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Improvement of physical and thermal properties of polyvinyl butyral coating with nanosilica

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Abstract

In this paper, polyvinyl butyral (PVB) coatings with different nanosilica contents (0- 1.5 weight percent (wt%) were prepared for improving properties such as mechanical properties, corrosion protection, thermal oxidation stability of coating. Presence of nanosilica in coating was characterized by FT-IR. Corrosion resistance of PVB coatings containing nanosilica was investigated by salt mist testing. Effects of nanosilica on adhesion, flexural strength and relative hardness and thermal oxidation stability of PVB coatings were also examined. Nanosilica with content of 1.2 wt% significantly improved mechanical properties, corrosion resistance and thermal oxidation stability of PVB coatings.

Keywords: Coating for aluminum, corrosion protection, nanosilica, polyvinylbutyral coating, paint, polymer.

1. Introduction

Polyvinyl butyral (PVB) can be used as a binder for wash primers, stoving enamels, varnishes and lacquers for different substrates. PVB coating is tough, flexible, high impact resistance, transparent and weather resistant (Rodger, 2007; Arthur, 2006). It has a very good adhesion to metals, plastics and leather as well, but the most important application of PVB in paint is wash primer for aluminum, aluminum alloy (Rike, Carsten, Thomas, Boris., & Anne, 2021; Agnieszka & Krzysztof, 2016; Zhu, Ma, Sun & Zhang, 2019; Arieh, 2008). Although it is a thermoplastic, PVB itself contains functional groups so it can participate in curing with other resins as phenolic, epoxy, nitrocellulose for making paints (Hideki & Yuya, 2021; Edwin & Agnieszka, 2011; Manjunatha, Taylor, Kinloch & Stephan, 2009; Motawie, Badr, Amer, Moustafa & Ali, 2008; Yinze, Zhaolei, Liang, Yu & Yanmin, 2017; Saad, Najat & Adnan, 2010) studied PVB blended epoxy with a weight ratio of 40 wt% epoxy resin and 60 wt% PVB at about 160 °C in 30 minutes for improving mechanical properties of PVB coating. (Guiyu et al., 2019) investigated on improving anticorrosion of PVB coating with graphene oxide and poly (methylhydrosiloxane) for aluminum alloy. Corrosion resistance of the coating in 3.5 wt% NaCl solution was done. The long-term immersion experiment indicated that studied coating could effectively protect the aluminum for up to 1200 hours. (Igor et al., 2016) studied the influence of potassium polytitanate on mechanical properties of PVB coating. Results showed that surface modification of potassium polytitanate with different coupling agents significantly improved PVB coating's mechanical properties as adhesion, tensile strength and strain at break.

Some authors have used nanosilica to enhance properties of coatings or polymer composite (Thanh, 2022a; Malaki, Tehrani & Hashemzadeh, 2018; Meiling et al., 2020; Tsai, Huang, & Cheng, 2011). Results showed that nanosilica had enhanced tensile strength, flexural strength and thermal oxidation resistance of nanocomposite based on epoxy. Results also showed that nanosilica had considerably enhanced tribological and mechanical properties of acrylic polyurethane coatings, etc.

Even nanosilica particles have been introduced in matrixes as epoxy, acrylic, polyurethane, etc. but hardly published papers related to PVB paints or coatings. This article will present effects of nanosilica on mechanical properties, thermal oxidation stability, salt mist stability of PVB coating so as to confirm that some properties of PVB coating had been improved with nanosilica. Fourier transform infrared spectroscopy (FTIR) was also used to identify the presence of nanosilica in coating. Besides that, the anticorrosion performance of coatings with and without nanosilica was investigated by scanning electron microscopy (SEM) through salt spray testing.

2. Materials and methods

2.1 Chemicals

Binders: Polyvinyl butyral, B-08HX (Chang Chung Group, Taiwan) with main specifications: Specific gravity: 1.05- 1.10, Butyral content: 76- 82 %, Hydroxyl content: 18- 21 %, Acetyl content □ 2 %, Third amine group: 5- 9. Pigments: Dichromium zinc tetraoxide and carbon black (N330): Industrial products (China). Solvents: Xylene, Ethanol, Methyl Ethyl Ketone (MEK): Industrial products (China). Filler: Talc, Industrial products (China).

