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Aging of Environmentally Friendly Alkyd Coating Containing Tinuvin 292 under Effect of UV Radiation

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Abstract. This study presents durability of environmentally friendly alkyd coating containing Tinuvin 292 (a liquid hindered amine light stabilizer) under UV-thermo-humidity condition. Coatings were accelerated under UV-thermo-humidity complex for 100 cycles. FT-IR, TGA and SEM were used to value the changes of before and after accelerated weathering tested coatings. Results showed that gloss loss, adhesion, flexural strength, impact resistance, relative hardness of tested coating were much improved with 1.5 weight percent (wt.%) of Tinuvin 292. FT-IR spectrums of initial and aged coatings without Tinuvin 292 illustrated the significant changes on intensity of CH_2 and C=O (ester) groups. Meanwhile, coating with Tinuvin 292 exhibited that intensity of CH_2 and ester groups had been changed slightly. SEM images indicated that surface morphology of samples changed differently depending on the presence Tinuvin 292. After aging process, surface of aged coating without Tinuvin 292 became worse than that of coating with Tinuvin 292. TGA also showed that 1.5 wt.% of Tinuvin 292 had improved thermo oxidation stability of environmentally friendly coating.

Keywords: Aging coating, environmentally friendly alkyd paint coating, polymer, Tinuvin 292, UV degradation

1 Introduction

Aging or degradation of paint or varnish coatings under weather factors such as UV radiation, humidity, oxygen, high temperature, etc. leads to the blistering, chalking, losing adhesion [1-3]. To reduce the aging of coatings exposed to UV radiation, many kinds of UV additives have been added in coatings [3-5]. Hu et al. [6] investigated on aging behavior of acrylic polyurethane varnish coating in a fluorescent UV/condensation weathering device, a xenon lamp exposure and weathering equipment with different time. Results showed that degradation rate in UV condition was higher than in Xenon testing condition. Crescenzo et al. [7] studied on photochemical degradation of some binders and pigments in 800 h, results showed that acrylic or styrene-acrylic were more stable than vinyl. Kahrizsangi et al. [8] showed that there was no microcracks on epoxy coating with 2.5 wt.% of carbon black after 1000 h of UV exposure. In addition, this coating generated much less carbonyl group (from chain scission) than neat epoxy coating. Some other authors used graphene oxide, zinc oxide (ZnO), titanium oxide (TiO_2) to prevent coatings from degrading. The fact that, carbon black, zinc oxide or titanium oxide particles are intend to agglomeration together, it is difficult for them to be well dispersed in coatings [9-12].

Recently, environmentally friendly alkyd paints have been studied by combining or modifying with chitosan, lignin, starch, shellac,

polyhydroxyalkanoates, wool fibers, vegetable oils, etc. to reduce volatile components. In spite of having been developed for a long time, hardly any papers mentioned on aging of environmentally friendly alkyd coatings [13-17].

In other paper, author had studied on manufacturing environmentally friendly from alkyd and polysaccharide [18]. Results showed that with reduction of about 20 % of solvents, environmentally friendly alkyd paint could remain its properties the same as common alkyd paint.

Tinuvin 292 is a liquid hindered amine light stabilizer. It is an almost pure mixture of two active ingredients of Bis (1, 2, 2, 6, 6-pentamethyl-4-piperidyl) sebacate and Methyl 1, 2, 2, 6, 6-pentamethyl-4-piperidyl sebacate. The efficiency of Tinuvin 292 provides significantly extended lifetime to coatings by minimizing paint defects such as cracking and loss of gloss [19]. Because Tinuvin 292 is a liquid so it can be easily distributed in coatings and overcome disadvantages of above anti-UV additives. This paper presents effect of Tinuvin 292 content on degradation of environmentally friendly alkyd coating based on alkyd and polysaccharide under UV-thermo-humidity condition. Surface's morphology, gloss loss, mechanical properties, thermal oxidation resistance of coatings were investigated. In addition, chemical changes of functional groups were identified by FT-IR. Environmentally friendly alkyd paint based on alkyd and polysaccharide is a new kind of paint. The published papers on its aging is still limited. Therefore, in this article, investigation on the effect of Tinuvin 292 light stabilizer on durability of the coating under UV-thermo-humidity conditions is a novelty work.

