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Original Article

Polyvinyl Butyral/Graphene Oxide Composite Coating for Properties Improvement

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Abstract: In this paper, polyvinyl butyral (PVB) composite coating was prepared with graphene oxide (GO) to improve mechanical properties, corrosion protection, and thermal oxidation stability. Fourier-transform infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), Field Emission Scanning Electron Microscopy (FESEM),... were used to examine the results. The presence of GO in the composite coating was characterized by FT-IR. Corrosion protection of PVB coating containing GO was determined with salt mist testing with four cycles in 5% NaCl. Effects of GO on adhesion, flexibility, impact resistance, relative hardness, and thermal oxidation stability of PVB composite coatings were also investigated. Results showed that GO content in PVB composite coating of 1.5 wt.% had significantly enhanced mechanical properties, and corrosion resistance of PVB composite coating. The thermal oxidation resistance of PVB composite coating with 1.5 wt.% of GO was much higher than that of PVB composite coating without GO.

Keywords: Polyvinyl butyral/Graphene oxide composite coating, physico-mechanical properties, anti-corrosion protection FT-IR, salt mist testing.

1. Introduction

Polyvinyl butyral (PVB) is used in the coating field because of its excellent film-forming properties, impact resistance, high flexibility, and toughness. It has excellent adhesion to metals, plastics, as well as leather [1-3]. One of the most critical applications of PVB coating is a wash primer for aluminum and aluminum alloy [4-7]. The presence of functional groups in PVB resin provides it more possibilities for chemical modification, and it can be cured with acid or other resins such as phenolic, epoxy, nitrocellulose,… [8-12].

Recently, graphene and graphene oxide (GO) have been used as an additive for improving mechanical properties or UV- resistance for polymer coatings or polymer composites [13-15]. Jingjing Si et al., [16] investigated on influence of GO on the thermal

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stability of polymer composite based on phenolic. Results showed that polymer composite with GO had a higher initial degradation temperature of about 14 °C than that of neat phenolic resin. Rama Layek et al., [17] used GO in methylcellulose coating, and GO had improved mechanical properties of coating, and oxygen permeation of coating also decreased about 98%. Guiyu Zhu et al., [18] studied on nanocomposite coating based on PVB and GO to improve the anti-corrosion ability for aluminum alloy. Results showed that the coating could effectively protect aluminum substrate for up to 1200 h. Anhang Li et al., [19] used polyaniline-graphene oxide (PANI-GO) to add to PVB primer to prepare anti-corrosion coating for aluminum alloy. Poly (methylhydrosiloxane) was also introduced to enhance the crosslinking degree of the coating. Results showed that the coating had a higher protection for aluminum alloy than the neat PVB coating. The coating expressed long-term corrosion protection to aluminum alloy for over 70 days. Mortaza Hajian et al., [20] investigated nanocomposites of PVB with graphene via solution blending. Nanocomposites showed considerable thermal and mechanical properties than neat PVB. The nanocomposites also expressed good toughness and flexibility.

Previous studies have generally conducted GO in PVB and cured with phenolic, Poly (methylhydrosiloxane), epoxy, and so on. These papers' common weakness was done at temperatures above 60 °C to create the crosslinking network. In fact, some substrates could not suffer from the temperature above 60 °C or coated big things cannot be put into ovens for baking. To overcome the weakness of the above-mentioned researches, PVB cured with phosphoric acid at room temperature would be introduced. This article will show the effects of GO on adhesion, flexibility, impact resistance, and relative hardness of PVB coating. Besides thermal oxidation stability, salt mist resistance of PVB coating was also investigated to evaluate the role of GO in PVB coating.

2. Materials and Experiment

2.1. Chemicals

Binders: Polyvinyl butyral, B-08HX was a Chang Chung Group (Taiwan) product. Specific gravity: 1.05- 1.10. Butyral content: 76-82%. Hydroxyl content: 18-21%. Acetyl content ≤ 2%.

Hardener: Phosphoric acid 85% was supplied by Chongqing Chemdad CO., Ltd (China).

