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MECHANICAL, THERMAL PROPERTIES AND MORPHOLOGY OF COMPOSITE COATING BASED ON ACRYLIC EMULSION POLYMER AND GRAPHENE OXIDE

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Abstract. Effects of graphene oxide content on mechanical, thermal properties and morphology of composite coating based on acrylic emulsion R4152 and graphene oxide (GO) have been investigated. Obtained results showed that GO particles had insignificant effect on adhesion of composite coating but GO improved abrasion resistance of composite coatings. The abrasion durability of coatings increased with GO ratio rising to 0.5 % and then abrasion resistance of coatings decreased with GO ratio continuously growing up. SEM images presented that GO particles dispersed homogenously into polymer matrix if the GO ratio is of 0.5 % wt. While the ratio increased to 1 % wt., the agglomeration of GO particles in composite coating could be seen clearly in SEM images. It is assumed that the abrasion resistance decreased if using the GO ratio more than 0.5 % wt. TGA results also demonstrated the thermal property of GO composite coating was improved than that of neat coating.

Keywords: acrylic waterborne, graphene oxide, SEM image, abrasion resistance, thermal stability.

Classification numbers: 2.5.3.

1. INTRODUCTION

Graphene, a 2D structure material made up of carbon atoms, was discovered by Andrei Geim and Konstantin Sergeevich Novoselov (Nobel Prize 2010). Graphene and its derivatives (*i.e*. graphene oxide, reduce graphene oxide, etc.) have proven their worth recently and been considered as “magical materials” to help solving scientific and technique issues with the applications in various fields such as super capacitor, solar cell, battery, biomaterials, biosensor, drug delivery, water treatment, anticorrosion, etc.; because of their superior physico-mechanical properties (1050 GPa of Young modulus, 130 GPa of tensile strength), thermal conductivity (4840 -5300 W/m.K), electrical conductivity (10^{-8} Ω/m of resistivity) and huge specific surface area (2630 m^2/g), etc. [1-3]. Among graphene’s derivatives, GO is, more or less, the most popular due to simple synthesis and cheap cost. GO, which can be synthesized by oxidizing graphite or some other methods, has large specific surface area and contains lots of functional groups such as hydroxyl (-OH), epoxy on the surface and carboxyl (-COOH) on the edge [4]. As a result, GO is a highly hydrophilic material, with good dispersion into some of other substrates and good biocompatible ability.

Due to good physico-mechanical properties, GO has been used to improve different limitation of organic coatings. GO-added composite coating based on poly (vinyl alcohol)/starch with 2 mg/mL concentration of GO, has some improved characteristics such as humidity resistance, tensile strength and thermo-property in comparison with non-GO coating [5]. It can be explained that GO has lots of polar functional groups which help GO to be compatible to PVA and starch. Therefore, GO disperses well polymer substrate and it causes significant improvements of PVA/starch/GO coatings' properties. Composite PVA/starch/GO is concerned as promising biodegradation material. It is also investigated that GO contributes to improve physico-mechanical properties of materials in other studies, e.g. tensile strength and module Young of epoxy/GO composite increased to double than the original materials [6]. In presence of GO, chemical durability (acid and base resistance) and water durability of composite acrylic/GO were substantially improved [7] since GO having functional groups like OH, COOH, carbon double bonds, up to a point, cross-linked with polymer matrix leading to establish closed network in composite materials.

Besides, the published studies pointed out that GO can play a role as nanoparticles auxiliary dispersion. Weixin Hou and his coworkers studied effect of GO and nanodiamond (ND) on epoxy coating properties [8]. Their results showed that while ND improved hardness of coating composite, GO increased the coating's flexibility. Nanocomposite coatings reached the best mechanical properties at 5/1 wt. the ratio of ND/GO. In presence of GO, Zeta potential results indicated the raise in stability of nanocomposite epoxy/ND (Zeta potential of GO and ND were – 43.1 mV and 48.4 mV, respectively) [8]. However, dispersion level of GO into polymer substrate depended on much oxidation degree of GO. If oxidation degree of GO levels off at low or high level, GO indicates bad dispersion since GO particles agglomerate [9]. It was also investigated that GO improved thermal property [10] and anticorrosion of materials [11,12].