2 Materials and methods

2.1 Chemicals

Binders: Alkyd resin, QA 7812 (Taiwan) and Polysaccharide Resin, LPR 76 were supplied by Lorama Group Inc- Canada). Pigments: TiO_2 (Rutile R-996) was supplied by Sichuan Lomon Corporation (China) and carbon black (N330) was supplied by Shanxi Lixin Chemical Company Limited (China). *Solvents:* Xylene was an industrial product (China) and Kerosine was supplied by Petrolimex (Vietnam). *Additives:* Dioctyl phthalate (DOP) was a plasticizer, bentonite was a thickener, octoate cobalt was a drying agent: Industrial products (China). Tinuvin 292 (Bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate and 1-(Methyl)-8-(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate) was supplied by Kremer Pigmente GmbH & Co. KG (Germany).

2.2 Paint preparation [18]

Emulsion Intermediate preparation

Raw materials were prepared as Table 1. Alkyd resin was stirred at 1,200- 1,500 rpm, then kerosine and xylene were added gradually. Speed was adjusted to 3,000 rpm before adding LPR 76 and continued stirring for 20 minutes. Lastly, water was added and stirred at 3,000 rpm in about 30 minutes until getting a homogeneous emulsion intermediate solution.

Table 1. Composition of Emulsion Intermediate (EI)

No.	Components	Weight percent (Wt.%)
1	Alkyd resin	17
2	Polysaccharide resin	13
3	Kerosine	10.5
4	Xylene	7
5	Water	52.5

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Paint preparation

Raw materials were prepared as in Table 2. The process included four stages, (1) Primary grinding: 90% of xylene were added with all other materials and stirred at 20- 40 rpm for an hour. The mixture was kept being conditioned for 24 hours. (2) Fine grinding: The mixture was subjected to fine grinding at a speed of 1,300-1,500 rpm to reach the paint fineness of ≤ 30 μm. (3) Preparation: The rest of xylene (another 10%) was added and stirred for an hour. (4) 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 coarse particles or dirt in this stage. Then, it was followed by the canning step for storing purposes.

Table 2. Composition of paint

No.	Components	Weight percent (Wt.%)
1	Alkyd resin	14.5-16.5
2	Kerosine	12
3	Xylene	10
4	TiO_2	17
5	Bentonite	0.5
6	Octoate cobalt	1
7	Carbon black	3
8	Tinuvin 292	0-2.0
9	EI solution	40

2.3 Sample preparation

Testing samples 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) ^oC 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).

2.4 Analysis methods

UV-thermo-humidity complex stability was performed in UV/condensation weathering chamber Atlas UVCON UC-327-2 with UVB-313 fluorescent lamps and a cycle including 8 hours of UV irradiation at 60 °C then following by 4 hours of dark water condensation at 50 °C as ASTM D4587-11. Infrared spectroscopy (FT-IR) was conducted on Fourier FTIR-8700 series converter. Morphology of coating was observed by FESEM Hitachi S4800 machine with magnification of 5,000 times and voltage of 5 KV.

Gloss of coating was determined in accordance with ISO 2813:2014 with angle of 60 degrees. Impact resistance of coating was determined in accordance with ISO 6272-1:2011, flexural strength of coating was determined in accordance with ISO1519:2011, adhesion of coating was determined in accordance with ISO 2409:2013 and relative hardness of coating was determined in accordance with ISO 1522:2006. Fineness of paints was determined in accordance with ISO 1524: 2020. Thermal oxidation resistance: Thermogravimetric analysis (TGA) was analyzed by NETZSCH TG 209F1 LIBRA in the air with a heating rate of 10 ^oC/minute from room temperature to 600 ^oC.

3 Results and discussion

3.1 Effect of anti-UV content on gloss and mechanical properties coating

To study effect of anti-UV (Tinuvin 292) content on gloss loss and mechanical properties of before and after tested coatings, samples were prepared with Tinuvin 292 content of 0; 0.5; 1.0; 1.5; 2.0 wt.% named as M0, M1, M2, M3, M4 and tested for 100 UV-thermo-humidity complex cycles. Samples were covered on standard panels (ISO 1514:2016) and kept at room

temperature for 7 days before testing. Results were shown in Table 3.

