Effect of Graphene Oxide on Mechanical and Anticorrosive Properties of Graphene Oxide-urushiol Formaldehyde Polymer Composite Coating

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Abstract. Modified graphene oxide (MGO) was dispersed in urushiol formaldehyde polymer by mechanical mixing and ultrasonic dispersion, and MGO/urushiol formaldehyde polymer (UFP) coatings with different MGO contents were fabricated. The effects of the MGO additive on the microstructure, phase composition, physico-mechanical properties and anticorrosion properties of the MGO/UFP composite coating were studied. The results demonstrated that GO successfully incorporated into UFP through chemical bond and the well-dispersed MGO in UFP could markedly improve anticorrosive properties of the UFP coating. The hardness and the adhesion on the UFP coating was significantly enhanced.

1. Introduction

Raw lacquer, a renewable raw resource derived from lacquer trees grown in Asia region, [1] has been considered as a promising natural coating material due to superior barrier properties against oxygen and water, good durability, chemical resistance, and mechanical properties. However, the shortcomings of slowly drying speed and poor workability of oriental lacquer form a major obstacle for its application. In view of this, it is necessary to modify raw lacquer or develop a new lacquer based materials. The urushiol-formaldehyde polymer (UFP) coating, a type of modified urushiol paint having excellent physical and chemical properties, was mainly developed to apply in coating field with high properties, e.g. heavy anticorrosive properties. [2-4] Nevertheless, the development of UFP suffers from several limitations due to the presence of the low toughness and low alkaline resistance, which make it exhibit the poor membrane feature. In recent years, the superior properties of graphene oxide (GO) as potential nanofiller for the polymer composite coating have attracted great attention in both academic and industrial fields by a few researchers. The astounding properties of GO for its application in the field of anti-corrosion coating include remarkable liquid and gas barrier [5] excellent chemical stability and thermal stability,[6,7]compelling mechanical stiffness and strength, anti-corrosion, anti-microbial and anti-fouling features.[8] Therefore, GO has been successfully used as anticorrosive additives to improve the formulation of the polymer coatings and conventional organic coatings.[9-11] The development of GO-polymer-functionalized composite coatings is a potential method to enhance effectively anti-corrosion properties and physico-mechanical properties of the coatings used for industrial equipment anticorrosion protection.[12] At present, the dispersibility of GO is a bottleneck for the preparation of GO-polymer composite coatings, which strongly restricts its application in various fields. Physical dispersing methods such as ultrasonic dispersion can improve the dispersion of graphene in
polymer to some extent. [13] Comparatively, chemical modification can not only suppress the stacking and aggregation of GO, but also overcome the shortcoming of poor compatibility with polymers. To date, the modification of GO by grafting of chemical groups using silane such as vinyltris (2-methoxyethoxy) silane (TMEVS), 3-aminopropyltrimethoxysilane (APS), (3-aminopropyl) triethoxysilane (APTES), γ-(2,3-epoxypropoxy) propyltrim-ethoxysilane (GPTMS) and 3-methacyrloxypropyltrimethoxysilane (MPS) have been applied in the preparation of nanocomposite.[12,14-16] The challenge is the option of the silane coupling agents to synthesize well distributed silane-functionalized monolayer GO for the composite coatings.

In this work, the modified graphene oxide/urushiol-formaldehyde polymer (MGO/UFP) coatings from raw lacquer were prepared in order to improve the physico-mechanical properties and enhance the corrosion resistance of the UFP coating. The effects of the type of silane coupling agents on the dispersion stability of graphene oxide in UFP were investigated. The effects of MGO content on the morphology, structural composition, and physico-mechanical properties of as-fabricated MGO/UFP composite coatings were discussed. Also, the corrosion resistance of the novel MGO/UFP composite coated onto tinplate was evaluated through electrochemical measurements and acid, alkali and salt immersion tests. The potential application of the MGO/UFP composite coatings based on natural high polymer from raw lacquer was evaluated in the study.