Binder is the most important component of organic coatings, which are used widely as protective and decorative materials for various substrate materials. Depending on physical properties – solvable characteristics, binders are divided into two main types: solvent-borne and water-borne binder. Raising the environmental awareness, water-borne binders have been widely used because of low VOC, producing high quality coating, easy to process and clean. That is the way water-borne binders get the attention of scientists and manufacturers [13-16], especially the acrylic emulsion polymers, which are more popular. This type of polymers can be applied as binders for wood paints, architectural paints and topcoat in metal paint systems. The research groups of Institute for Tropical Technology have performed a number of studies on acrylic emulsion polymers with valuable and promising results. Besides that, studies on improving quality of waterborne acrylic coating have been implemented and figured out that weather durability of acrylic emulsion AC 261 coatings increased in presence of nano rutile TiO_2 [13,14]. Adding ZnO nanoparticles into acrylic emulsion polymer AC261 can create a transparent coating with high UV-shielding ability (> 96 %) [15]. Acrylic emulsion R4152 coating with 1%wt. of nanosilica acquired high weather resistance and better thermo-property [16].

This work aims to enhance some properties, *i.e.* mechanical and thermal properties of acrylic emulsion R4152 coating by adding GO synthesized by Hummer method. Effect of content of GO on physico-mechanical, thermal properties and morphology of composite coating will be presented.

2. EXPERIMENTAL

2.1. Materials

Acrylic emulsion Plextol R4152 was provided by Symthomer having 49 ± 1 % of solid content, 7 - 8.5 of pH. Texanol (2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate) obtained from Dow Chemical company was used as coalescing agent.

Other chemicals: graphite natural flake (≤ 20 µm) was obtained from Sigma Aldrich, sulfuric acid 98 %, hydro peroxide 30 % and sodium nitrate (P grade) were purchased from China, and potassium permanganate was supplied by Duc Giang Chemical Company (Viet Nam) and some other relevant solvents.

Graphene oxide was synthesized by the Hummer method [17] as to the following description. Firstly, 3 g of graphite and 1.5 g of $NaNO_3$ were added in 57 mL H_2SO_4 (98 %). The obtained mixture was stirred at 0 ^oC for 30 minutes. After that, 7.5 g $KMnO_4$ was added slowly into the mixture (the temperature of mixture was kept to be not over 20 ^oC), and then the temperature of mixture was increased to 35 ± 3 ^oC during 30 minutes for oxidation reaction of graphite. 115 mL distilled water was added to lead temperature of mixture raising to 98 ^oC and maintained temperature of mixture at this in 30 minutes. Finally, 200 mL distilled water and 25 mL H_2O_2 30 % were added to reduce amount of MnO_4^- abundance. After the oxidation process, the mixture became bright brown, and it was treated by ultrasonic with suitable time. GO was collected by centrifuge and then it was rinsed by acetone and dried at 100 ^oC. The FT-IR spectra (recorded by Nicole Nexus 670), Raman spectra (performed by Horiba Xplus Raman Spectroscopy) and morphology images (by scanning electron microscope Hitachi S4800) of GO were presented in Figure 1 and Figure 2, respectively.