Table 3 showed that after 100 cycles of UV-thermo-humidity complex testing, the more content of Tivunin 292, the less reduction of adhesion, flexural strength, impact resistance, gloss loss of coating. Besides that, when Tinuvin 292 content increased, relative hardness had not been changed much, respectively. It can be explained that Tinuvin 292 had prevented polymer chains from breaking or cutting which led to the limitation of polymer aging by UV rays [19-21]. With Tinuvin 292, mechanical properties of environmentally friendly alkyd coating were better than those of coating without Tinuvin 292 after testing and that was also the same to gloss loss of coating. Results also showed that Tinuvin 292 with content of 1.5 wt.% and above, properties of coating did not change much after 100 UV-thermo-humidity complex cycles testing. Meanwhile, coating without Tinuvin 292 (M0), adhesion, flexural strength and relative hardness of coating became much higher, it meant that the coating was more rigid or brittle and lost its adhesion [22]. After testing, properties of M3 and M4 were the same, so M3 was chosen for further study.

Table 3. Gloss and mechanical properties of coating before and after 100 cycles testing

Gloss and mechanical properties of coating before testing					
Samples	**Gloss at 60°**	**Mechanical properties of coating**			
		Adhesion (Points)	**Flexural strength (mm)**	**Impact resistance (Kg.cm)**	**Relative hardness**
M0	75	1	2	200	0.37
M1	74	1	2	200	0.38
M2	75	1	2	200	0.37
M3	75	1	3	200	0.38
M4	75	1	3	200	0.38
Gloss and mechanical properties of coating after 100 cycles testing					
Samples	**Gloss at 60°**	**Mechanical properties of coating**			
		Adhesion (Points)	**Flexural strength (mm)**	**Impact resistance (Kg.cm)**	**Relative hardness**
M0	30	4	5	100	0.59
M1	46	3	3	160	0.48
M2	59	2	2	180	0.43
M3	69	1	2	200	0.40
M4	70	1	2	200	0.39

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3.2 Infrared spectroscopy (FT-IR) analysis

Aging of polymer material, initially, may not be observed obviously with its appearance but by chemical changes of functional groups. FT-IR spectroscopy was used to investigate chemical changes of functional groups of before and after aging process of 100 UV-thermo-humidity complex cycles coatings. M0 and M3 were used for testing. Results were shown in Figures 1a, 1b, 1c and 1d.

Figures 1a and 1b showed that [23] peak intensity of CH_2 (2922.67) decreased sharply, even peak 2852.69 in Figure 1a disappeared in Figure 1b. This can be explained that polymer molecular chain had been cut and molecular length was much shorter. At the same time, intensities of ester group peaks (1723.85 of C=O and 1256.15 of C-O) decreased and ester bond was altered to form new bonds such as ketones due to optical oxidation or groups were stretched and rocked [4, 19-21]. However, the vibration was small and low intensity, because TiO_2 worked as an UV-absorber and a photocatalyst [21, 22]. As can be seen in Figures 1c and 1d, there was a little difference between before and after-aging samples. These showed that environmentally friendly alkyd coating with Tinuvin 292, peak intensities of CH_2 (2922.50) and ester groups (1723.96 of C=O and 1253.85 of C-O) were also stretched but intensities and vibrations of these peaks reduced insignificantly in comparison between before and after testing samples. Photo-degradation of polymers may happen to chain scissions or macroradical disproportionation, leading to terminal double bonds [19, 21, 22]. For coating with Tinuvin 292, there was little difference after aging. Because macroradical disproportionation attacked polymer chains to produce C=C bonds, coating containing Tinuvin 292, macroradicals would attack the conjugated double bonds of Tinuvin 292. In other words, Tinuvin 292 absorbed UV rays and thus reducing the degradation of environmentally friendly alkyd coating [23-25].