Pigments: TiO_2, Rutile R-996: was a Sichuan Lomon Corporation (China) product. Crystal form: Rutile. TiO_2 Content > 93%. Average particle size: 23 μm. Oil absorption (g/100g) < 22; Zinc tetroxy chromate was a product of Sona Synthetics Products (India). Purity ≥ 97%. Specific gravity: 3- 3.2; Carbon black (N330) is a Hangzhou Epsilon Chemical Co.,Ltd (China) product. Iodine absorption: 77-87 g/kg. Tinting strength: 98-108%. Residue on 45μm sieve ≤ 0.1.

Solvents: Xylene, Ethanol, Methyl Ethyl Ketone (MEK): Industrial products (China).

Additive: ACS Material Graphene Oxide-GO was an ACS MATERIAL LLC (USA) product. Appearance form: powder. Color: brown Molecular weight: 4.239,48 g/mol. Carbon> 85%. Oxygen > 14.95%.

2.2. Paint Reparation

Table 1. Composition of paint

No.	Components	Weight percent (wt. %)
Part A		
1	Polyvinyl butyral	24
2	Zinc tetroxy chromate	6
3	TiO_2	10
4	Carbon black	1
5	Xylene	20
6	Methyl Ethyl Ketone (MEK)	24
7	Ethanol	13-15

8	Graphene Oxide	0-2
Part B		
1	Phosphoric acid 85%	15
2	Ethanol	65
3	Water	20

For Part A: Raw materials were prepared as in Table 1. There were three stages of paint preparation involved: *i) Primary grinding*: 90% of xylene was added with all other materials of zinc tetroxy chromate, polyvinyl butyral, TiO_2, MEK, ethanol, and stirred at 20- 40 rpm for an hour. The mixture was kept to be conditioned for 24 hours*; ii) Fine grinding*: The mixture was subjected to fine grinding at a speed of 1,300- 1,500 rpm to reach the paint fineness of $\leq$ 20 µm*; and iii) Preparation*: The remaining xylene (another 10%) was added and stirred for an hour. After that, the paint samples for testing were acquired through filtering before proceeding with the canning step. A 100 hole/mm^2 mesh was used to remove any dirt or coarse particles. It was followed by the canning step for storing purposes. The GO content was calculated as the percentage of it to the total volume of paint. For example, the content of GO was 2 wt.%, which meant the ratio of GO was 2 wt.%, and 98 wt.% was for the rest ingredients.

For Part B: Components were poured together.

2.3. Preparation of Samples

Mechanical properties measurement and salt mist testing samples were prepared on steel panels (ISO 1514:2016). The composite coatings were deposited on the cleaned panels using a sprayer under pressure of 4 kg/cm^2. These coatings were dried at (25±2) oC and humidity (50±5)% for seven days before testing. The thickness of dried coatings was (50±3) µm.

2.4. Analysis Methods

The adhesion of the coating was determined according to ISO 2409:2013. The impact resistance of the coating was determined according to ISO 6272-1:2011. The relative hardness of the coating was determined according to ISO 1522: 2006. The flexibility of coating was determined according to ISO 1519:2011. The fineness of paints was determined according to ISO 1524: 2020. Fourier-transform infrared spectroscopy (FT-IR) was done on the Fourier FTIR-8700 series converter. The thermal oxidation stability of the coating was evaluated by thermogravimetric analysis (TGA). TGA was analyzed by NETZSCH TG 209F1 LIBRA in the air with a temperature rate of 10 ^{o}C/minute from room temperature to 600 ^{o}C. Salt mist, cyclic testing (5% NaCl) was determined according to IEC 60068-2-52: 2017 with four cycles, each cycle included 2 hours of spraying at (35±2) ^{o}C, kept in humidity condition for seven days at (40± 2) ^{o}C with a relative humidity of (93 ± 2) %. Morphology of composite coating was observed by the FESEM Hitachi S4800 machine with a magnification of 10,000 times and voltage of 5 KV.

3. Results and Discussion

3.1. Effect of GO Content on Physisco-Mechanical Properties of Coating

To investigate the effect of GO content on adhesion, flexibility, impact resistance, and relative hardness of PVB composite coating, samples were prepared with a ratio of Part A/Part B as 4/1 [7] and GO content of 0; 0.5; 1.0; 1.5 and 2.0 wt.%. Samples were named M0, M1, M2, M3 and M4, respectively. Samples were covered on standard panels. Results are shown in Table 2.

