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MODIFICATION OF GRAPHENE OXIDE BY CURCUMIN AND APPLICATION IN POLYURETHANE COATING

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Abstract. Curcumin modified graphene oxide (GO-CR) was prepared using the adsorption method and polyurethane (PU) coating containing 0.3 wt% GO-CR was prepared on carbon steel. Synthesized GO-CR was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and zeta potential measurement. Corrosion protection property of polyurethane coating containing GO-CR was evaluated and compared with that of blank polyurethane coating and coating containing GO by electrochemical impedance spectroscopy. The results showed that GO-CR has a layer structure like GO with lower crystallinity. In GO-CR, structure curcumin was attached on GO surface. The presence of curcumin on GO-CR surface provided corrosion inhibition action for PU coating and also improved the dispersion of GO in PU coating.

Keywords: graphene oxide, curcumin, corrosion protection, polyurethane coatings.

Classification numbers: 2.4.4, 2.9.4, 2.5.3.

1. INTRODUCTION

Corrosion of metals causes high economic loss, especially in tropical weather conditions. Therefore, corrosion protection of metals is important and necessary. A lot of researches have been concentrated on using graphene oxide to develop environmentally friendly organic coatings. Graphene oxide can be formed on steel to provide good corrosion protection coatings [1 - 3]. Carbonyl iron (CI) particles were treated with 4-aminobenzoic acid (A-CI) then coated by graphene oxide by adsorption method. Electrochemical impedance measurements showed that GO coating passivated A-CI surface and increased the charge transfer resistance of A-CI sample [1]. GO coating was formed on mild steel surfaces by electrophoretic (EPD) method and

heat treated at 200 ^{o}C for 4 h. GO coating increased charge transfer of mild steel and decreased it's corrosion rate by 2 times [2]. In other works, GO prepared with different drying procedures were deposited on steel substrate by electrophoretic method for corrosion protection. The results showed that the drying temperature influenced the dispersion degree of GO in water, as well as on the protection performance of GO coating. GO dried at lower temperature provided higher barrier and corrosion protection coating on steel [3]. GO has also been studied as an additive to improve corrosion protection properties of organic coatings. GO was often modified or combined with other additives in order to improve the effect of GO in organic coatings [4 - 7]. Graphene oxide modified by P-phenylenediamine improved corrosion protection of epoxy coatings [4]. Surface treatment by aminosilane and 1,4-butanediol diglycidyl improved their GO dispersion in epoxy matrix and effects on corrosion resistance of epoxy coatings [5]. GO modified by 3-(Triethoxysilyl)propyl isocyanate and 3-aminopropyltriethoxysilane significantly improved corrosion resistance and adhesion properties of silane/epoxy coatings on steel surface [6]. GO was grafted with polyethylenimin and applied in waterborne epoxy coating for corrosion protection of carbon steel [7].

Recently many researches focused on the development of corrosion inhibitors based on plant extracts. Curcumin, a polyphenol compound derived from turmeric, showed inhibition effect for carbon steel [8 - 10]. M.K. Mohammed *et al*. studied the corrosion inhibition of carbon steel in 3.5 % NaCl by curcumin. It was shown that curcumin can be adsorbed on steel surface, and inhibition efficiency was about 86 % at concentration of 2.7×10^{-5} M [8]. Curcumin formed a protective film on steel surface and showed both anodic and cathodic inhibition effect in 0.5 M H_2SO_4 [9]. Combination of curcumin and Zn^{2+} exhibited corrosion inhibition efficiency of 93 % for carbon steel in seawater [10].

In this study, GO was modified by curcumin (GO-CR) and applied in polyurethane coatings for corrosion protection of carbon steel. Synthesized GO-CR was analyzed by FTIR, XRD and SEM. The corrosion resistance of polyurethane coatings containing GO-CR was evaluated by electrochemical impedance spectroscopy.

2. MATERIALS AND METHODS

2.1. Materials

Natural graphite was purchased by Sigma-Aldrich. $KMnO_4$ and H_2SO_4 (95 - 98 %) were all supplied by Merck. Curcumin was extracted from turmeric powder from Thanh Son, Phu Tho, Viet Nam using acetone as a solvent.

The polyurethane coating was based on a hydroxyl-bearing polyacrylate (ACRY) as base and an aliphatic polyisocyanate (ALIP) as hardener. They were obtained from Nippon Polyurethane Industry (NPU).

