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Enhancing properties of environmentally friendly alkyd coating with nanosilica

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Abstract - In this article, environmentally friendly alkyd coatings with different nanosilica content (0-2.0 weight percent (wt%) were prepared for improving some properties as mechanical properties, corrosion protection, thermal resistance, etc. Nanosilica in coating was characterized by FT-IR. Effects of nanosilica on mechanical properties of environmentally friendly alkyd coatings with and without nanosilica such as adhesion, flexural strength and relative hardness and thermal stability were investigated. Coatings with and without nanosilica was also investigated with salt mist testing. Nanosilica with content of 1.5 wt% significantly improved mechanical properties, corrosion resistance, thermal oxidation resistance of environmentally friendly alkyd coatings.

Keywords: Corrosion protection, nanosilica, environmentally friendly alkyd coating, paint, polymer.

1. Introduction

Improving mechanical properties of polymers with additives have been studied for long time (Samad *et al.*, 2018; Talbert, 2007; Cheumani *et al.*, 2021; Zhu *et al.*, 2018; Zhu *et al.*, 2019). Wen *et al.* (2016) investigated polyurethane composite coating with graphene oxide and IP-GO (made by modified graphene oxide (GO) with isophorone diisocyanate (IPDI), in comparison to GO, IP-GO had improved its dispersion and compatibility in water polyurethane matrix. Results also showed that composite materials with 0.3 wt% of IP-GO had the lowest water absorption and the highest mechanical properties. With GO and IP-GO, anticorrosion efficiency of composite coating had been significantly enhanced. Chen *et al.*, (2021) used graphene-based hybrid in coatings and have got good results in anti-corrosion application because of paints' high strength and impermeability. Research showed that GO sheets were functionalized with tetraethoxysilane (TEOS) by a sol-gel method first and then added into resin. Functionalized graphene oxide (FGO) sheets with active-Si-OH groups had been increased surface wrinkles and decreased layers. Si-OH groups transformed FGO into tubular structure. FGO sheets made a better dispersion and interfacial interaction. Coatings were formed with high cross-linking density, toughness, flexibility,etc. Malaki *et al.*, (2018) used fumed and precipitated nano-silica to reinforce acrylic-based polyurethane polymer composites. It showed that nanosilica considerably enhanced tribological and mechanical properties of coatings. It also indicated that precipitated nanosilica clearcoat was hard enough, tough, and very resistant against weather, etc. Depending on the applications, some kinds of additives such as CeO_2, TiO_2, carbon black, nanosilica, etc. have been added to improve mechanical properties or anticorrosion, etc. (Han *et al.*, 2018; Mansourabad *et al.*, 2020; Gao *et al.*, 2021; Pourhashem *et al.*, 2017; Kahrizsangi *et al.*, 2015).

Environmentally friendly paints have been studied by using lignin, polysaccharides, shellac, wool fibers, etc. so as to reduce volatile components but hardly any papers mentioned about using nanosilica as an additive for enhancing mechanical properties those kind of paints (Pascual & Rahdar, 2021; Mikkonen *et al.*, 2019; Kumar & Baghel, 2019; Porfyris *et al.*, 2021; Neši´c *et al.*, 2020; Thanh, 2022a).

And in my last paper, the author had studied on manufacturing environmentally friendly alkyd paint (EFAP) from alkyd and polysaccharide (Thanh, 2022a). Through using polysaccharide to make "Emulsion Intermediate" before adding to alkyd paint and gained environmentally friendly alkyd paint with less volatile organic compounds (about 20% of solvents less). Results showed that mechanical properties (impact resistance, flexural strength, adhesion) of friendly alkyd coating were the same as alkyd ones. Besides that thermal stability, UV-thermo-humidity complex stability, thermal shocking at temperatures of +50 ^{o}C and-50 ^{o}C of friendly alkyd coating and alkyd coating were also investigated so as to express that environmentally friendly alkyd paint has less volatile organic compounds, with a smaller amount of toxic solvents, while its properties were comparable to those of alkyd paint and to confirm that it can be replaced alkyd paint for indoor and outdoor purposes. Current paper presents effect of nanosilica on mechanical properties, thermal oxidation stability, salt mist stability of environmentally friendly alkyd so as to prove that properties of coating had been enhanced with nanosilica.

2. Materials and methods

2.1. Chemicals

- Alkyd resin, QA 7812 (Taiwan).

- Polysaccharide resin, LPR 76 is supplied by Lorama Group Inc (Canada).