Table 2 showed that GO content increased from 0.5-1.5 wt.% relative hardness increased, and adhesion and flexibility of coating were the best and unchanged. Meanwhile, when GO content reached 2 wt.%, the relative hardness of the composite coating was slightly increased, but impact resistance was lightly reduced, but the adhesion and flexibility of the coating decreased sharply. It can be explained that the hardness of GO particles was much higher than that of PVB, so the more GO content, the harder the relative hardness of composite coating [13, 20].

However, if GO content increased continuously to high enough (2 wt.%), GO particles tended to agglomerate into larger particles, so the adhesion, flexibility, and impact resistance of coating would be decreased [16, 21, 22]. M3 expressed the best properties of all, so it was chosen for further study.

Table 2. Effect of GO content on physisco-mechanical properties of composite coating

Samples	Adhesion (Points)	Flexibility (mm)	Impact resistance (kg. cm)	Relative hardness
M0	1	2	200	0.58
M1	1	2	200	0.61
M2	1	2	200	0.63
M3	1	2	200	0.65
M4	3	4	180	0.66

3.2. Fourier-Transform Infrared Spectroscopy (FT-IR) Analysis

To examine the appearance of GO in PVB composite coating, infrared spectroscopy (IR) of PVB composite coating with and without GO were conducted by Fourier FTIR-8700 series transformers. Results are shown in Table 3 and Figure 1.

Figure 1a showed that [23] peaks 3386.81 cm^{-1} and 3363.48 of the OH group in PVA (raw material for the synthesis of PVB); peaks 2957.18, 2956.83, 2871.46, and 2869.43 of CH group of aliphatic hydrogens; 1643.06 and 1641.25 cm^{-1} of C=C of alkene; 1236.69 and 1228.86 cm^{-1} of acetates; 1101.42 and 1100.12 cm^{-1} of -C-O-C (Symmetry) of second alcohol, 996.07 and 995.82 cm^{-1} of =C-C (Bending) of trans RCH=CHR.

There were some new peaks in Figure 1b, in which peak 1623.06 cm^{-1} was C=C vibration of graphite; peak 937.78 cm^{-1} represented for vibration of C=C-H (out of plane), and peak 1228.86 cm^{-1} was typical for the vibration of the C-OH group of GO, which proved in the captured sample FT-IR spectrum with GO [20, 21, 24].

Table 3. Selected measured IR bands of coating

No.	Typical spectrum	Wavenumbers (cm-1)
1	νOH	3386.81
2		3363.48
3	Nch (Aliphatic hydrogens)	2957.18
4		2956.83
5		2871.46
6		2869.43
7	νC=C (alkene)	1643.06
8		1641.25
9	νC=C	1623.06
10	νC-OH	1236.69
11		1228.86
12	ν_aC-O-C (asymmetry)	1101.42
13		1100.12

14	C=O	1052.88
15	ν_a C-O-C (symmetry)	1048.08
16	νC=C-H (out of plane)	937.78
17	νC-H (aromatic-bending)	808.91
18		784.18

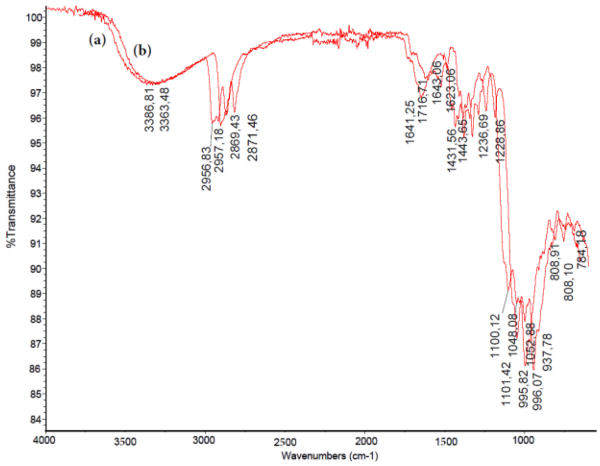


Figure 1. IR spectra of PVB composite coating without GO (a) and with GO (b).

3.3. Salt Mist Stability of Composite Coatings

To study the effect of salt mist on the protection of PVB composite coating with and without GO, samples M0 and M3 were conducted. Coatings were tested in a salt mist chamber with 5 wt.% NaCl for four cycles. The images of PVB-coated surfaces were taken before and after the salt mist cyclic tested coatings surface.