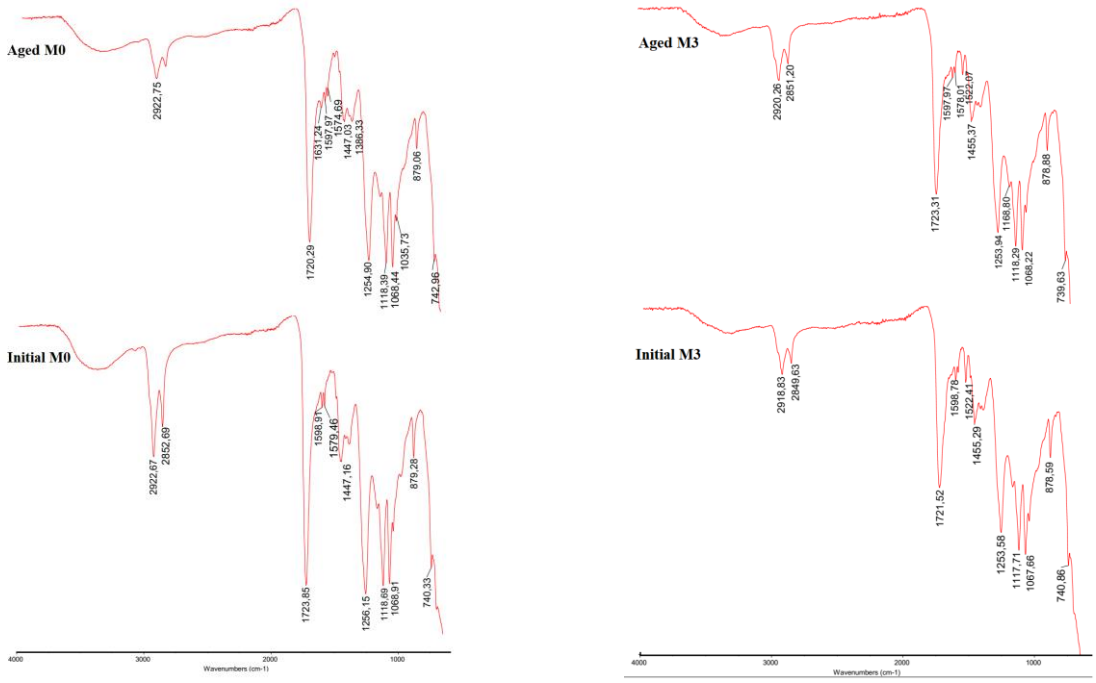
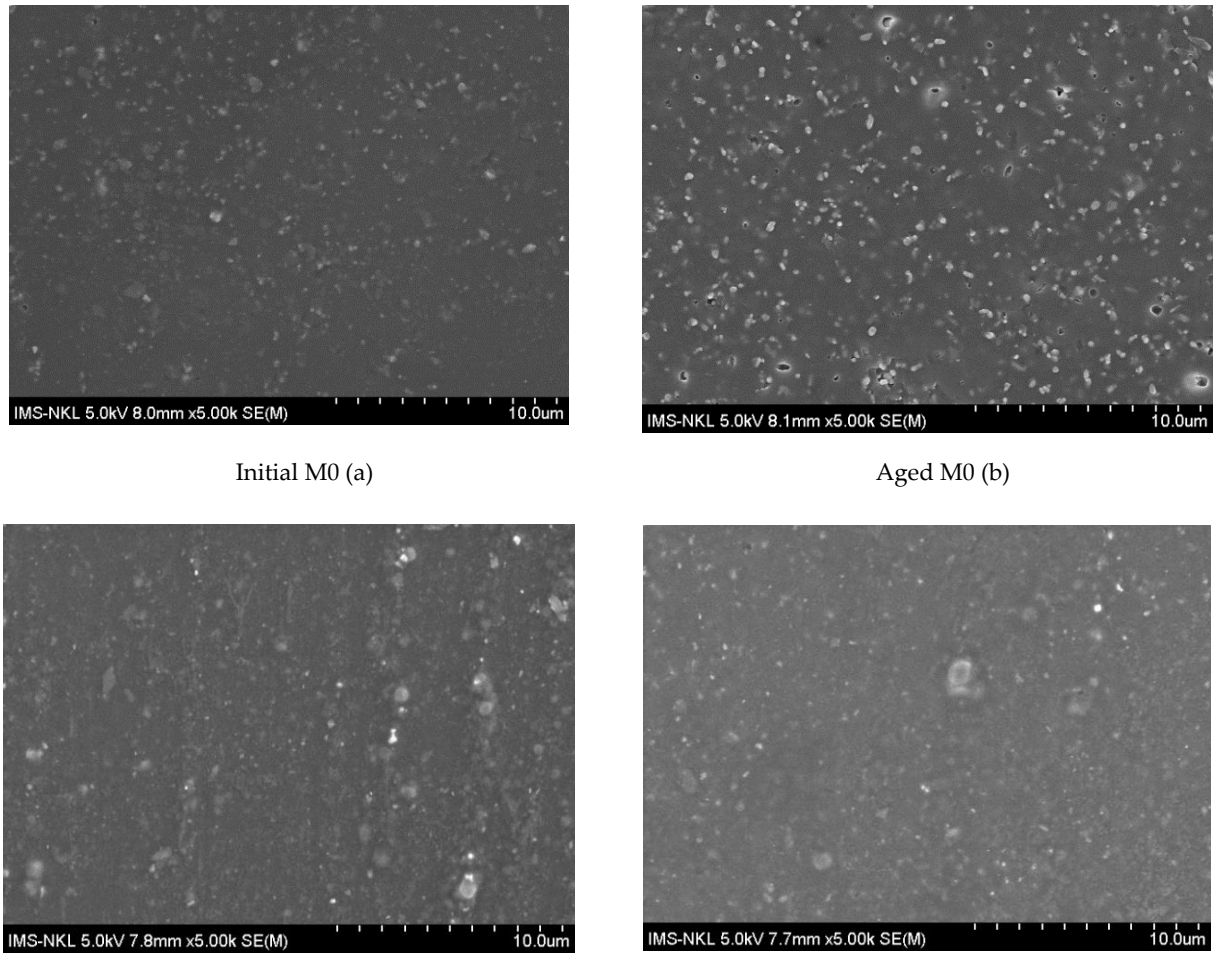