- Xylene, Dioctyl phthalate (DOP), bentonite, octoate cobalt, carbon black (N330): Industrial products (China).

- Kerosine is supplied by Petrolimex (Vietnam).

- TiO_2 (Rutile R-996): is a product of Sichuan Lomon Corporation (China).

- Nanosilica, Sigma-Aldrich: Fine powder, Purity: 99.8%, Average size: 12nm, Specific surface area: 175-225 m^2/g (according to BET method).

2.2. Sample preparation (Thanh, 2022b)

2.2.1. Emulsion Intermediate preparation

Table 1. Composition of Emulsion Intermediate (EI)

No.	Components	Weight percent (wt%)
1	Alkyd resin	18
2	Polysaccharide resin	12
3	Kerosine	12.5
4	Xylene	7
5	Water	50.5

- The composition of preparing raw materials was as in Table 1.

- Stirring alkyd resin of 1,200-1,500 rpm, adding kerosine and xylene gradually.

- Speeding up to 3,000 rpm, adding LPR 76 and stirring in 20 minutes.

- Adding water and stirring at 3,000 rpm in about 30 minutes until getting a homogeneous emulsion intermediate solution.

3.2.2. Paint preparation

Table 2. Composition of paint

No.	Components	Weight percent (wt%)
1	Alkyd resin	14.5-16.5
2	Kerosine	10
3	Xylene	12
4	TiO_2	16
5	Bentonite	0.5

Table 2. Composition of paint (cont.)

No.	Components	Weight percent (wt%)
6	Octoate cobalt	1
7	N330	3
8	Nanosilica	2.0
9	EI solution	41

- Raw materials were prepared as Table 2.

- Primary grinding: Adding 90% of xylene and all others to stir at 20-40 rpm for an hour. Keeping mixture for 24 hours.

- Fine grinding: Grinding at speed of 1,300-1,500 rpm, until paint fineness £ 30 µm.

- Preparation: Adding the rest xylene, stirring for 01 hour. Getting 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.

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) ^{o}C and humidity of (50±5)% for 7 days before testing. The thickness of dried coatings was (30±3) µm (measured with Minitest 600 Erichen digital meter).

Samples for FTIR analysis were prepared on glass substrates with 15 µm of dried thickness These coatings were dried at temperature of (25±2) ^{o}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) ^{o}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.

- Drying time of coating was determined according to ISO 9117-6:2012.

- Fineness of paints was determined by ISO 1524: 2020.

- Infrared spectroscopy (FT-IR) 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 ^{o}C/minute from room temperature to 600 ^{o}C.

- Morphology of coating film was observed by FESEM Hitachi S4800 machine with a magnification of 2,000 times and voltage of 5 KV.

-Salt mist, cyclic testing (5% NaCl) was determined by IEC 60068-2-52: 2017 with 4 cycles, each cycle included 2 hours spraying (at (35 ± 2) ^{o}C), keeping humidity condition for 7 days at (40± 2) ^{o}C, relative humidity of (93 ± 2)%.

3. Results and discussion

3.1 Effect of nanosilica content on mechanical properties of coating

Investigating effect of nanosilica content on adhesion, flexural strength and relative hardness of environmentally friendly alkyd coating, samples were prepared with composition as on Table 2 with nanosilica content of 0; 0.5; 1.0; 1.5; 2.0 wt%. Samples were named M0, M1, M2, M3, M4. Samples were covered on standard panels and kept at room temperature for 7 days before testing. Results were shown in (Table 3).

Table 3. Effect of nanosilica content on mechanical properties of coating

Samples	Adhesion (Points)	Flexural strength (mm)	Relative hardness
M0	1	2	0.39
M1	1	2	0.43
M2	1	2	0.46
M3	1	2	0.50
M4	2	4	0.52

Table 3 showed that nanosilica content increases to 1.5 wt%, relative hardness increases, meanwhile adhesion and flexural strength were the best. However, when nanosilica content was 2.0 wt%, hardness increases slightly but adhesion and flexural strength coating decreased sharply. This can be explained that nanosilica particles have much higher hardness than environmentally friendly alkyd matrix, so the more nanosilica content the harder relative hardness of coating would be. However, when nanosilica concentration continuously increased to 2.0 wt%, those nano particles tended to agglomerate together to make larger particles so as to release surface energy and adhesion together with flexural strength would be decreased (Saranya *et al.*, 2014; Huang *et al.*, 2017; Selim *et al.*, 2017).