Coatings were examined by cross-cut test, and SEM was also taken with a magnification of 10.000 times to observe the surfaces of coatings. Results are shown in Figure 2 and Figure 3.

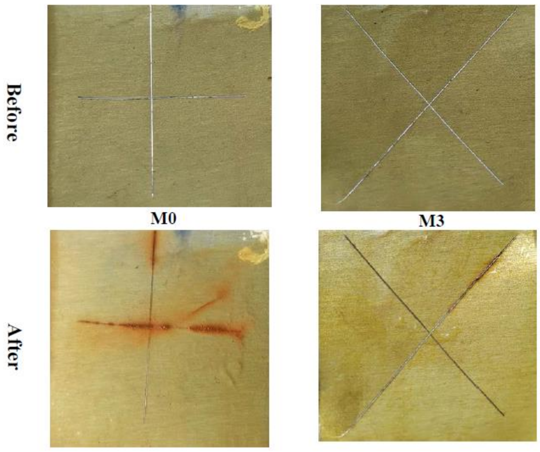
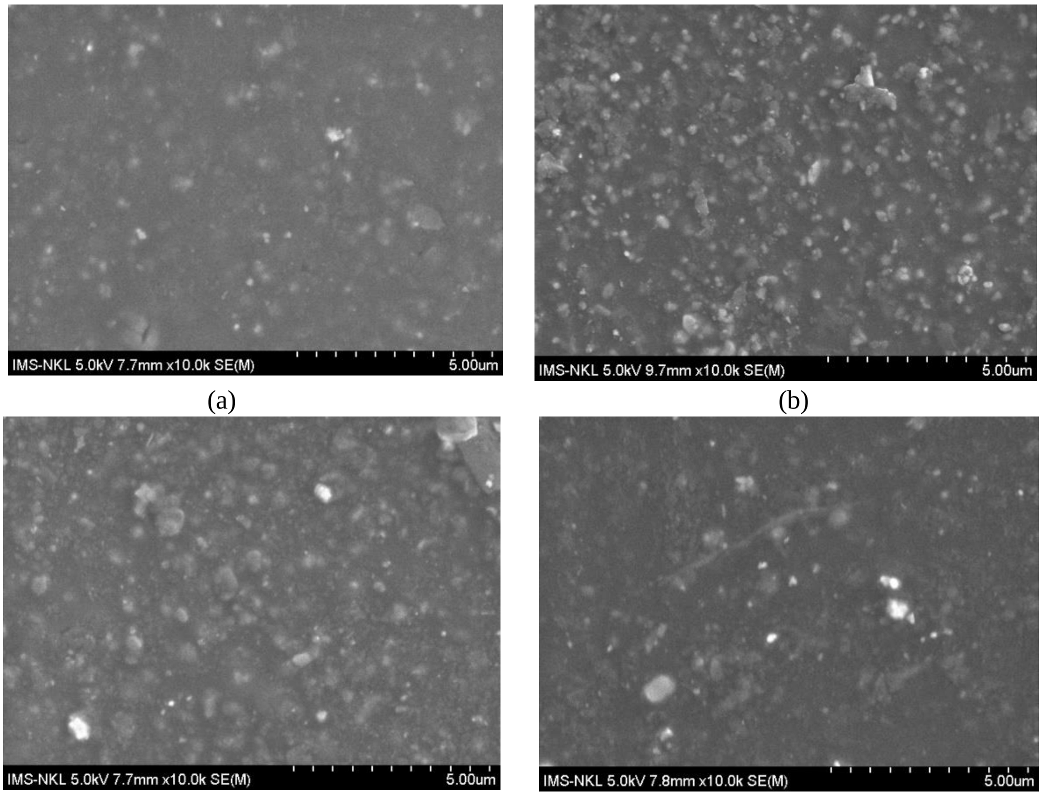


Figure 2. Optical photographs on the surface of examined coatings before and after salt mist testing.

Figure 2 showed that after four cycles of salt mist testing of coatings appeared, rust spots on samples, PVB coating sample without GO had larger blistering; meanwhile, PVB coating with GO had some smaller spots blistering. This indicated that the steel surface under coating had been corroded and the adhesion degraded. It meant that PVB coating with GO could protect the substrate better than PVB coating without GO [22, 25]. This can be explained by the fact that good adhesion came from the role of GO. On the surface of GO, there were C-OH groups (peak 1228.86 cm^{-1}), which could create physical bonding to the steel substrate. The strong adhesion guaranteed the long-term protection of PVB coating with GO, and the damage happened electrochemically, so SEM images (Figure 3) could not clearly express the differences between samples [13, 21, 25].