Additive: Nanosilica, Sigma-Aldrich with specifications as: Fine powder, Purity: 99.8%, Average size: 12nm, Specific surface area: 175- 225 m^2/g (according to BET method). Phosphoric acid 85%: Industrial product (China). Water was use as industrial fresh water.

2.2 Paint preparation

Table 1. Composition of PVB coating.

No.	Components	Content (wt%)
	Part A	
1	Polyvinyl Butyral (B-08HX)	25
2	Dichromium zinc tetraoxide	5
3	Talc	10
4	Carbon black (N330)	1
5	Xylene	24
6	Methyl Ethyl Ketone (MEK)	20
7	Ethanol	13-15
8	Nanosilica	0-2
	Part B	
1	Phosphoric acid 85%	15
2	Ethanol	70
3	Water	15

For Part A: Raw materials were prepared as Table 1. Primary grinding: Adding 90% of xylene and all dichromium zinc tetraoxide, B-08HX, Talc, MEK, ethanol to tank to stir at 20- 40 rpm for an hour. Keep the mixture for 24 hours. Fine grinding: Grinding at speed of 1,300- 1,500 rpm, until paint fineness □ 20 µm. Preparation: Adding the rest xylene, stirring for 02 hours. Getting a paint sample for testing. Filtering - canning - storage: Using a 100 hole/mm^2 mesh to remove any coarse particles or dirt, then switch to canning for storing.

For Part B: Just pouring components together.

2.3 Sample preparation

Samples for mechanical properties measurement and salt mist testing were prepared on steel panels (ISO 1514:2016). Paint coatings were deposited on the cleaned panels by using a sprayer (4 kg/cm^2 of pressure). These coatings were dried at temperature of (25±2) °C and humidity of (50±5) % for 7 days before testing. The thickness of dried coatings was (30±3) µm.

Samples for FTIR analysis were prepared on glass substrates with 15 µm of dried thickness. These coatings were dried at temperature of (25±2) °C and humidity of (50±5) % for 7 days before testing.

Samples for morphology on glass substrates with 150 µm of dried thickness and then dried at temperature of (25±2) °C and humidity of (50±5) % for 7 days before testing.

2.4 Analysis methods

Adhesion of coating determined according to ISO 2409:2013. Flexural strength of coating was determined according to ISO 1519:2011. Impact resistance of coating was determined according to ISO 6272-1:2011. Relative hardness of coating was determined according to ISO 1522: 2006. Fineness of paints was determined by ISO 1524: 2020. Drying time of coating was determined according to ISO 9117-6:2012. Infrared spectroscopy (FTIR) was done on the Fourier FTIR-8700 series converter. Thermal oxidation stability: Thermal gravimetric analysis (TGA) was analyzed by NETZSCH TG 209F1 LIBRA in air with temperature speed of 10 °C/minute from room temperature to 600 °C. Morphology of coating film was observed by FESEM Hitachi S4800 machine with a magnification of 5,000 times and voltage of 5 KV. Salt mist, cyclic testing (5% NaCl) was determined by IEC 60068-2-52: 2017 with 04 cycles, each cycle included 02 hours spraying (at (35 ± 2) °C), keeping humidity condition for 7 days at (40± 2) °C, relative humidity of (93 ± 2) %.

3. Results and discussion

3.1 Effect of phosphoric acid content on mechanical properties of PVB coating

As coating comprises two components so the ratio of Part A and Part B will strongly affect the mechanical properties of PVB coating. By investigating the effect of Part B (phosphoric acid) content on mechanical properties of coating, the best suitable ratio of Part A and Part B would be determined. Samples were made as Part A without nanosilica and Part B content of 10; 15; 20; 25; 30 wt%. Samples were covered on standard steel panels (ISO 1514:2016) with a thickness of 30 µm. Results were shown in Table 2.

Table 2. Effect of phosphoric acid content on mechanical properties of PVB coating.