Fig. 1. IR of initial M0- aged M0 (a), initial M3- aged M3 (b)

3.3 Morphology coatings' surface

To investigate effect of UV-thermo-humidity complex cycles on surface of coatings, M0 and M3 were tested with 100 cycles. Paint was covered on standard panels (ISO 1514:2016) and kept at room temperature for 7 days before testing. Results were shown in Figure 2.

Figure 2 showed that there were no cracks, blisters or surface changes on aged M3. In comparison with initial coating surface, tested sample's surface seemed to be unchanged. For M0, in comparison with initial sample, aged sample's surface had pinholes. This meant that coating's surface was damaged. It might be taken place by oxidation process and led to the generation of micro-cavities and micro-holes at coating's surface [24-27]. Besides that, under the effect of UV-thermo-humidity complex, oxidation happened and the adhesion between components in the coating became worse so TiO_2 particles would not be enclosed by binder, and they were easily observed on the surface and micro-holes or micro-cavities were created on the surface of coating and surface's cracks became wider and deeper, as well [6, 26-28].



Initial M0 (a) Aged M0 (b)

Initial M3 (c) Aged M3 (d)

Fig. 2. SEM of initial and aging of coatings' surfaces

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3.4 Effect of Tinuvin 292 on thermal oxidation resistance of coating

Thermogravimetric analysis (TGA) was performed on M0 and M3 samples to investigate the effect of Tinuvin 292 content on the thermal oxidation resistance of before and after testing coatings. Results were shown in Table 4 and Figure 3.