(a) (b)

(c) (d)

Figure 3. SEM micrographs of initial M0 (a), tested M0 (b), initial M3 (c), and tested M3 (d).

3.4. Effect of GO Content on Thermal Oxidation Resistance of PVB Composite Coating

To study the effect of GO content on the thermal oxidation resistance of PVB composite coating, Thermogravimetric analysis (TGA) was carried out with samples M0 (PVB coating) and M3 (PVB coating with GO). Results are shown in Table 4, Figure 4a, and Figure 4b.

Table 4 and Figures 4a, and 4b showed that the slopes of TG curves of different samples were not the same. At different temperatures decomposition of samples was different, too. There were two decomposition steps: i) Under 200 ^{o}C: decomposition of low molecular substances and residual solvents; and ii) Up to 350 ^{o}C and above: decomposition occurred with residual functional groups in polymer branches, and low molecular substances [10, 17, 20]. Results also showed that at 500 ^{o}C PVB coating had an ash content of 39.82%, and with the presence of GO, the ash content of the coating was much higher, up to 44.14%. It can be explained that polymer chains were cut and oxidation had taken to organic substances in a high temperature with the presence of oxygen. At that time, oxygen had promoted the formation of free radicals and polymer would be degraded sharply, forming lower molecular compounds containing oxygen.

These particles for PVB coating with GO prevented heat and oxygen penetration from inside the PVB's structure. In addition, the thermal decomposition of GO would be coked to form a stable structure like ceramic. Hence, GO had improved the thermal oxidation resistance of PVB composite coating [18, 19, 24, 25].

Table 4. Effect of GO content
on the thermal oxidation resistance of PVB composite coating

Samples	Weight loss (%)		
	300 °C	350 °C	500 °C
M0	33.43	42.56	60.18
M3	34.82	44.28	55.86

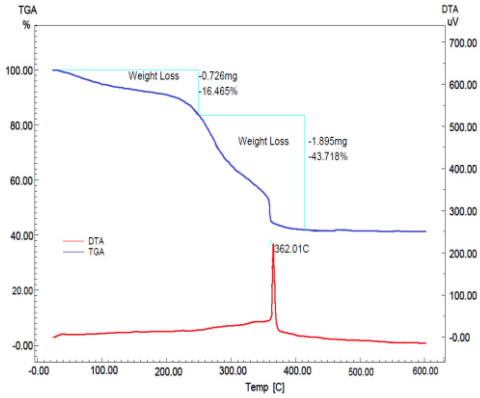


Figure 4a. TGA of M0.

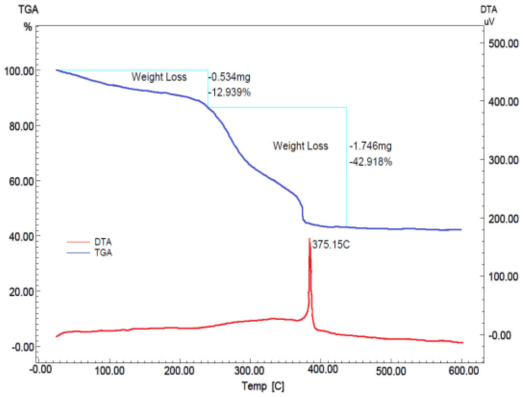


Figure 4b. TGA of M3.

4. Conclusion

Graphene oxide (GO) content increases from 0-1.5 wt.%, adhesion, impact resistance, and flexibility of PVB composite coatings are the best; meanwhile, relative hardness increases from 0.58 to 0.66. The physisco-mechanical properties of PVB composite coating would be the best when the GO content of 1.5 wt.%. GO improves anti-corrosion protection of PVB composite coating from salt mist cyclic. PVB composite coating with 1.5 wt.% of GO could protect the substrate better than PVB composite coating without GO. The thermal oxidation resistance of PVB composite coating with GO is much higher than that of PVB composite coating, and the weight loss of PVB composite coating is 60.18%, but that of PVB composite coating with GO is 55.86%, respectively.

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