

Degradation of acrylic-melamine based varnish containing Tinuvin 292 with accelerated exposure in fluorescent UV and condensation

Trung Thanh Nguyen*

Institute of Technology, General Department of Defence Industry, Dong Ngac Ward, Bac Tu Liem District, Hanoi, Vietnam

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Abstract:

The durability of an acrylic-melamine (AC-ML) based varnish containing Tinuvin 292 when exposed to 100 cycles of accelerated exposure testing in fluorescent UV and condensation was investigated. Fourier-transform infrared (FT-IR) spectroscopy, thermal gravimetric analysis (TGA), and scanning electron microscope (SEM) were used to evaluate the changes between the initial and aged coatings. The obtained results showed that gloss loss, adhesion, flexibility, impact resistance, and relative hardness of the AC-ML varnish were enhanced with 2.5 wt.% of Tinuvin 292. FT-IR spectrums of the initial and aged samples without Tinuvin 292 illustrated strong changes in intensity of CH_2 and C=O (ester) groups. AC-ML varnish with 2.5 wt.% of Tinuvin 292 exhibited changes in the peaks of the CH_2 and ester groups after accelerated exposure testing. SEM images showed that the surface of the aged AC-ML varnish without Tinuvin 292 was rougher than that of the coating with Tinuvin 292. TGA results also showed that 2.5 wt.% of Tinuvin 292 had improved thermal oxidation stability of the AC-ML based varnish.

Keywords: accelerated exposure testing, acrylic-melamine varnish coating, degradation, FT-IR, physico-mechanical properties, thermal oxidation resistance, Tinuvin 292.

Classification numbers: 2.2, 2.3

1. Introduction

Degradation of polymers, in general, and paint coatings, in particular, under high temperature, humidity, oxygen, thermal changing, and UV radiation result in the damage of polymers or adhesion losses, chalking, or blistering, etc. [1-4]. Many authors have studied how to reduce coating degradation under UV light by using carbon black, graphene oxide, nanosilica, zinc oxide (ZnO), and inorganic pigments [5-8]. Unfortunately, these above anti-UV additives tend to agglomerate or cluster, so they are difficult to disperse in coatings and thus cannot be used for varnishes due to losing their transparency [9-11].

AC-ML paint with its high relative hardness, polish, and chemical resistance is widely used for electrical details, household items, insulating materials, and automotive products [12-15]. Even baking acrylic-melamine coatings are widely used for outdoor purposes, but publications on their degradation have been limited [14-16]. In our last article, the authors studied the effects of acrylic-melamine ratio and baking temperature on mechanical properties, thermal resistance, and chemical resistance to determine the optimal ratio and drying temperature for the AC-ML varnish coating. From which, the conditions of acrylic-melamine ratio (wt.%) of 35/15, baking temperature of 140°C , and baking time of 60 min were determined as optimal. Results also showed that the AC-ML varnish was capable of being used to protect metal parts under several chemical conditions [17].

Tinuvin 292 is a liquid hindered amine light stabilizer that is especially developed for protecting coatings from UV radiation. It is useful for varnish in UV radiation protection [18].

This article will address the effect of Tinuvin 292 on the degradation of AC-ML varnish when subjected to accelerated exposure in fluorescent UV and condensation with FT-IR analysis. Besides that, mechanical properties, gloss loss, surface morphology, and thermal oxidation resistance of initial and aged AC-ML varnish coatings were also investigated.

2. Materials and methods

2.1. Materials

Acrylic resin (trade name of Eterac 7108-X-54) was supplied by Eternal Chemical Co., Ltd (Taiwan), with an appearance of clear/clean, acid value (mg KOH/g): 5-9, and solid content of $(60\pm 1)\%$.

Melamine resin (trade name of MF268) was purchased from Synpol Products Private Ltd. (India), with free formaldehyde $\leq 3\%$, acid value (mg KOH/g) $\leq 3\%$, and solid content $(60\pm 2)\%$.

Xylene, acetone, and butyl acetate were purchased from Industrial Products (China).

Tinuvin 292 (Bis(1,2,2,6,6-pentamethyl-4-piperidiny)-sebacate and 1-(Methyl)-8-(1,2,2,6,6-pentamethyl-4-piperidiny)-sebacate) was supplied by Kremer Pigmente GmbH & Co. KG (Germany).