Table 4 and Figure 3 showed that different samples had different curve slop. TGA curve slop of aged M0 was the highest. At different temperature, weight loss of samples was different, too. Results also showed that Tinuvin 292 had enhanced thermostability of environmentally friendly alkyd coating, remarkably [8, 21, 30]. This can be explained that at temperature of under 200 ^{o}C, decomposition occurred with low molecular substances and residual solvents as well. Decomposition volume was about 2-5 %. To about 300 ^{o}C, the decomposition happened with residual functional groups in polymer branches, low molecular substances. Aged M0 (without Tinuvin 292), polymer chains had been broken stronger than that of aged M3 and its decomposition was the strongest of all. Meanwhile, Tinuvin 292 had prevented polymer chains from breaking so aged M3 had lower decomposition [5, 19, 29]. For the total decomposition volume from room temperature to 400 ^{o}C, aged M0 had the highest decomposition of 52.17 %. M3 had the lowest decomposition of 50.14 %. This can be explained that Tinuvin 292 had prevented chemical bonds of polymer matrix from breaking that led to slit reduction in material structure. Hence, oxygen permeation in material would be reduced and thermal oxidation resistance of material increased. Up to 500 ^{o}C and above, the decomposition of samples was not different much because at that temperature, all organic components had been burnt or decomposed and inorganics of samples were the same [24, 29, 31]. Decomposition temperature and weight loss of samples were shown in Table 4.

Table 4. Decomposition temperature and weight loss.

Samples	Weight loss (%)		
	300 ^{o}C	**400 ^{o}C**	**500 ^{o}C**
Initial M0	21.72	51.10	72.01
Aged M0	26.85	52.17	72.24
Initial M3	21.46	50.14	71.81
Aged M3	21.74	51.35	72.06