2.2. Preparation of graphene oxide

Graphene oxide was synthesized from expanded graphite powder by modified Hummer's method according to the same procedure described in our previous report [11]. Graphite and $KMnO_4$ were gradually added into concentrated H_2SO_4 solution at 2 ^{o}C. Then the temperature of the mixture was increased to 35 ^{o}C and kept for 2 hours. After that distilled water was poured to the mixture with stirring over 1 h, and then H_2O_2 was poured to the mixture with stirring over 1 h. GO was filtered, washed with distilled water and dried in a vacuum oven at 50 ^{o}C for 24 h.

2.3. Preparation of curcumin modified graphene oxide

0.05 g GO was dispersed in 50 mL distilled water using ultrasonics during 20 min. 20 mL ethanol solution containing 0.02 g curcumin was added progressively to the GO solution with magnetic stirring. The mixture was then kept at room temperature with stirring for 24 h. After that the GO-CR powder was centrifuged, washed with water, and dried at 80 ^{o}C in vacuum.

2.4. Preparation of polyurethane coatings containing GO-CR

Polyurethane coatings containing GO-CR and GO at concentration of 0.3 wt% were prepared on carbon steel. The dimension steel sample was 15 × 10 × 0.2 cm. The steel samples were abraded by abrasive papers 400 grades and washed with distilled water and ethanol and then dried. GO and GO-CR were dispersed in ACRY resin under magnetic stirring and ultrasonic condition, and then the hardener was added to resin containing GO or GO-CR. The polyurethane coatings were applied on steel plates by spin coating method. These coatings were dried at room temperature for 14 days. The thickness of dried coatings was 30 ± 3 μm.

2.5. Analytical characterization

The FTIR spectra were obtained using the KBr method on a Nexus 670 Nicolet spectrometer operated at 1 cm^{-1} resolution in the 400–4000 cm^{-1} region.

XRD patterns were taken by using Siemens diffractometer D5000 with CuKα radiation (0.15406 nm).

The scanning electron microscope images were taken by using Field emission scanning electron microscope Hitachi S-4800.

The zeta potential measurements of the GO and GO-CR were realized by using MALVERN Zetasizer Nano ZS.

2.6. Electrochemical impedance test

The corrosion resistance of coating samples was investigated by electrochemical impedance test using a Biologic SP300. A three-electrode system was used: coated steel as working electrode, saturated calomel (SCE) as reference electrode and platinum grid as counter electrode. The electrochemical impedance test was done with frequency intervals from 10 mHz to 100 kHz and the corrosion medium was 3 % NaCl solution. For each coating system, three samples were tested.

3. RESULTS AND DISCUSSION

3.1. Characterization of curcumin modified graphene oxide

Structure of curcumin loaded GO was characterized at first by FTIR. FTIR spectra of curcumin, GO and GO-CR are shown in Fig. 1. The spectrum of GO revealed the presence of C=O, C-O and C=C at 1719, 1385 and 1624 cm^{-1} respectively [12]. In the spectrum of curcumin, the band at 1628 cm^{-1} was characteristic of aliphatic C=O and C=C. The bands at 1510 and 1284 cm^{-1} were attributed to C=C and C-O, respectively [13]. Spectrum of GO-CR presented the bands characteristic of C=O, C-O and C=C in GO at 1719, 1385 and 1624 cm^{-1}. The bands characteristic of C-O in CR were observed also in the spectrum of GO-CR. The band characteristic of C=C and C=O of CR at 1628 cm^{-1} was overlapped by the band characteristic of C=C in GO. These results revealed the presence of curcumin in GO-CR.

The XRD patterns of GO and GO-CR are presented in Fig. 2. It is observed that GO-CR has the same interlayer distance of 0.79 nm as GO. The pattern of GO is sharper than that of GO-CR. This result indicates that GO-CR maintains the structure of GO with lower crystallinity.

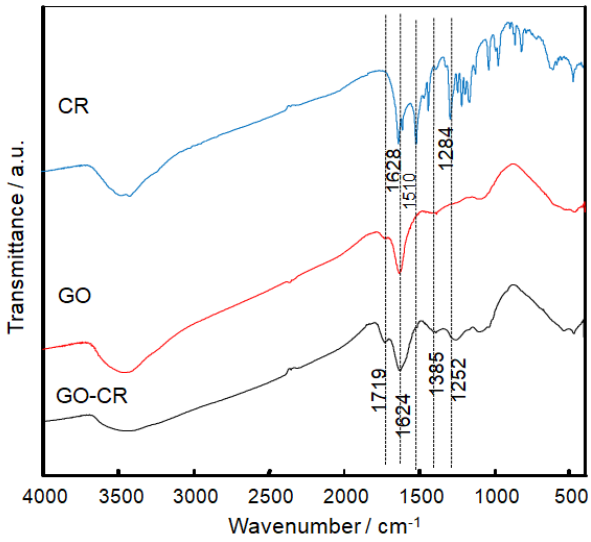

Figure 1. FT-IR spectra of curcumin, GO and GO-CR.