*Email: nguyentrunghanh42@gmail.com

2.2. Varnish preparation [17]

Raw materials were prepared as given in Table 1. Acrylic resin and melamine resin were dissolved in xylene, then acetone and butyl acetate was added. The varnish was well mixed and the samples were formed (according to ISO 15528:2013) on steel panels according to ISO 1514:2016 for testing of mechanical properties.

Table 1. Composition of AC-ML varnish.

No.	Components	Weight percent (wt.%)
1	Acrylic, Eterac 7108-X-54	35
2	Melamine, MF268	15
3	Xylene	30
4	Butyl acetate	12-15
5	Acetone	5
6	Tinuvin 292	0-3.0

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 spray gun with pressure of 4 kg/cm².

These coatings were prepared and kept at a temperature of (25±2)°C and humidity of (50±5)% for one day, then baked at 140°C for 60 min, and then kept at room temperature for five days before testing [17]. The thickness of the dried coatings was (30±3) µm as measured with a Minitest 600 Erichsen digital meter.

2.4. Analysis methods

Accelerated exposure testing was performed in a UV/condensation weathering chamber (Atlas UVCON UC-327-2) with UVB-313 fluorescent lamps and operated under conditions of one cycle including 8 h of UV irradiation at 60°C following by 4 h of dark with water condensation at 50°C in accordance ASTM D4587-11. FT-IR spectroscopy was conducted on a Fourier FTIR-8700 series converter.

Morphology of the coating film was observed by FE-SEM (Hitachi S4800) with a magnification of 1,000 times and voltage of 5 kV.

Gloss of the coating was determined according to ISO 2813:2014 with an angle of 60 degrees. Adhesion of the coating was determined according to ISO 2409:2013. Flexibility of the coating was determined according to ISO 1519:2011. Impact resistance of the coating was determined according to ISO 6272-1:2011. Finally, relative hardness of the coating was determined according to ISO 1522:2006.

Thermal oxidation resistance was determined by TGA as analysed by a NETZSCH TG 209F1 LIBRA with a heat rate of 10°C/min from ambient temperature to 600°C in air atmosphere.

3. Results and discussion

3.1. Effect of Tinuvin 292 content on physico-mechanical properties of AC-ML varnish when subjected to accelerated exposure of fluorescent UV and condensation

To study the effect of Tinuvin 292 content on gloss loss and mechanical properties in AC-ML varnish after accelerated exposure testing, samples with thickness of 30±3 µm were prepared with Tinuvin 292 content of 0, 1.0, 2.0, 2.5, and 3.0, which were named M0, M1, M2, M3, and M4, respectively. Results from 100 cycles of ageing testing are shown in Tables 2 and 3.

Table 2. Gloss and mechanical properties of initial AC-ML varnish coatings.

Samples	Gloss at 60°	Mechanical properties of coating			
		Adhesion (points)	Flexibility (mm)	Impact resistance (kg.cm)	Relative hardness
M0	81	1	2	200	0.59
M1	81	1	2	200	0.59
M2	81	1	2	200	0.59
M3	80	1	2	200	0.59
M4	80	1	2	200	0.59

Table 3. Gloss and mechanical properties of aged AC-ML varnish coatings.

Samples	Gloss at 60°	Mechanical properties of coating			
		Adhesion (points)	Flexibility (mm)	Impact resistance (kg.cm)	Relative hardness
M0	43	5	6	80	0.71
M1	49	4	5	140	0.68
M2	61	2	3	180	0.64
M3	76	1	2	200	0.60
M4	77	1	2	200	0.60