2. Materials and methods

2.1. Materials

Raw lacquer sap was purchased from a local company located in AnKang, Shaanxi Province, China. The pure urushiol was obtained through xylene extraction as described in the literature. [17] Potassium permanganate, sulphuric acid, hydrogen peroxide, hydrochloric acid, methanol, ethanol, acetone, xylene, aqueous ammonia solution, formaldehyde, vinyltris (2-methoxyethoxy) silane (TMEVS), (3-aminopropyl)-trimethoxysilane (APS), (3-aminopropyl)triethoxysilane (APTES), 3-methacryloxypropyltrimethoxysilane (MPS) and other chemical reagents were of analytical reagent grade. Graphite powder (particle size <20 μm) was provided by Chinese Academy of Sciences Chengdu Organic Chemical Co., Ltd.

2.2. Synthesis of the MGO/UFP composite coatings

MGO/UFP composite coatings with different compositions were prepared by solution blending method (see Table 2). Urushiol formaldehyde polymer (UFP) was synthesized according to described previously method.[3] In a typical procedure for the synthesis of MGO/UFP, 3.0 wt.% of GO/MPS (1:2, w/w) was dispersed in 10 ml of xylene as a solvent through ultrasonication for 120 min to achieve a uniform dispersion. Next, 10.0 g of UFP (UFP: MGO, 100:3) was added into the MGO suspension with xylene/MGO ratio of 100/3 (ml/w). Then, the solution was mixed at room temperature by a mechanical stirrer at 1000 rpm/min until getting a uniform dope solution. The as-prepared MGO/UFP samples were labeled as MGU, respectively.

2.3. Preparation of the MGO/UFP composite films

The liquid composite coatings was poured and painted on clean dried tinplate and glass sheets by roll coating method at ambient temperature, and the coated samples were kept at room temperature for 24 h before measurement. The films formed on tinplates with a size of 120 mm × 50 mm × 2 mm were used for mechanical tests including thickness, adhesion, and hardness. Drying time and chemical corrosion resistant properties of the samples were obtained using the glass sheets (60 mm× 20 mm × 2 mm). The films were peeled from the glass sheets (30 mm × 50 mm × 2 mm) by immersing into deionized water under 100 °C for 5 min, then the films were dried in an thermostatic drying oven at 120 °C for 2.5 h to determine the cross sectional and surface morphologies (SEM). In addition, the UFP film without GO and the GO/UFP film without silane coupling agent were also prepared on the tinplates and glass sheets as a reference sample.
2.4. Characterization of the MGO/UFP composite coatings
The physico-mechanical properties tests including thickness (Coating thickness gauge), drying time (Drying time tester), adhesion (QFDT type electric paint film adhesion tester), and hardness (QHQttype pencil hardness test apparatus) of the MGO/UFP composite coatings were performed. The surface chemistry of the UFP, MGO/UFP, and GO/UFP coating were analyzed by a Perkin Elmer FTIR spectroscopy. The FTIR test was carried out in the wavelength range of 400-4000 cm\(^{-1}\). The surface morphologies of the prepared coatings were examined by S-4800 field emission scanning electron microscopy (SEM, Hitachi Ltd., Japan) analysis. The phase crystallinity and composition of the prepared coatings were measured by XRD (D8 ADVANCE A25, Bruker). Cu Ka was used as the radiation source at the voltage of 40 kV and the emission current of 30 mA.

2.5. Chemical corrosion resistant property.
In order to characterize the anticorrosive performance of the MGO/UFP composite coating, the corrosive experiment in chemical solution was carried out. The coated glass plates as samples were immersed in 30% H\(_2\)SO\(_4\), 10% NaOH and 3% NaCl solution for 14 days at room temperature and visual observations were carried out for the loss of light, color, or the formation of foam on the coatings surface. The samples were checked every 24 h and images were recorded.

3. Results and discussion

3.1. Characterization of the MGO/UFP composite coatings

3.1.1. FT-IR Analysis. As shown in Figure 2a, after reacting with HCHO, several peaks intensity decreased in the spectrum of UFP compared with those of fresh urushiol. Peaks at 3500, 1180 and 1250 cm\(^{-1}\) could be ascribed to the O–H stretching vibration and C–O and \(\beta\) O-H stretching vibration, respectively, probably owing to the decrease in the number of the hydroxyl group on the phenyl ring and the formation of polymers corresponding to the hydroxyl group on the phenyl ring of urushiol.[18]