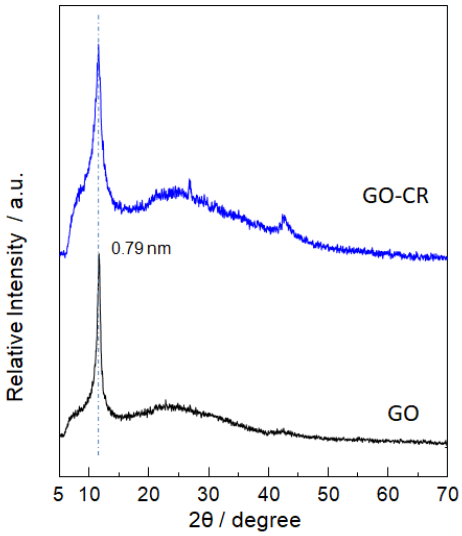

Figure 2. XRD patterns of GO and GO-CR.

SEM images of GO and GO-CR are shown in Fig. 3. GO has a layer structure with a large surface. GO-CR exhibits also layer structure similar to GO. The surface of GO is smoother than the one of GO-CR. This can be explained by the presence of curcumin on GO-CR surface [14].

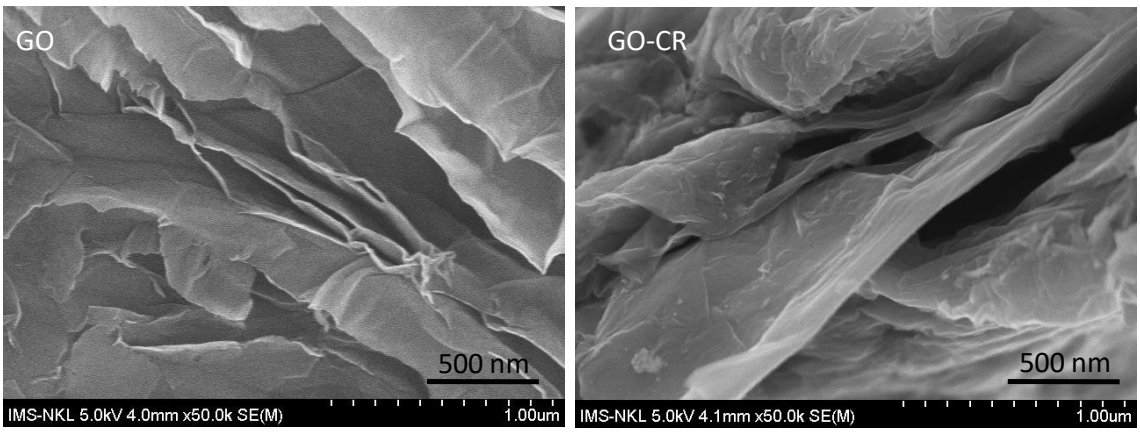

Figure 3. SEM photographs of GO and GO-CR.

Surface property of GO-CR was investigated by measuring zeta potential of GO and GO-CR at a concentration of 0.03 % in distilled water (Fig. 4). The zeta potentials of GO and GO-CR were -49.0 mV and -29.1 mV, respectively. In comparison with GO, the zeta potential of GO-CR moved in a positive direction. The change of zeta potential indicates the presence of curcumin on GO-CR surface [14].

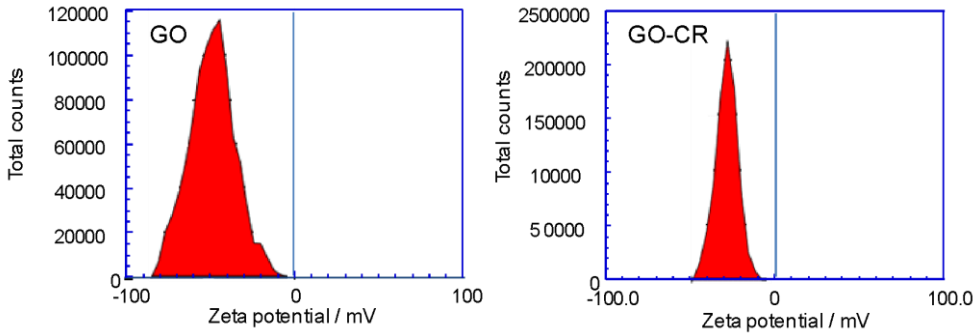

Figure 4. Zeta potentials of GO and GO-CR.