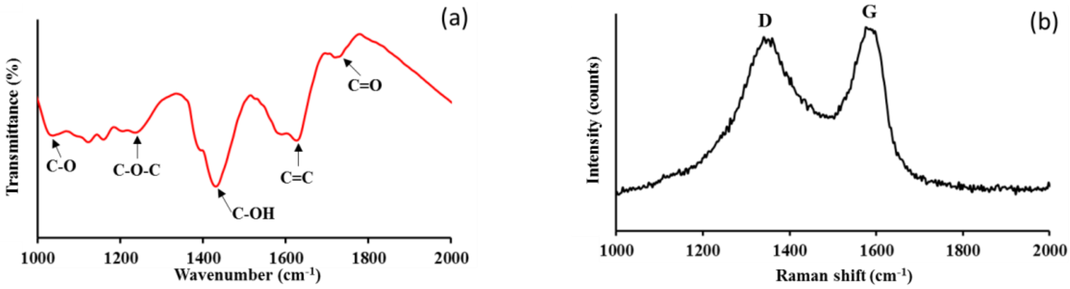

Figure 1. IR spectrum (a) and Raman spectrum (b) of graphene oxide.

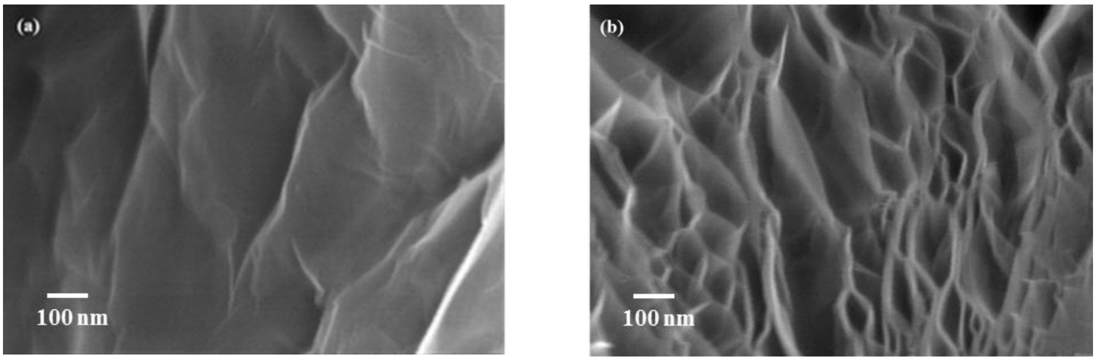

Figure 2. SEM images of GO’s surface (a) and cross-section (b).

As in the IR spectra, GO particles contained several functional groups like hydroxyl, carbonyl and carbon double bond [17]. Due to the oxidation of graphite, Raman spectra of GO indicated two peak known as D band (at 1340 cm^{-1}) and G band (at 1575 cm^{-1}) with intensity ratio of $I_D/I_G = 0.97$, while Raman spectra of graphite illustrated that the intensity of band G was much higher than that of band D, i.e. with $I_D/I_G = 0.102$ [18]. This means the oxidation reaction of graphite produced C_{sp3}, consequently, leading to defects and disorder of C_{sp2} network. In addition, oxidation of graphite shifted the band G toward higher wavenumber (1575 cm^{-1}) in comparison with band G of graphite itself (at 1568 cm^{-1} [18]). In addition, the increase of band D intensity investigated that graphite structure was exploited from multilayers to single layers with formation of defects and disorder. SEM images also showed that multilayer structure of graphite was exploited and GO was formed in a wrinkled sheet-like structure.

2.2. Sample preparation

Solid GO was dispersed in distilled water by ultrasonic treatment for 03 hours (Mixture A) with weight ratio of GO/water = 1/10. Texanol was dispersed in acrylic emulsion R4152 with 3 % wt. by ultrasonic treatment during 1 hour (Mixture B). And then, mixture A was mixed with mixture B by ultrasonic equipment (TPC-120, Switzerland) during an hour. Weight ratios of constituents in investigated coatings were presented in Table 1.

Table 1. Components' ratio of coatings.

Sample	GO (g)	Water (g)	R4152 (g)	Texanol (g)
0 %	0	0.8	8	0.12
0.25 %	0.01	0.8	8	0.12
0.5 %	0.02	0.8	8	0.12
1 %	0.04	0.8	8	0.12
2 %	0.08	0.8	8	0.12

Investigated coatings containing various GO contents were fabricated by Film Applicator model 306 (Erichsen) on glass with wet thickness of 60 µm for IR analysis and of 120 µm for weight loss measurement. Samples for adhesion testing and abrasion resistance measurement were prepared on mortar sheets and steel, respectively.