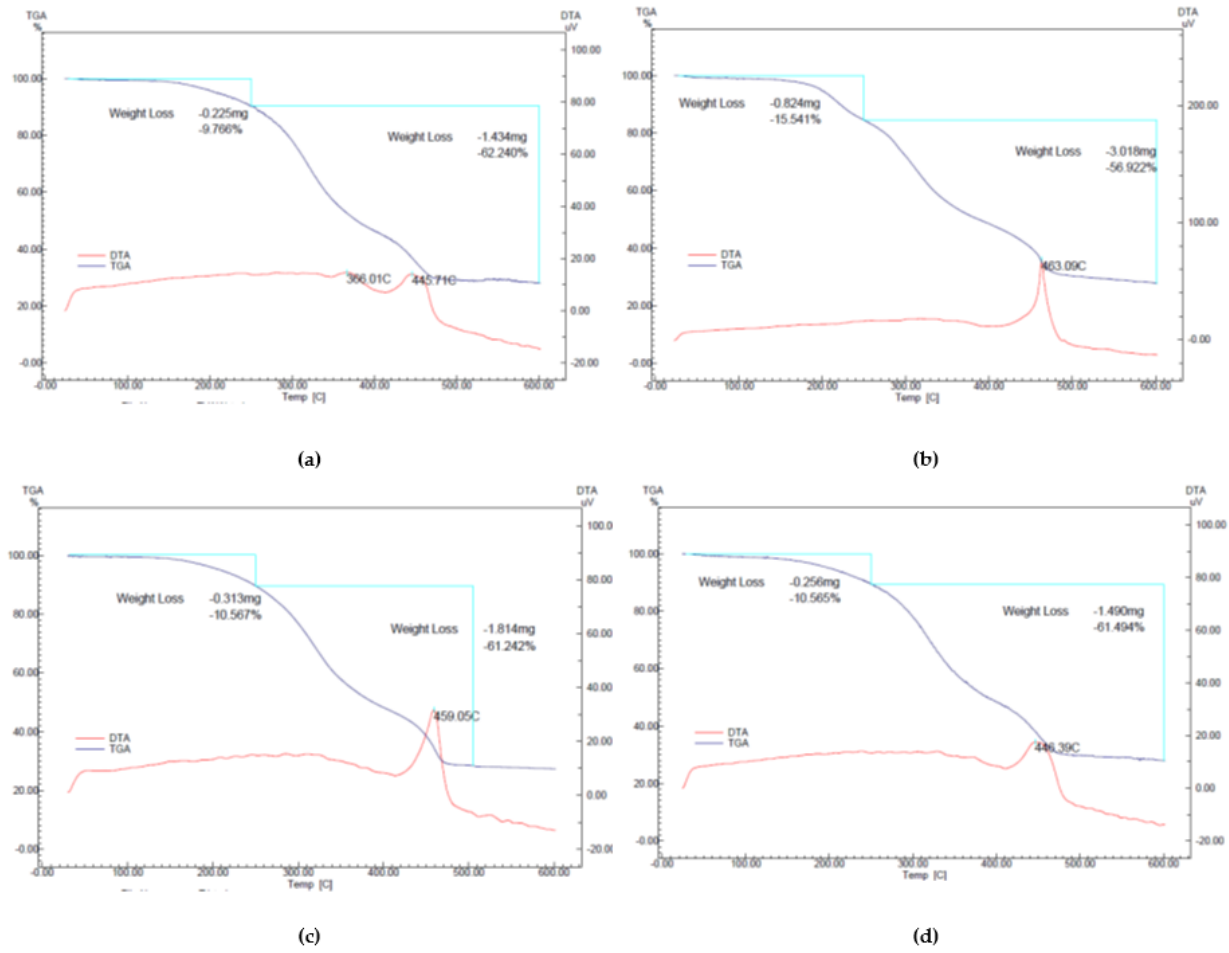

Fig. 3. TGA of initial M0 (a), aged M0 (b), initial M3 (c), aged M3 (d)

4 Conclusions

The aim of this research was to compare stability of environmentally friendly alkyd coating with and without Tinuvin 292. After 100 UV-thermo-humidity complex cycles, with Tinuvin 292 of 1.5 wt.%, coating became more stable in adhesion, flexural strength, impact resistance, relative hardness and gloss loss. Under UV irradiation, bonds of group ~CH_2 and ester groups of samples without Tinuvin 292 decreased more strongly than that of sample with Tinuvin 292. Thermal oxidation resistance of coating with 1.5 wt.% Tinuvin 292 was much higher than that of sample without Tinuvin 292.

References

1. Thanh NT. Modification of Alkyd with Epoxy and its Application for Paint Part 1: Epoxy Alkyd Ester Manufacturing and some Properties of Paint made from this Ester. VNU Journal of Science: Natural Sciences and Technology. 2020;36(1):36-44.
2. Decker C, Masson F, Schwalm R. Weathering resistance of water based UV-cured polyurethane-acrylate coatings. Polymer Degradation and Stability. 2004;83(2):309-320.
3. Kızılkonca E, Erim FB. Development of Anti-Aging and Anticorrosive Nanoceria Dispersed Alkyd Coating for Decorative and Industrial Purp. Coatings. 2019;9(10):610.
4. Queant C, Blanchet P, Landry V, Schorr D. Comparison of two encapsulation systems of UV stabilizers on the UV protection efficiency of wood

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eISSN 2615-9678

clear coats. Journal of Polymer Engineering. 2019; 39(1):94-103.