3.2. Characterization of PU coatings containing GO-CR

The dispersion degree of GO-CR and GO in PU coating was investigated by SEM. The SEM images of cross-section surface of PU coatings containing GO and GO-CR are shown in Fig. 5. For PU coatings containing 0.3 wt% GO we can see the layer structure of GO and the gaps between GO and PU resin. The size of the gaps were about 150-200 nm. For PU coating containing GO-CR, the structures of GO-CR can be also observed, but the slits between GO-CR and PU resin were much lower that of PU coatings with GO. The size of the slits was about 50-100 nm. The results showed that modification by curcumin improved the dispersion of GO-CR in PU matrix.

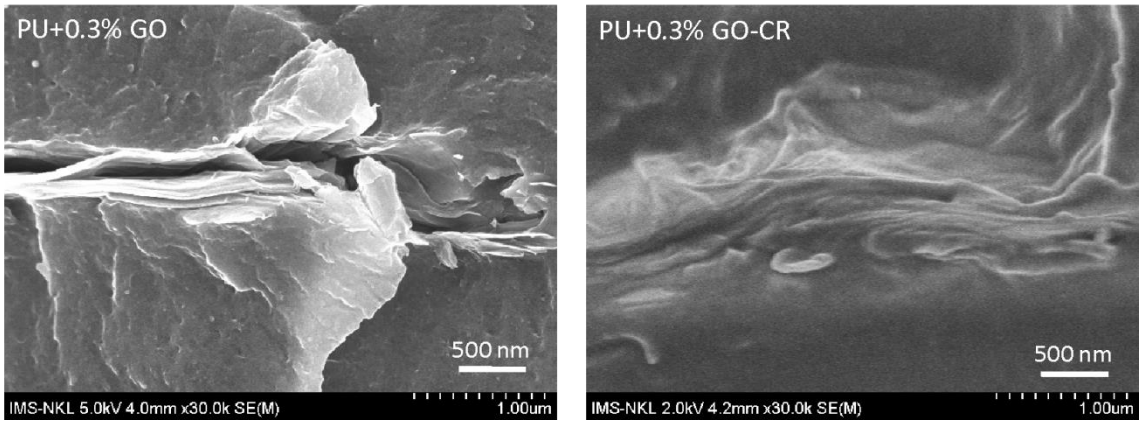

Figure 5. SEM images of polyurethane coatings with GO and GO-CR.

Corrosion resistance of coating samples was investigated by electrochemical impedance test. Fig. 6 presents the impedance diagrams of PU coating, PU containing 0.3 % GO and PU coating containing 0.3 % GO-CR after 35 days immersion in 3 % NaCl solution. The impedance modulus of PU coating with GO and GO-CR were very high and much higher than that of blank PU coatings and the impedance modulus of sample with GO-CR was higher than that of sample with GO. The increase of impedance modulus of sample with GO-CR in comparison with that of coating with GO can be explained the inhibition effect of curcumin on GO-CR surface [8]. From impedance diagrams, impedance modulus at a frequency of 100 mHz ($Z_{100\ mHz}$) were extracted to evaluate the corrosion resistance of samples [15]. The variations of $Z_{100\ mHz}$ of samples during the test are shown in Fig. 7.