All of samples were dried naturally during 7 days and conditioned at 25 ^oC and 60 % humidity during 24 hours before conducting tests.

2.3. Analysis

2.3.1. Morphology

Scanning electron microscope (SEM) images of investigated coatings were taken by FESEM S-4800 (Hitachi, Japan).

2.3.2. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis was determined by LABSYS EVO TGA (Setaram – France). The sample was heated from ambient temperature to 900 ^oC with temperature scanning rate of 10 ^oC/min in argon atmosphere with gas flow rate of 50 cm^3/min.

2.3.3. Physico-mechanical properties

- *Adhesion*: The adhesion of coatings to mortar sheet substrate was measured by cutting test method in accordance with ISO 2409:2013 standard.

- *Abrasion resistance*: the abrasion resistances of coatings were determined in accordance with ASTM D968-15 standard. Abrasion resistance was calculated as the following formula: AR = V/d (L/mil), with V is volume of sand (L) and d is thickness of coatings (mil).

All of tests were conducted three times to obtain average values.

2.3.4. X-ray diffraction pattern (XRD)

XRD analysis of GO particles, acrylic coatings with 0.5; 1 % GO and without GO was carried out by XRD EQUINOX 5000 (France).

3. RESULTS AND DISCUSSION

3.1. Physico-mechanical properties of investigated coatings

Adhesion and abrasion resistance of coatings based on acrylic emulsion polymer R4152 with different GO contents were presented in Table 2.

Table 2. Adhesion and abrasion resistance of coatings.

	0 % GO	0.25 % GO	0.5 % GO	1 % GO	2 % GO
Adhesion (Point)	1	1	1	1	1
Abrasion resistance (L/mil)	46.18	50.8	74.70	55.03	55.03

The adhesion results in Table 2 showed that the adhesion values of acrylic emulsion R4152 coatings were independent with GO content, but the abrasion durability of investigated coatings depended on the added GO content. The abrasion resistance value increased with the raise of added GO content and reached the highest value of 74.70 L/mil in the composite coating with 0.5 % wt. GO. When the GO content added into coatings continuously increased to 1 %, the value of abrasion resistance of coatings reduced to 55.03 L/mil. It can be explained that structure of composite coating became tighter with 0.5 %w t. GO-added, while GO content added into coatings at high level, e.g. 1 and 2 %, that means the density of GO particles was raised up, thus, GO particles were more easily agglomerated together. It is assumed to phase interaction reduction and defects in coatings' structure and thus decreasing abrasion durability of coatings.

3.2. Morphology of composite coating

Coatings' characteristics are affected significantly by the dispersion of GO into polymer matrix. If the dispersion process is homogeneous, the characteristics of coatings are improved, and vice versa. SEM image of composite coatings were displayed in Figure 3. The X-ray diffraction patterns of GO, neat coating, and composite coatings filled by 0.5 and 1 % GO were presented in Figure 4.

As can be seen from SEM images (Fig. 3a and 3b) of the composite coating containing 0.5 % wt. GO, GO particles dispersed homogenously in the coating. GO particles were the small pieces (which had brighter color than the background) and dispersed on the surface of composite coating (Fig. 3b). For composite coating containing GO of 1 % wt. (Figure 3c), the white points represented to the GO agglomeration on the coating surface. Due to the electro-conductivity performance of e_π system of GO, that caused the image of GO agglomeration points much brighter.