3.2 Infrared spectroscopy (FT-IR) of environmentally friendly alkyd coating with and without nanosilica

To prove the appearance of nanosilica in environmentally friendly alkyd coating, infrared spectroscopy (IR) of coating with and without nanosilica were carried out with Fourier FTIR-8700 series transformers. Results were shown in (Figures 1a, 1b).

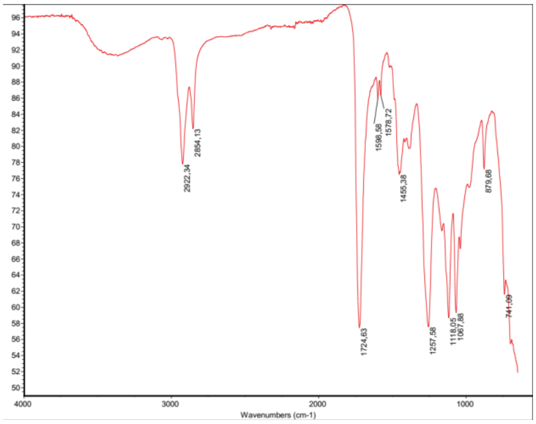

Figure 1a. IR of EFAP coating

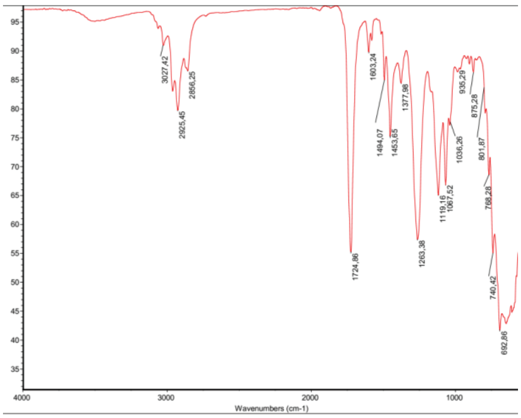

Figure 1b. IR of EFAP coating with nanosilica

Table 4. Selected measured IR bands of coating

No.	Typical spectrum	Wavenumbers (cm-1)
1	νCH (Aliphatic hydrogens)	3027
2		2925
3		2922
4		2856
5		2854
6	νC=O vibration	1724
7	νC-OH	1225
8	νaC-O-C (symmetry)	1067
9	νSi-OH	935
10	νCH (bending)	879
11		874
12	νSi-O-Si (stretching)	768

Figures 1a and 1b showed that (Moore, 2014). peaks 3027 cm-1, 2925 cm-1, 2922 cm-1, 2856 cm-1 and 2854 cm-1 as CH group of aliphatic hydrogens. Peak characteristic of C=O vibration at 1724 cm-1. The vibrations of C-OH and C-O group can be shown at 1263 cm-1, 1257 cm-1, and of C-O group 1067 cm-1 respectively. There had some new peaks on figure 1b, in which, peak 935 cm-1 represented for vibration of Si-OH bond, and peak 768 was typical for the stretching vibration Si-O-Si bond (Thanh, 2022c; Huang *et al.*, 2017), which proved in the captured sample FT-IR spectrum with nanosilica.

3.3 Salt mist resistance of environmentally friendly alkyd coating with and without nanosilica

To investigate effect of salt mist on protection of coating with and without nanosilica, samples M0 and M3 as mentioned above were done. Samples were covered on standard panels. After making, samples were kept at room temperature for 7 days before testing 4 cycles in salt mist chamber with 5% NaCl. To observe surfaces of coatings before and after testing, optical photographs on the surface of coatings examined by cross-cut test (cross-cut surface of coating was scratched, cleaned carefully) before and after salt mist cyclic testing and SEM also was taken with magnification of 2,000 times. Results were shown in (Figures 2a, 2b, 2c, 2d and Figure 3).