5. Cogulet A, Blanchet P, Landry V. Evaluation of the Impacts of Four Weathering Methods on Two Acrylic Paints: Showcasing Distinctions and Particularities. Coatings. 2019;9(2):121.
6. Hu J, Li X, Gao J, Zhao Q. Ageing behavior of acrylic polyurethane varnish coating in accelerated weathering environments. Progress in Organic Coatings. 2009;65(4):504-509.
7. Crescenzo MMD, Zendri E, Pons MS, Lospez LF, Marco DJY. The use of waterborne paints in contemporary murals: Comparing the stability of vinyl, acrylic and styrene-acrylic formulations to outdoor weathering conditions. Polymer Degradation and Stability. 2017;107:285-293.
8. Kahrizsangi AG, Neshati J, Shariatpanahi E, Akbarinezhad H. Improving the UV degradation resistance of epoxy coatings using modified carbon black nanoparticles. Progress in Organic Coatings. 2015;85:199-207.
9. Pourhashem S, Vaezi MR, Rashidi A, Bagherzadeh M R. Exploring corrosion protection properties of solvent based epoxy-graphene oxide nanocomposite coatings on mild steel. Corrosion Science. 2017;115:78-92.
10. Bahreini Z, Heydari V, Namdari Z. Effects of nano-layered silicates on mechanical and chemical properties of acrylic-melamine automotive clear coat. Pigment and Resin Technology. 2017;46(2):333-341.
11. Das S, Pandey P, Mohanty S, Nayak SK. Investigation into the Influence of UV Aging on Green Polyurethane/Nanosilica Composite Coatings Based on Transesterified Castor Oil and Palm Oil Isocyanate. Journal of Inorganic and Organometallic Polymers and Materials. 2017;27(3):641-657.
12. Pintus V, Wei S, Schreiner M. Accelerated UV ageing studies of acrylic, alkyd, and polyvinyl acetate paints: Influence of inorganic pigments. Microchemical Journal. 2016;124:946-961.
13. Selim MS, Shenashen MA, Elmarakbi A, El-Saeed, AM, Selim MM, El-Safty SA. Sunflower oil-based hyperbranched alkyd/spherical ZnO nanocomposite modeling for mechanical and anticorrosive applications. RSC Advance. 2017;7:21796-21808.
14. Thanh NT. Improvement of Environmentally Friendly Alkyd Composite Coating with Graphene Oxide. Malaysian Journal on Composites Science & Manufacturing. 2022;7(1):1-10.
15. Murillo EA, Lopez B. Waterborne hyperbranched alkyd-acrylic resin obtained by miniemulsion polymerization. Polimeros. 2016;26(4):343-351.
16. Murillo EA, Lopez B. Novel waterborne hyperbranched acrylated-maleinized alkyd resins. Progress in Organic Coatings. 2011;72(4):731-738.
17. Mikkonen KS, Kirjoranta S, Xu C, Hemming J, Pranovich A, Bhattarai M, et al. Environmentally compatible alkyd paints stabilized by wood hemicelluloses. Industrial Crops and Products. 2019;133:212-220.
18. Thanh NT. Study on Manufacturing Environmentally Friendly Alkyd Paint, VNU Journal of Science: Natural Sciences and Technology. 2022;38(1):27-33.
19. Shenoy MA, Marathe YD. Studies on synergistic effect of UV absorbers and hindered amine light stabilisers. Pigment and Resin Technology.2007;36(2):83-89.
20. Vuong NT, Hung DP, Linh DK, Hoan DQ, Trung VQ. Effect of R-TiO2 and ZnO nanoparticles on the UV-shielding efficiency of water-borne acrylic coating. Progress in Organic Coatings. 2017;110:114-121.
21. Yousif E, Haddad R. Photodegradation and photostabilization of polymers, especially polystyrene: review. Springerplus. 2013;2(1):398.
22. Queant C, Blanchet P, Landry V, Schorr D. Effect of Adding UV Absorbers Embedded in Carbonate Calcium Templates Covered with Light Responsive Polymer into a Clear Wood Coating. Coatings. 2018;8(8):265.
23. Moore E. Fourier transform infrared spectroscopy (FTIR): methods, analysis, and research insights. New York: Nova Science Publishers, Inc; 2017.
24. Kotnarowska D. Influence of Ageing with UV Radiation on Physicochemical Properties of Acrylic-Polyurethane Coatings. Journal of Surface Engineered Materials and Advanced Technology. 2018;8(4):95-109.
25. Malshe V, Waghoo G. Weathering study of epoxy paints. Progress in Organic Coatings. 2004;51(4) 267-272.
26. Rus AZM, Kemp TJ, Clark AJ. Degradation studies of polyurethanes based on vegetable oils. Part 1. Photodegradation. Progress in Reaction Kinetics and Mechanism.2008;33(4):363-391.

27. Thanh NT. Study on effects of isocyanate on some properties of epoxy varnish. Vietnam Journal of Chemistry. 2022;60(1):15-20.

28. Nikafshar S, Zabihi O, Ahmadi M, Mirmohseni A, Taseidifar M, Naebe M. The Effects of UV Light on the Chemical and Mechanical Properties of a Transparent Epoxy-Diamine System in the Presence of an Organic UV Absorber. Materials (Basel). 2017;10(2):180.

29. Kozak A. Multi-criteria assessment of an acrylic coating exposed to natural and artificial weathering. Procedia Engineering. 2015;108:664-672.

30. Trung Thanh N. Influence of nanosilica on the properties of nanocomposite based on K-153 epoxy resin. Suan Sunandha Science and Technology Journal. 2022;9(1):5-11.

31. Huang DD, Xu F, Du XS, Lee ZH, Wang XJ. Temperature effects on rigid nano-silica and soft nano-rubber toughening in epoxy under impact loading. Journal of Applied Polymer Science. 2015;134(38):45319.