets, as the results mentioned above, it is confirmed that GO acts as a dispersion adjunct, making the ZnO nanoparticles easily disperse, spread and achieve homogeneity in the polymer matrix [19, 20]. Moreover, the band gap energy of GO/ZnO nanocomposite was lower than that of ZnO nanoparticles, 3.26 eV for the former and 3.30 eV for the later. As a result, electrons easily jumped from valence band to conduction band, consequently leading to forming more positive charge holes and enhancing more electron excitation. Therefore, the photocatalytic activity of GO/ZnO nanocomposite was higher than that of ZnO nanoparticles.

Besides, Román and his colleagues supposed that oxygen functional groups on GO sheets interacted with hydroxyl groups on the surface of ZnO nanoparticles leading to aligning energy

levels at the GO-ZnO interface. Hence, electron excitation easily transferred from ZnO to GO upon UV exposure. Consequently, the recombination of electron and hole (taking positive charge) was decreased and thus promoting the oxidation reaction with analysts and medium via remaining positive charges (holes) in the valence band of ZnO [20].

3.4. Morphology of nanocomposite coating

SEM images of cross surface of nanocomposite coatings filled by 2 wt.% ZnO nanoparticles as well as by 0.5 wt.% GO and 2 wt.% ZnO nanoparticles were illustrated in Fig. 6.

For nanocomposite coating filled by 2 wt.% ZnO nanoparticles, SEM images obviously showed that the coating was heterogeneous and there were agglomerations of nanoparticles, while the nanocomposite coating filled by 0.5 wt.% GO and 2 wt.% ZnO nanoparticles was homogeneous. The ZnO nanoparticles having an average diameter of approximately 100 nm dispersed uniformly in an acrylic polymer matrix. Due to uniform dispersion, R4152/GO/ZnO nanocomposite coating had a higher photocatalytic activity than R4152/ZnO nanocomposite.

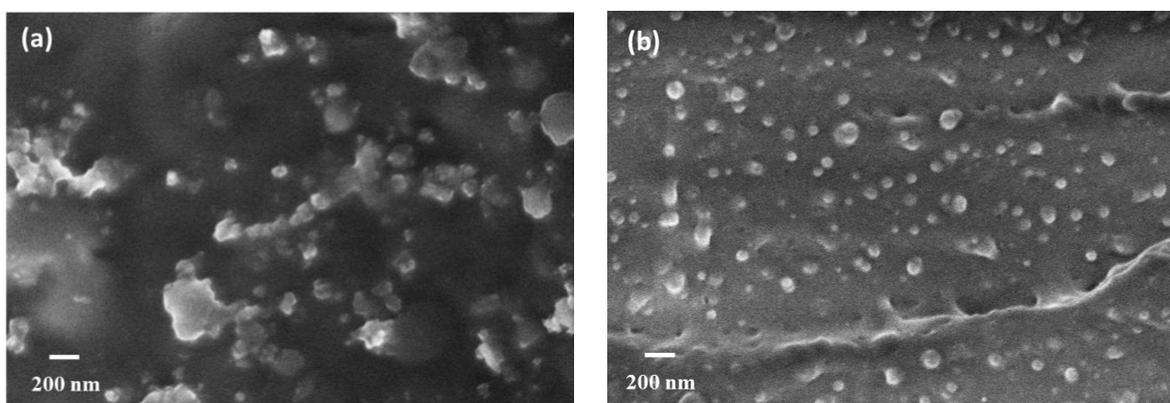


Figure 6. SEM images of cross surface of R4152/ZnO (a) and R4152/GO/ZnO (b) nanocomposite coating

ZnO nanoparticles can homogeneously disperse in an acrylic polymer matrix thanks to graphene oxide, which has a lot of functional groups such hydroxyl, ether, ester at the edge of the sheet. ZnO nanoparticles could interact with functional groups of GO sheets. Consequently, ZnO nanoparticles uniformly distributed on GO as mentioned above as well as in an acrylic polymer matrix. It may say that graphene oxide acts as dispersion aids of ZnO nanoparticles [20].

4. CONCLUSIONS

GO/ZnO composite could be obtained by simple synthesis - a suspension mixing method. ZnO nanoparticles distributed uniformly on GO sheets as well as in a polymer matrix. As a result, the addition of ZnO nanoparticles improved physico-mechanical properties of the nanocomposite. Moreover, GO reduced band gap energy of ZnO nanoparticles. Hence, the combination of ZnO nanoparticles and graphene oxide produced a synergistic effect of photocatalytic activity of nanocomposite. Nanocomposite coatings based on R4152, graphene oxide and ZnO nanoparticles showed higher methylene blue degradation ability than nanocomposite coating filled by only 2 wt.% ZnO nanoparticles. However, due to the interaction

of ZnO nanoparticles and acrylic polymer, the initial decomposition temperature of R4152/GO/ZnO nanocomposite coatings was lower than that of R4152/GO nanocomposite coating.

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Declaration of competing interest. 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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