Table 2 showed that Tinuvin 292 did not affect the mechanical properties and gloss of AC-ML varnish. Table 3 showed that after 100 cycles of ageing testing, as the content of Tinuvin 292 increased, adhesion, flexibility, impact resistance, and gloss of coatings had less of a reduction. After ageing testing, impact resistance of M0 (the sample without Tinuvin 292) decreased strongly from 200 to 80 kg.cm, relative hardness increased from 0.60 to 0.71, and flexibility increased from 2 to 6 mm. This meant that the coating became more brittle and lost its adhesion. Meanwhile, samples M3 (sample with 2.5 wt.% of Tinuvin 292) and M4 (sample with 3 wt.% of Tinuvin 292) only showed slight changes to adhesion, flexibility, impact resistance, and gloss loss. The results also showed that for Tinuvin 292 content over 2.5 wt.%, the relative hardness of aged coatings did not increase. This can be explained that Tinuvin 292 (light stabilizer) had prevented polymer chains from breaking down and being severed, so ageing of the polymers by UV rays was limited [18-20]. Hence, with Tinuvin 292, mechanical properties of AC-ML varnish are better than those without Tinuvin 292 after 100 cycles of accelerated exposure testing, and the same also occurred with the gloss value

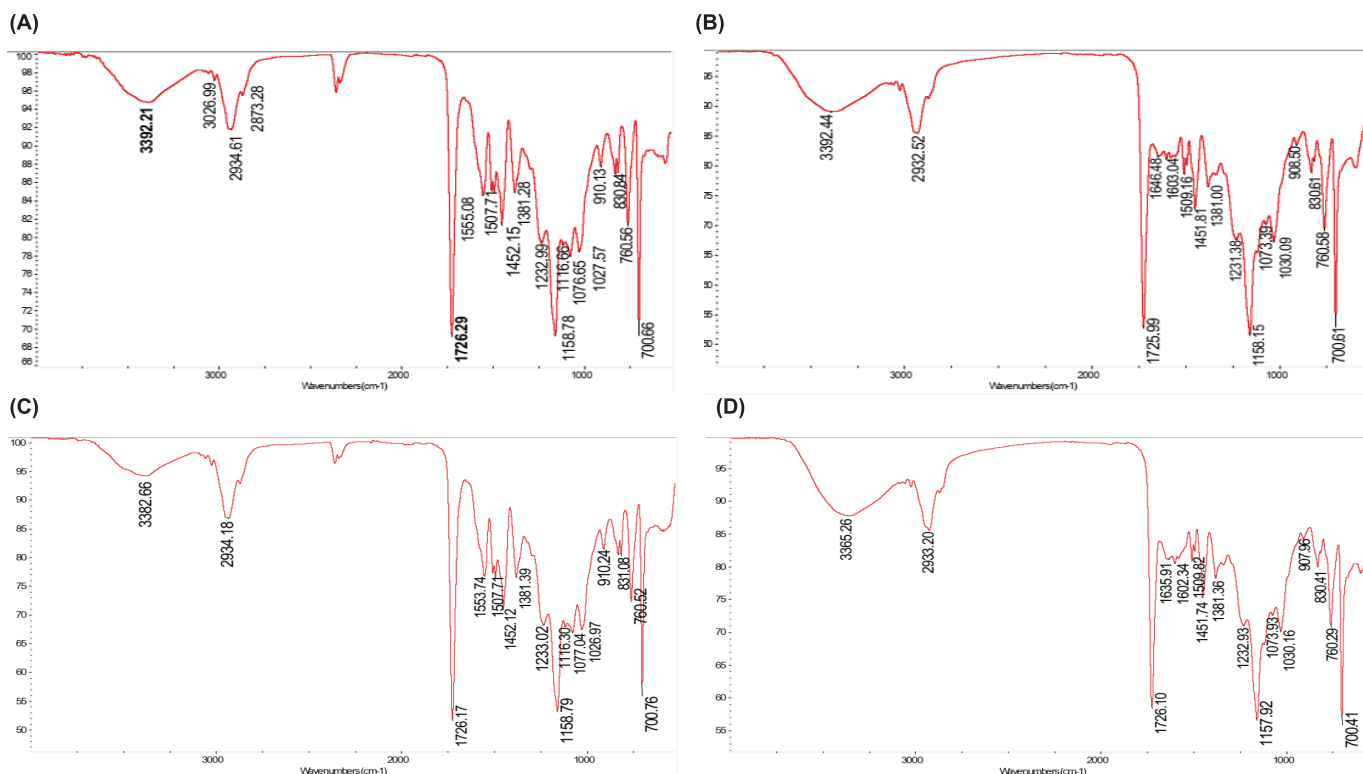


Fig. 1. IR spectra of M0 (A) before and (B) after accelerated exposure testing and M3 (C) before and (D) after accelerated exposure testing.

of AC-ML varnish [21, 22]. Therefore, Tinuvin 292 enhanced the mechanical properties and gloss of the AC-ML varnish under UV radiation conditions. Based on above results, M3 was chosen for further study.