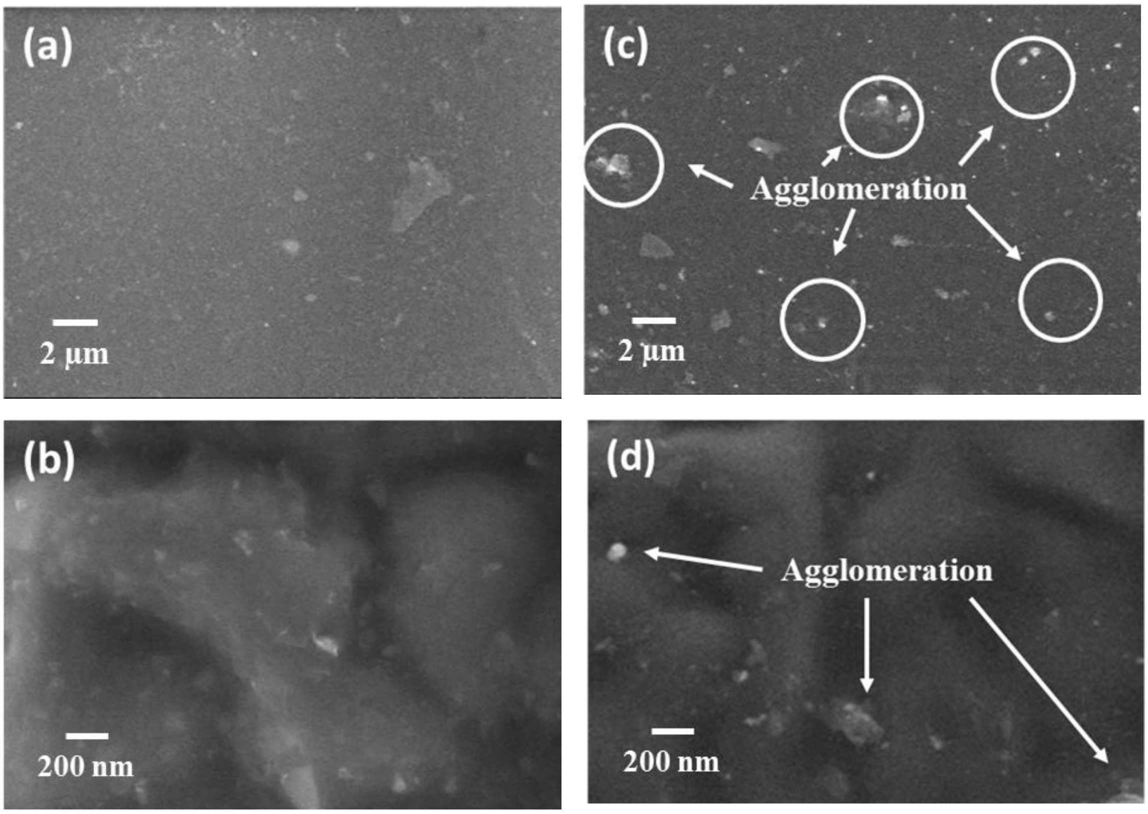

Figure 3. SEM images composite coatings containing 0.5 % GO (a, b) and 1 % GO (c, d) in various magnifications.

The X-ray diffraction in Figure 4 showed that GO and neat coating had diffraction peaks at $2\theta = 13.6^o$ for the former and $2\theta = 19.8^o$ for the later. Both of diffraction peaks were fairly sharp. For composite coating containing 0.5 % wt. GO, the diffraction peak was at $2\theta = 19.8^o$, less sharp and wider than in coating. For composite coating with 1 % wt. GO, in addition to the shape was wider and less sharp than of neat coating, there is a peak shoulder appeared at $2\theta = 10^o$. Overall, it led to a possible conclusion that GO showed better dispersion into polymer matrix at low concentration of 0.5 % wt., lower dispersion ability received at high content of 1 % wt. GO.

GO contains a lot of polar functional groups such as hydroxyl, carboxylic etc. (which was confirmed by IR spectra of GO), these polar functional groups established hydrogen bonds with other polar functional groups of polymer. Hence, GO showed well dispersion into acrylic emulsion polymer [19]. GO content increased to 1 % wt., that means GO particles had more chance to interacting with each other by hydrogen bonding and Van der Waals force and thus producing larger particles. The agglomeration of GO particles reduced phase interaction and produced defects in the coatings' structure. This phenomenon might contribute to explain how the abrasion resistances of composite coatings reduce when content of GO rising from 0.5 % wt. to 1 % wt.