Samples	Part A/ Part B (Wt%)		Mechanical properties of coating			
	Part A	Part B	Adhesion (Points)	Flexural strength (mm)	Impact resistance (Kg.cm)	Relative hardness
M1	100	10	3	3	160	0.31
M2	100	15	2	2	180	0.45
M3	100	20	1	2	200	0.53
M4	100	25	1	2	200	0.59
M5	100	30	2	4	180	0.61

Table 2 showed that with different percentages of Part B (or phosphoric acid content), different values of coating's adhesion, flexural strength, impact resistance, and relative hardness gained. Results also showed that Part B increased from 10-25 wt%, mechanical properties changed strongly except flexural strength. It can be explained that PVB coating was formed by curing the OH group of PVB and OH group of phosphoric acid (Saad, Najat & Adnan, 2010). More Part B or more phosphoric acid meant more stereo-linkages occurred and adhesion, impact resistance, and relative hardness of coating would be improved. When content of Part B reached 30 wt%, three-dimensional network increases while adhesion, flexural strength, impact resistance, relative hardness of coating decreased because coating was harder and more brittle (Olagoke & Kolapo, 2015). Results also showed that M4 expresses the best properties of all, so this was chosen for further research.

3.2 Effect of nanosilica content to adhesion, flexural strength and relative hardness of coating

For Investigating effect of nanosilica content on adhesion, flexural strength and relative hardness of PVB coating, samples were prepared with M4 of Table 2 and nanosilica content of 0.5; 0.8; 1.2 and 1.5 wt%. Samples were named M6, M7, M8 and M9. Samples were covered on standard panels with a thickness of 30 µm. Results presented in Table 3.

Table 3. Effect of nanosilica content on adhesion, flexural strength and relative hardness of coating.

Sample	Adhesion (Points)	Flexural strength (mm)	Relative hardness
M4	1	2	0.59
M6	1	2	0.61
M7	1	2	0.62
M8	1	2	0.64
M9	3	4	0.65

Table 3 showed that nanosilica content increased from 0.5- 1.2 wt% besides, relative hardness increased, while adhesion and flexural strength were the best. However, when nanosilica content reached 1.5 wt%, hardness of coating increased slightly however, adhesion and flexural strength of coating were higher. It meant that the coating was more rigid or brittle and lost its adhesion. It can be explained that nanosilica particles had high surface energy so they tended to agglomerate into larger particles to release surface energy. In this case, when content of nanosilica in paint was high enough they would be agglomerated together and adhesion beside flexural strength of coating would be decreased (Guiyu et al., 2019; Pritom, Irthasa, Vinoy, Praveen & Giridhar, 2018).

3.3 Infrared spectroscopy (FT-IR) analysis

To investigate the appearance of nanosilica in PVB coating, infrared spectroscopy (IR) of PVB coating with and without nanosilica were conducted by Fourier FTIR-8700 series transformers. Results presented in Table 4 and Figures 1a, 1b.

Table 4. Selected measured IR bands of coating.

No.	Typical spectrum	Wavenumbers (cm^{-1})
1	νOH	3387.85
2	νCH (Aliphatic hydrogens)	2955.89
3		2912.10
4		2869.49
5	νC=C (alkene)	1646.27
6	ν_aC-O-C (asymmetry)	1100.13
7	ν_a C-O-C (symmetry)	1049.04
8	νSi-OH	936.27
9	νSi-O-C	768.15

Figure 1a shows that (Emily, 2017) peak 3387.85 cm-1 of OH group in PVA (raw material for making PVB), peaks 2955.89, 2912.10, 2869.49 as CH group of aliphatic hydrogens, 1646.27 as C=C of alkene, 1378.51 of methyl group, 1239.68 of acetates, 1100.13, 1049.04 as -C-O-C (Symmetry) of second alcohol, 994.80 as =C-C (Bending) of trans RCH=CHR, 807.90 as CH out of plane bending. There had some new peaks on figure 1b, in which, peak 936.27 cm-1 represented for vibration of Si-OH bond, and peak 768.15 is typical for the vibration of the Si-O-C bond, which proved that there had nanosilica particles in FT-IR spectrum captured sample.