FT-IR analysis was further carried out to verify the chemical grafting between GO and UFP. As shown in Figure 2b, after chemical grafting of the GO with UFP, the intensities of the FT-IR peaks of GO/UFP corresponding to the oxygen functionalities, such as the C=O stretching vibration peak at 1726 cm\(^{-1}\), the vibration and deformation peaks of O–H groups at 3395 and 1410 cm\(^{-1}\), respectively, the C-O (epoxy) stretching vibration peak at 1226 cm\(^{-1}\), and the C-O (alkoxy) stretching peak at 1052 cm\(^{-1}\) decreased dramatically, and some of them disappeared entirely. The groups between most oxygen functionalities in the GO and hydroxy groups in UFP were removed, which confirmed that GO was successfully grafted onto the UFP polymer matrix through the chemical reaction.

Upon treatment with MPS, the C=O stretching vibration at 1733 cm\(^{-1}\) in GO became obscured by the appearance of a stronger absorption at 1623 cm\(^{-1}\) that could be attributed to C=O from MPS as shown in Figure 2b. The new bending and asymmetric vibrations at 1646, 958 and 571 cm\(^{-1}\) could be assigned to Si-O-C, Si-OH, and Si-O-C bonds, respectively. The new band at 1096, 804 and 472 cm\(^{-1}\) could originate from the silanes moieties tendency to self-reaction in the bulk of solution instead of GO surface and corresponded to the coupling of the Si-O-Si stretching vibration with the silanes deformation vibration (Figure 2b), while those at 2800, 2770, and 2690 cm\(^{-1}\) could be assigned to the stretching vibration of CH\(_2\). Compared with typical CH\(_2\) bands (1350, 1465 and 2853, 2926 cm\(^{-1}\)), all the intensities of these bands was decreased, suggesting that it was characteristic of UFP with methylene groups. In addition, the characteristic peaks of UFP also appeared at 3370–3520 cm\(^{-1}\) in the spectrum of MGO/UFP, all bands shifted to a low wavenumber and became broader, which demonstrated the successful cross-link between UFP and MGO for formation of interpenetrating polymer networks at interfaces. Compared to the peaks of UFP, it was obvious from FT-IR spectra that silane molecules bond grafted on GO surface through the chemical reaction with functional groups and higher amount of MGO crosslinked onto the UFP as polymer matrix.

3.1.2. Phase Composition of the MGO/UFP Composite Coatings. XRD patterns of the UFP, GO/UFP and MGO/UFP samples were given in Figure 3. As can be seen, wide-angle X-ray diffraction showed
a very broad peak at 19.9° owing to the presence of amorphous structure domains in the UFP films which was characteristic of UFP. [19] The XRD pattern of the GO/UFP sample was similar to that of the UFP and no obvious characteristic diffraction peaks of GO were observed because of its low loading content and weak crystallization. Compared with the GO/UFP sample, the diffraction peaks at 19.9° of the MGO/UFP samples were sharp and intense, indicating their more highly crystalline nature than the GO/UFP sample. [12] This might be because graphene acting as nucleating agents promoted the heterogeneous nucleation of UFP polymer on the surface of MGO and further induced them to crystallize. Similar findings have been reported in previous studies, [20] which showed that the addition of graphene nanosheets could efficiently accelerate the crystallization rate of polypropylene in graphene/polypropylene nanocomposites. Thus, incorporation of MGO into the UFP matrix tended to modify its crystallinity, which could eventually improve the tensile strength of the pure UFP films.[21]

Additionally, there were a new decreased and diminished humps at 2θ=10.9°, indicating that the presence of GO. [12, 22] No impurity peaks were observed, confirming the high purity of the MGO/UFP films.