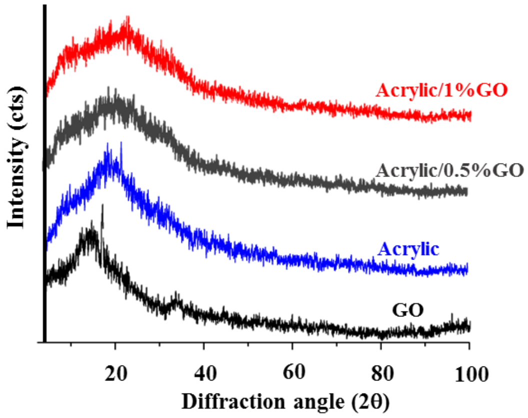

Figure 4. The X-ray diffraction patterns of graphene oxide, neat coating, and nanocomposite coatings filled by 0.5 and 1 % graphene oxide.

3.3. Thermal gravimetric analysis

TGA curves of neat coating and coating filled by 0.5 % GO were presented in Figure 5.

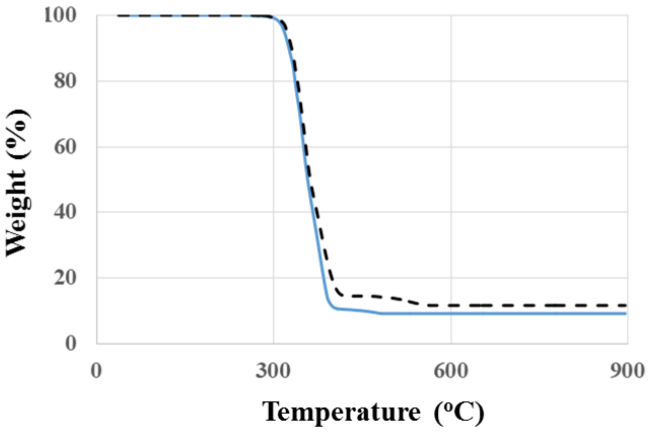

Figure 5. TGA curves of neat coating (−) and composite coating with 0.5 % wt. GO (---).

According to Fig. 5, the shape of TGA curves of the neat coating were similar to the coating filled by 0.5 % wt. GO. The thermal degradation of coatings occurred through 03 stages. The first stage is from ambient temperature to 300 °C, the coatings' weights were fairly stable. When the temperature was ranging from 300 - 400 °C, the weight of coatings sharply reduced. The thermal decomposition of the coatings started at 317.81°C for neat coating and 322.43 °C for composite coating. Decomposition peak temperatures (T_P) of coatings were 357.29 °C and 361.9 °C for neat coating and composite coating, respectively. That means thermal stability of coating with 0.5 % wt. GO was better than in neat coating sample. At the final stage, the weight of samples remained stable from the temperature from over 600 °C. One more notice is in the final stage, the weight of composite coating was higher than that of neat coating, leveling off at 11 % for the former and 9 % for the later.

It can be explained that GO was dispersed homogenously into polymer matrix in term of GO-added coating with 0.5 % wt. content as mentioned above. Hence, the network structure of composite coating became tighter and thus improving mechanical and thermal characteristics of coating.

4. CONCLUSION

Effect of GO content on morphological, thermal and mechanical properties of acrylic polymer coating has been investigated. Incorporation of GO (as nano-fillers, at content of 0.5 wt. %) in the polymer matrix, enhanced significantly the abrasion resistance and thermal stability of the coating, by 62 % (from 46.2 to 74.7 L/mil) and 4 ^{o}C (from 317.8 ^{o}C to 322.4 ^{o}C), respectively.

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