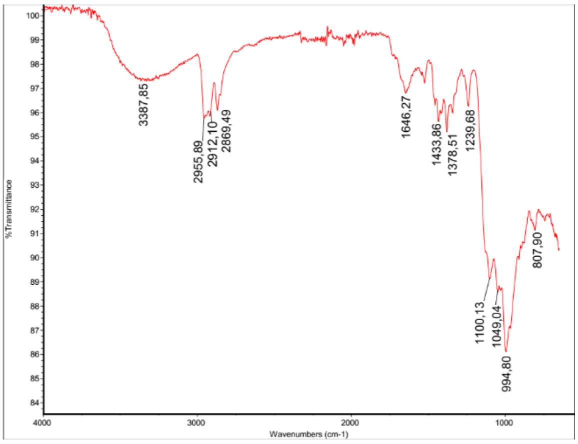

Figure 1a. IR of PVB coating.

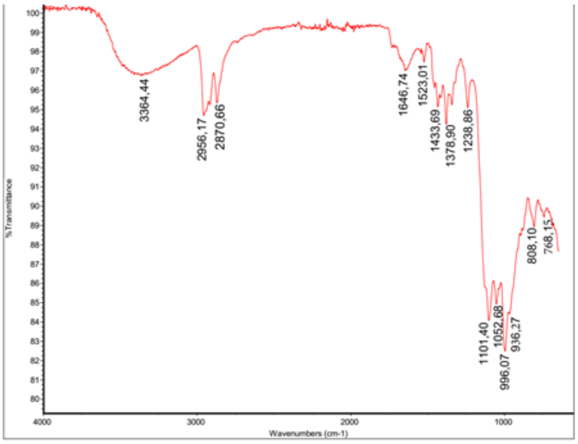

Figure 1b. IR of PVB coating with nanosilica.

3.4 Salt mist stability of PVB coating with and without nanosilica

To investigate the effect of salt mist on protection of PVB coating with and without nanosilica, samples M4 and M8 as mentioned above were conducted. Coatings were tested in a salt mist chamber with 5% NaCl for 04 cycles. Optical photographs on the surface of coatings were examined by cross-cut test (cross square on the surface of coating was scratched, cleaned carefully) before and after salt mist cyclic testing and SEM also was taken with magnification of 5,000 times to observe surfaces of coatings before and after testing. Results observed in Figures 2a, 2b, 2c, 2d and Figure 3.

Figures 2a, 2b, 2c, 2d showed that no obvious exfoliation phenomenon was observed in coatings after testing, which indicated that coating had a strong adhesion and was tightly bonded with steel substrate. Meanwhile, Figure 3 showed that after 04 cycles of salt mist testing of coatings, rust spots, PVB coating sample had larger blistering, PVB with nanosilica coating sample had some smaller spots blistering. They indicated that the steel surface under coating had been corroded and degraded adhesion. This meant that PVB coating with nanosilica could protect substrates better than PVB coating without nanosilica. This can be explained that good adhesion came from the role of nanosilica. On the surface of nanosilica, there were Si-OH groups which created physical bonding to substrate. The strong adhesion guaranteed the long-term protection of PVB with nanosilica coating. Results also indicated that salt mist testing happened electrochemically so SEM images could not clearly express the differences between samples (Hideki & Yuya, 2021; Yinze et al., 2017).

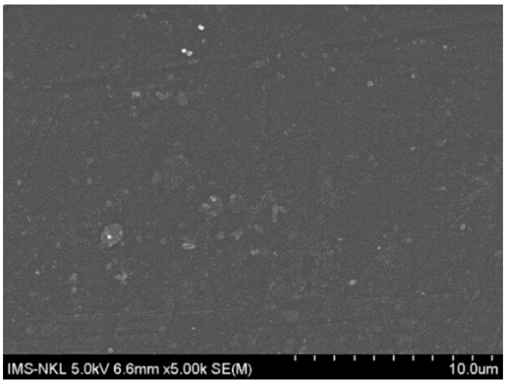

Figure 2a. SEM of M4 before salt mist testing.