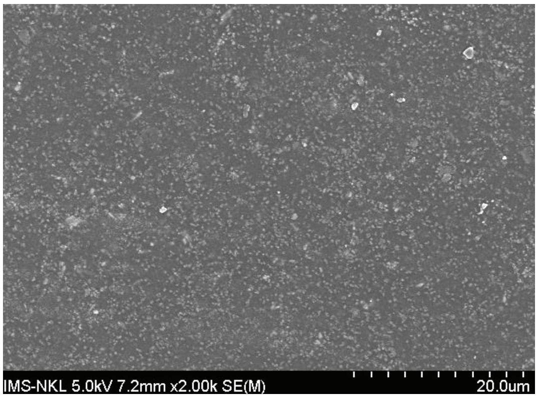

Figure 2a. SEM of M0 before salt mist testing

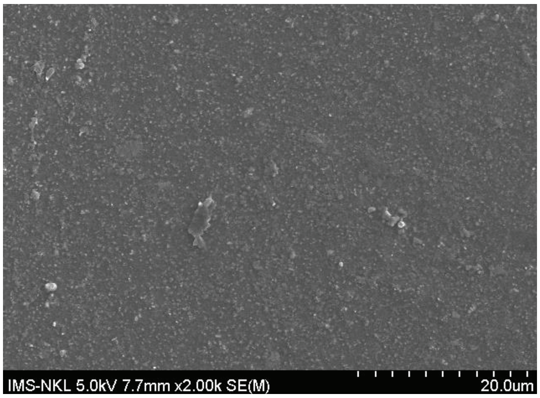

Figure 2b. SEM of M0 after salt mist testing

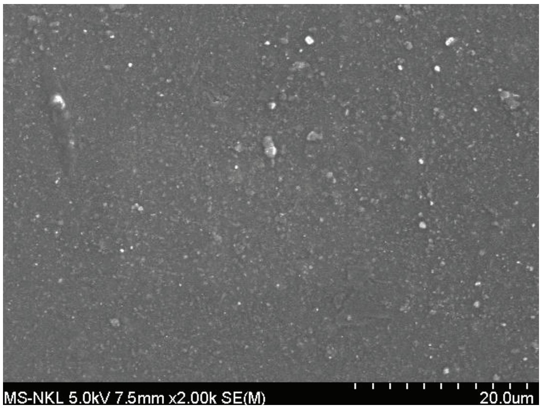

Figure 2c. SEM of M3 before salt mist testing

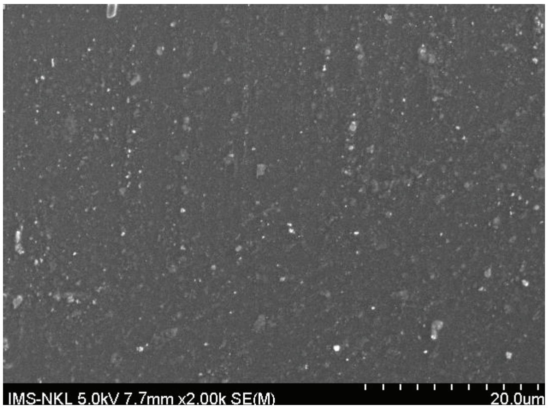

Figure 2d. SEM of M3 after salt mist testing

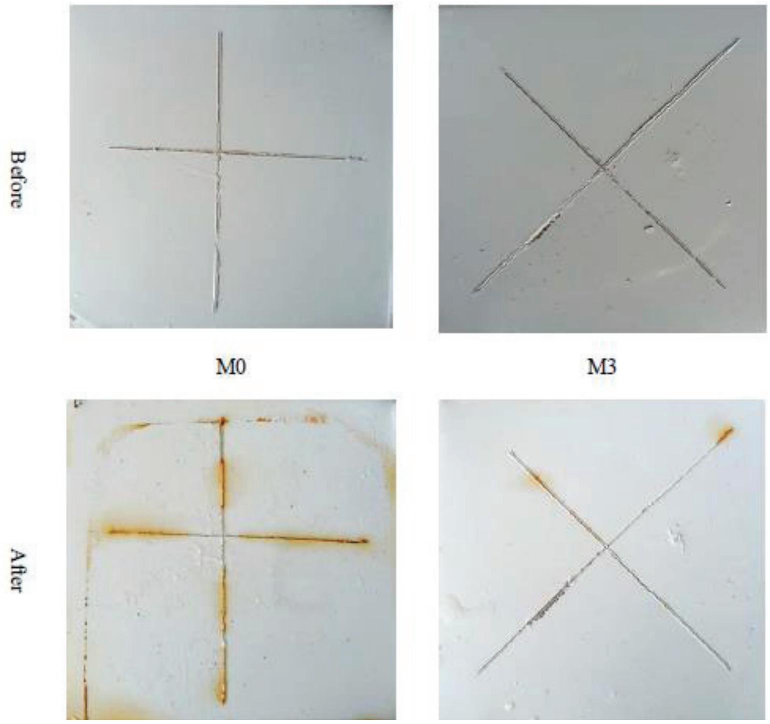

Figure 3. Optical photographs on surface of coatings examined before and after salt mist testing