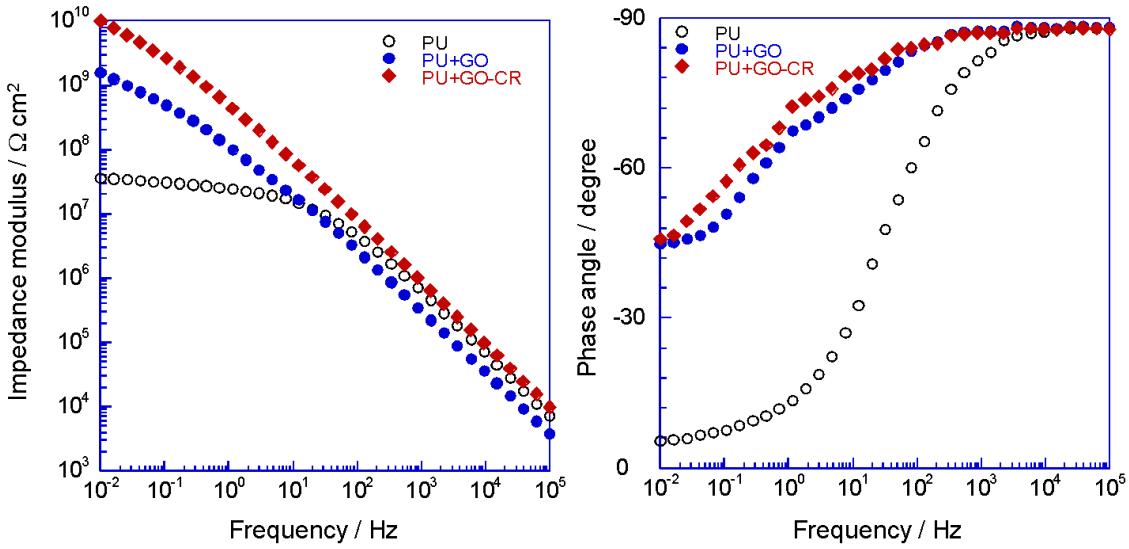

Figure 6. Electrochemical impedance diagrams obtained after 35 days test in 3 % NaCl for coating samples.

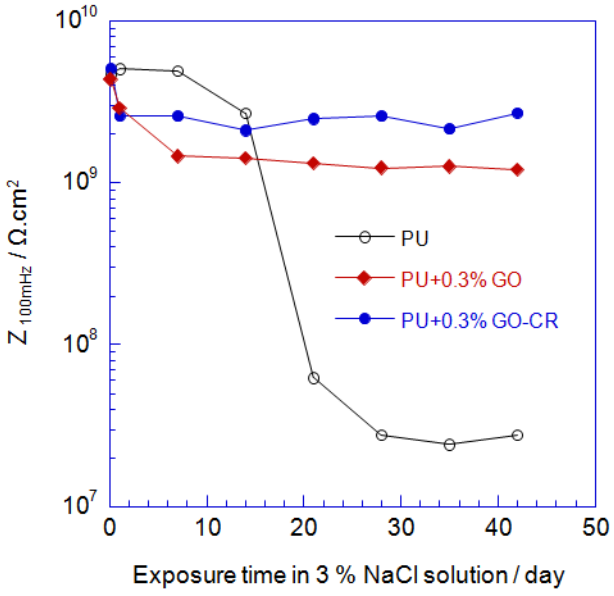

Figure 7. Variation of Z_{100mHz} values with exposure time to NaCl solution of coating samples.

After 1 h immersion in NaCl solution, the Z_{100mHz} values of all samples were very close and very high (> 10^9 Ω.cm^2). During the first 14 days of testing, The Z_{100mHz} values of all samples did not change much. After 21 days, the Z_{100mHz} value of blank PU sample decreased significantly, while the Z_{100mHz} values of PU samples with GO and GO-CR were stable. The decrease of Z_{100mHz} demonstrates the penetration of electrolyte in the coatings. After 42 days, the Z_{100mHz} of PU samples with GO and GO-CR were very high (> 10^9 Ω.cm^2), much higher than that of blank PU sample (< 10^8 Ω.cm^2). Sample with GO-CR exhibited higher Z_{100mHz} than sample with GO. Higher protection obtained by GO-CR compared with GO can be explained by the inhibition effect of curcumin presented in GO-CR and better dispersion of GO-CR in PU

resin. The presence of curcumin on GO-CR surface provided corrosion inhibition action at the steel/coating interface and improved the compatibility between PU and GO-CR.

4. CONCLUSIONS

Graphene oxide modified by curcumin was successfully synthesized by adsorption method. GO-CR has a layer structure like GO with curcumin attached on GO surface. Polyurethane coatings with GO and GO-CR at concentration of 0.3 wt% were prepared for corrosion protection of carbon steel. Corrosion resistance of coatings was evaluated by electrochemical impedance test. SEM results showed better dispersion of GO-CR in PU matrix than GO. PU coating containing GO-CR provided higher corrosion protection performance than PU coating containing GO. The presence of curcumin on GO-CR surface provided corrosion inhibition action at the steel/coating interface and enhanced the dispersion of GO-CR in PU matrix.

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