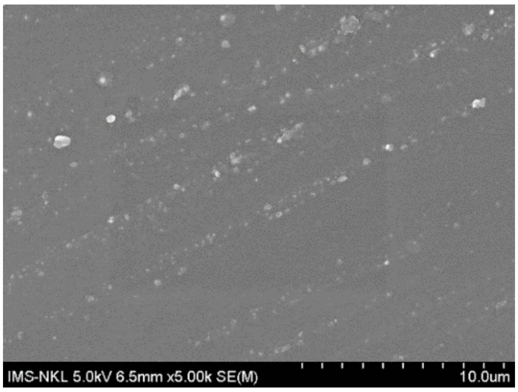

Figure 2b. SEM of M4 after salt mist testing.

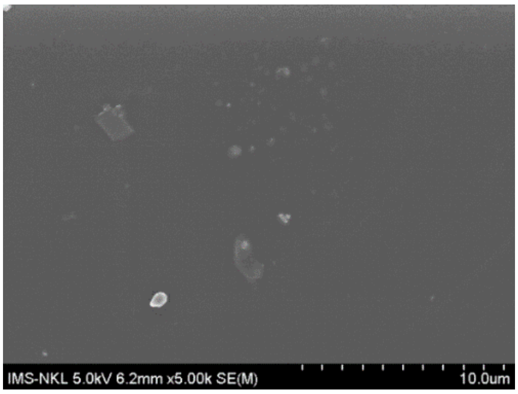

Figure 2c. SEM of M8 before salt mist testing.

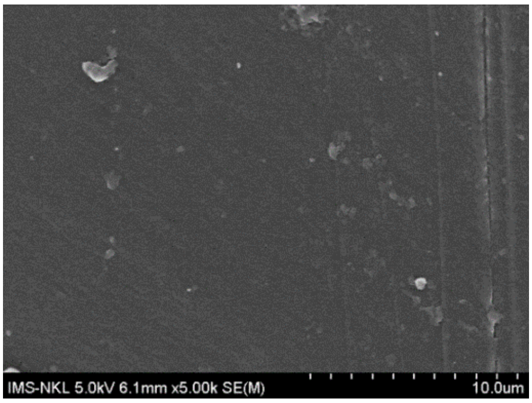

Figure 2d. SEM of M8 after salt mist testing.

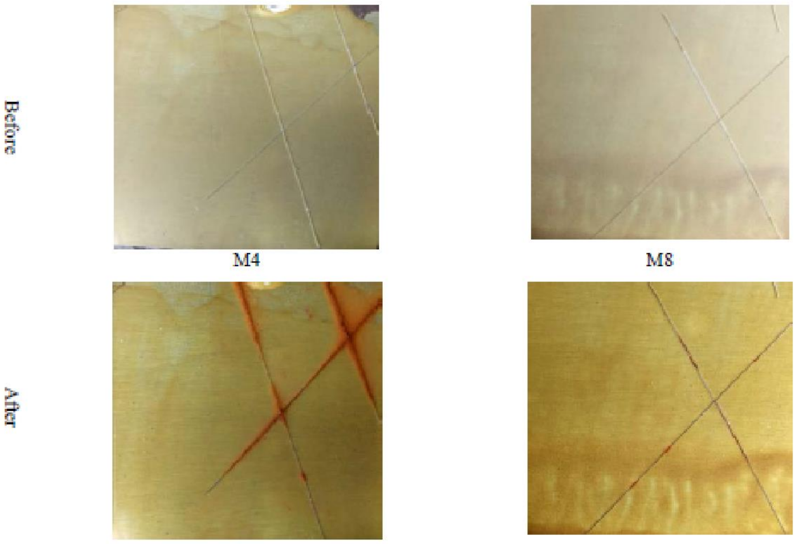

Figure 3. Optical photographs on surface of coatings examined before and after salt mist testing.

3.5 Effect of nanosilica content on thermal oxidation resistance of PVB coating

To study the effect of nanosilica content on thermal oxidation resistance of PVB coating, Thermogravimetric analysis (TGA) was done with samples M4 (PVB coating) and M8 (PVB with nanosilica coating). Table 5 and Figures 4a, 4b presented the results.