3.2. FT-IR spectroscopy analysis

In general, degradation of polymers may not be seen by their appearance but through the chemical changes of their functional groups. Therefore, to investigate the chemical changes of the initial and aged coatings' functional groups, FT-IR spectroscopy was performed on M0 and M3 of before and after ageing with 100 cycles of accelerated exposure. The results are shown in Figs. 1A-D and Table 4.

Figures 1A and 1B showed that the peak intensity of CH_2 (3026 or 2934) sharply decreased and even peak 2873 of CH_2 in Fig. 1A disappeared in Fig. 1B. This can be explained that the polymer molecular chain had been severed and the molecular length became much shorter. At the same time, the intensities of the ester group peaks (1726 of $\text{C}=\text{O}$ and 1232 of $\text{C}-\text{O}$) decreased as the ester bond was destroyed to form new bonds such as ketones due to optical oxidation or as $\text{C}=\text{O}$ and $\text{C}-\text{O}$ groups were stretched and rocked [19, 21]. As can be seen in Figs. 1C and 1D, there was only a small difference in intensities of peaks between the before- and after-aging samples. These results show that in varnish with Tinuvin 292, peak intensities of CH_2 (2934) and ester groups (1726 of $\text{C}=\text{O}$ and 1233 of $\text{C}-\text{O}$) also stretched but intensities and vibrations of these peaks reduced insignificantly compared to the initial sample. Photo-degradation of polymers may occur to chain scissions or macroradical disproportionation, leading to terminal double bonds [20, 21]. In the sample with Tinuvin 292 (M3), there was little

difference in peak intensities between before and after ageing. In the sample without Tinuvin 292, macroradical disproportionation attacked polymer chains to produce $\text{C}=\text{C}$ bonds. In the case of AC-ML varnish containing Tinuvin 292, macroradicals would attack the conjugated double bonds of Tinuvin 292. In other words, Tinuvin 292 absorbed the UV rays and, thus, reduced coating degradation [23-25].

Table 4. Fluctuations in infrared AC-ML varnish coatings.

No.	Typical spectrum	Wavenumbers (cm^{-1})
1	νCH , stretch	3392
2	$\nu\text{as}(\text{CH}_2=)$, asymmetry in vinyl group	3026
3	$\nu\text{as}(\text{CH}_2=)$, asymmetry in carbon chain	2934 2932
4	$\nu(\text{CO})$ of fat acid	1726 1725
5	$\nu(\text{C}=\text{C})$ in vinyl group	1646
6	$\nu\text{C}=\text{C}$ (epoxy aromatic ring)	1555
7	νCH	1232 1231
8	$\nu\text{C}-\text{O}$ stretch, vibrations	1158
9	$\nu\text{aC}-\text{O}-\text{C}$ (asymmetry)	1076 1073
10	$\omega(\text{CH}_2)$, oscillation of CH_2 near vinyl group	910 908
11	$\square(\text{CH})$, oscillation deformation of CH in aromatic ring	760