Figures 2a, 2b, 2c, 2d showed that, there was no change observed in coatings after salt mist testing, it meant that coating had a good adhesion and bonded tightly with substrates. And in figure 3, after 04 cycles of salt mist testing of coatings appeared rust spots, coating sample without nanosilica had larger blistering, coating with nanosilica had smaller spots blistering. It indicated that steel surface had been corroded and reduced its adhesion to coating. In comparison with initial coating in absence of nanosilica, tested sample surface (M0) was rougher, meanwhile, tested coating surface of coating with nanosilca (M3) was smoother. It meant that environmentally friendly alkyd coating with nanosilica could protect steel substrate better than coating without nanosilica. Nanosilica had played an very important role in adhesion between coatings and steel substrates. Because on surface of nanosilica, there are C-OH groups (peak 1225 cm-1) and Si-OH (peak 935 cm-1) which would create well physical bonding of coating to steel substrate. This bonding guarantees the long-term protection of environmentally friendly alkyd coating with steel substrate (Galpaya *et al.*, 2014; Haghdadeh *et al.*, 2018; Si *et al.*, 2013).

3.4 Effect of nanosilica content on thermal resistance of environmentally friendly alkyd coating

To study effect of nanosilica content on thermal resistance of environmentally friendly alkyd coating, Thermogravimetric analysis (TGA) was done with samples M0 and M3 as mentioned above. Results were shown in (Table 5 and Figures 4a, 4b).

Table 5. Effect of nanosilica on thermal resistance of environmentally friendly alkyd coating

Samples	Weight loss (%)		
	300 ^{o}C	350 ^{o}C	500 ^{o}C
M0	13.58	44.39	64.81
M3	9.86	37.86	59.99

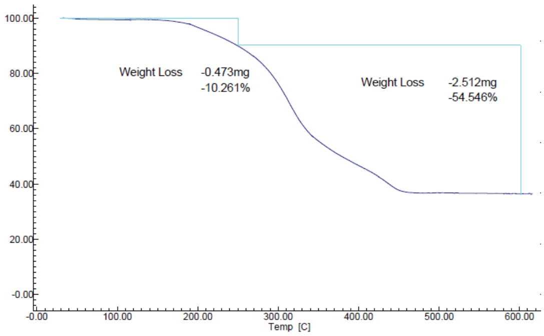

Figure 4a. TGA of M0

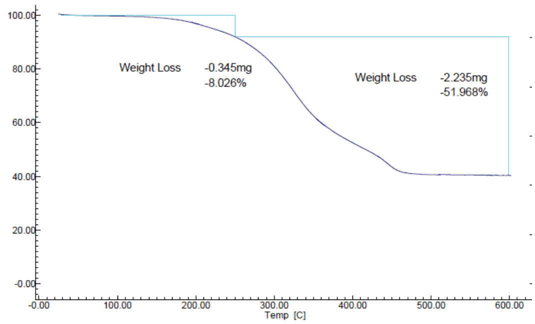

Figure 4b. TGA of M3

Table 5 and Figures 4a, 4b showed that the slops of TG curves of 02 different samples were not the same. At different temperatures, decomposition of samples were different, too. Under 200 ^{o}C: Decomposition mainly happened to low molecular substances as well as residual solvents. To 300 ^{o}C: Decomposition occurred with residual functional groups in polymer branches, low molecular substances, etc (Thanh, 2022c; Chen, 2021). Results also showed that, environmentally friendly alkyd coating had ash content of 35.19% and with nanosilica, ash content of coating was higher, up to 40.01%. It can be explained that under condition of high temperature polymers would be degraded sharply, leading to form lower molecular compounds. For environmentally friendly alkyd coating with nanosilica, these particles prevented penetration of heat into structure of alkyd chains, in addition, at high temperature, thermal decomposition of nanosilica would be coked to form ceramic. Thus, nanosilica had improved thermal oxidation resistance of environmentally friendly alkyd coating (Necolau & Pandele, 2020; Hou *et al.*, 2020).

4. Conclusions

- Nanosilica content increases from 0-1.5 wt%, adhesion and flexural strength of environmentally friendly alkyd coating increases, respectively, relative hardness increases from 0.39 to 0.50. Nanosilica content of 1.5 wt% gives the best mechanical properties of coating.

- Nanosilica improves anti-corrosion protection of environmentally friendly alkyd coating from salt mist cyclic. Coating with 1.5 wt% nanosilica could protect steel substrate better than coating without nanosilica.

- Nanosilica improves thermal resistance of environmentally friendly alkyd coating. Thermal resistance of coating with nanosilica is higher than that of coating without nanosilica. The weight loss of environmentally friendly alkyd coating is 64.81% but of coating with nanosilica is 59.99%, respectively.

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