Table 5 and Figures 4a, 4b showed that the slope of TG curves of different samples were not the same. At different temperatures, decomposition of samples was different, too. At a temperature of under 200 ºC: Decomposition occurred with low molecular substances and residual solvents as well. From room temperature to 300 °C: Decomposition happened with residual functional groups in polymer branches, low molecular substances, (Thanh 2020; Thanh 2022b). For the total decomposition volume from room temperature to 350 °C, aged M4 had the highest decomposition of 45.08 %. M8 had the lowest decomposition of 42.18 %. This can be explained that nanosilica had prevented chemical bonds of polymer from breaking that led to reduce slits in material structure, hence, oxygen permeation in material would be reduced and thermal oxidation resistance of material increased (M. Malaki et al., 2018; Olagoke, & Kolapo, 2015). Up to 500 °C and above, results also showed that PVB coating has ash content of 38.78 % and in the presence of nanosilica, ash content of coating was higher, up to 43.39 %. It can be explained that, in conditions of high temperature with presence of oxygen, polymer chains were cut and oxidation of organic substances. At that time, oxygen promoted formation of free radicals and polymers would be degraded deeply, forming lower molecular compounds containing oxygen. For PVB coating with nanosilica, nanosilica particles prevented penetration of heat and oxygen into structure of PVB, in addition, thermal decomposition of nanosilica would coke to form a stable structure like ceramic Thus, nanosilica had improved thermal oxidation resistance of PVB coating (Thanh, 2022a; De, Feng, Xu, Zheng & Xiao, 2017).

Table 5. Effect of nanosilica content on thermal oxidation resistance of PVB coating.

Samples	Weight loss (%)		
	300 °C	350 °C	500 °C
M4	33.96	45.08	61.22
M8	33.07	42.18	56.61

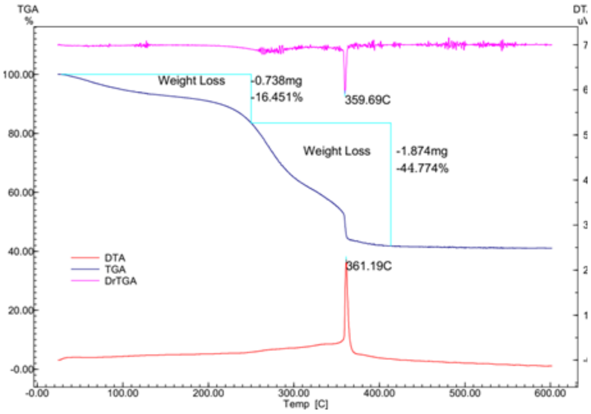

Figure 4a. TGA of M4.

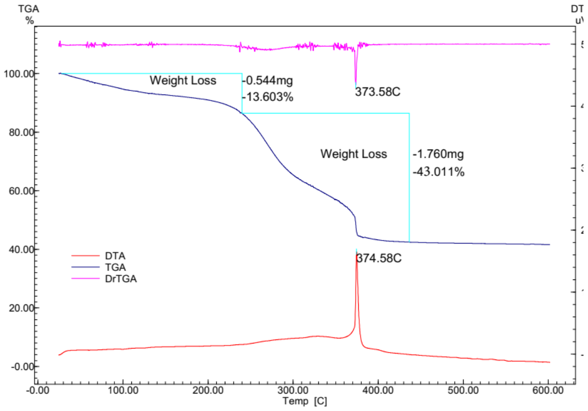

Figure 4b. TGA of M8.

4. Conclusions

- Nanosilica content increased from 0.5- 1.2 wt%, adhesion and flexural strength of PVB coating were the best, relative hardness increased from 0.59 to 0.64. nanosilica content of 1.2 wt% gave the best mechanical properties of PVB coating.

- Nanosilica improves anti-corrosion and protection of PVB coating from salt mist cyclic. PVB coating with 1.2 wt% nanosilica could protect substrate better than PVB without nanosilica.

- Nanosilica enhances thermal oxidation resistance of PVB coating. Thermal oxidation resistance of PVB coating with nanosilica is higher than that of PVB coating and ash of PVB coating is 38.78 % but of PVB coating with nanosilica is 43.39 %.

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