3.1.3. Microstructure and Chemical Composition of the MGO/UFP Composite Coatings. In this experiment, SEM micrographs in Figure 4 show the bulk structural information on the MGO/UFP, GO/UFP and pure UFP films. There were no visible agglomeration and protuberance or swelling behavior in the surface morphologies of the MGO/UFP (Figure 4a) composite films by comparing with the GO/UFP composite films (Figure 3c), indicating that the GO were well dispersed in the UFP since forming covalent bonding between MPS molecules and GO surface (hydroxyl on surface, carboxylic at edges and epoxide in the basal plane), which was similar to the one observed from the FT-IR results.[22] After silane molecule-grafted reaction with graphene oxide, the images on some agglomerations in the Figure 4b of MGO/UFP composite samples were related to strong interfacial interaction of MGO with UFP polymer matrix and GO molecules were aggregated on UFP (Figure 4c) compared to smooth surface of the MGO/UFP composite film (Figure 4a), which could be demonstrated that the microstructure compactness of the MGO/UFP composite coatings can be improved to act as a barrier against corrosive agents and effectively protect base metal from corrosion.[12,23,24] Meanwhile, the incorporation of MGO suspension in the UFP was supposed to improve the surface adhesion of the UFP coatings by establishing a interfacial interaction between MGO and UFP.[25]

3.2. Physico-mechanical Properties of the MGO/UFP Composite Coatings
The study of the physico-mechanical properties involving thickness, drying time, adhesion, and hardness in the resulting composite coatings is essential for its application. [2, 26] The physico-mechanical properties of the GO/UFP and MGO/UFP composite coatings with different GO content (GO, 0.5-2.0 wt. %) were studied and listed in Table 2. As can be seen, the addition of GO to the natural UFP significantly improved the adhesion and hardness at room temperature. The GO/UFP composite coatings consisting of 1.0 wt. % GO could much more resist scratching up to grades of hardness and adhesion 5H and 1 than the neat UFP. On the basis of this findings, it could be concluded that the incorporation of GO as reinforcement nanofillers had positively improved the hardness and adhesion.[27] The significant reinforcement was associated with interfacial interactions between GO and UFP matrix, such as covalent bonds, van der Waals forces and hydrogen bonding. [2, 28] Nevertheless, the hardness of sample GU3 and GU4 slightly reduced thereafter as the GO content further increased from 1.5 wt.% to 2.0 wt.%. The decrease of physico-mechanical properties in GO/UFP should be corresponded to the non-uniform dispersion level (not optimal) and nanometer effect between GO and UFP matrix.[29] That is, a non-uniform distribution of GO particles will cause uneven stress in the composite films.[2] The MGO at higher concentration (GO, 2.0 wt.% ) slightly increased a grade of the hardness to 6H and little decreased a grade of the adhesion to 2 for sample MGU4, indicating that the large silane molecules MPS leaded to a better dispersion of GO in UFP for preventing the GO sheets from agglomeration. Moreover, the silane molecules reduced the hydrophilicity of GO surface making it more compatible with polymer matrix and the excess MGO
could induce the interfacial interaction to form on the surface of the organic and the inorganic phases for UFP and GO. [22, 30]

3.3. Anticorrosive performance of the MGO/UFP composite coatings

In order to characterize the chemical corrosion resistance performance of the MGO/UFP composite coatings, the corrosive experiment in dilute sulphuric acid, sodium hydroxide solution and sodium chloride solution were carried out. The coated glass plates were immersed in 30% H$_2$SO$_4$, 10% NaOH and 3% NaCl solution for 14 days at room temperature and visual observations were carried out for the loss of light, color, the formation of foam on the coatings surface. Compared with UFP surface state, there was no visible superficial phenomenon formed on the MGO/UFP composite films immersed in 30% H$_2$SO$_4$ and 3% NaCl solution, but distinct foam could be observed on the MGO/UFP composite coatings surface immersed in 10% NaOH (Table 5). Therefore, the results indicated that the chemical corrosion resistance of the MGO/UFP composite coatings was enhanced by covering GO as a barrier to the diffusion of acid and saline water.

4. Conclusion

MGO/UFP composite coatings were successfully prepared through solution blending utilizing a mixture of MGO and UFP. It was found that the chemical grafting of silanes molecules MPS onto the GO surface enhanced the dispersion and compatibility of GO with UFP. The addition of GO in the appropriate amount was implied as an effective method to simultaneously improve the thermal stability, physico-mechanical property. At 1.5 wt. % and above, the MGO/UFP composite coating deriving from the reaction between MGO and UFP played as a major anti-corrosion coating, which could provide more effective barrier against corrosive ions ingress. Above 2.0 wt. %, increasing GO content had much effect on accelerating the corrosion rate, which could inhibit the dispersion of GO and the film-forming ability.

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6. References

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