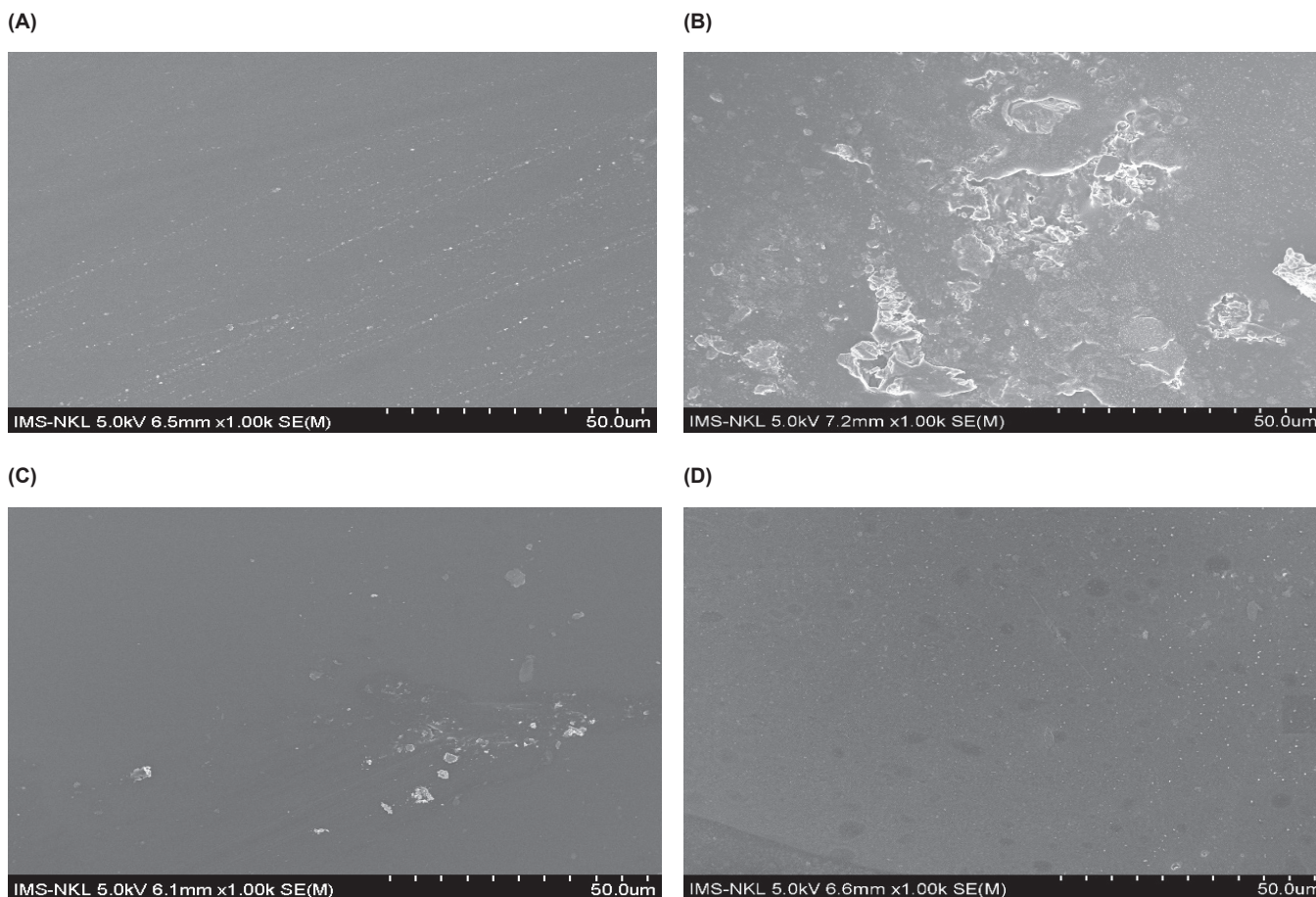


Fig. 2. Surface SEM images (A) before and (B) after accelerated exposure testing and M3 (C) before and (D) after accelerated exposure testing.

3.3. Morphology of varnish coating surface

Samples M0 and M3, as mentioned in Table 2, were selected to investigate the effect of 100 cycles of the accelerated exposure testing on the surface of AC-ML varnish coatings. The obtained results are shown in Fig. 2.

Figure 2D showed that after ageing testing, there were no cracks, blisters, or surface changes on M3. The surface of M0 and M3 after 100 cycles of accelerated exposure testing were rougher when compared with the initial sample surfaces. For M0, in comparison with initial sample, the sample surface after the aging testing was strongly damaged and had pinholes. This can be explained by the oxidation process that occurred, which led to the generation of micro-cavities and micro-holes on coating's surface [21, 23, 25]. These results indicate that Tinuvin 292 with a content of 2.5 wt.% is suitable for protecting AC-ML varnish from the effect of UV irradiation and humidity condensation impacts for long time (about 100 cycles).

3.4. Effect of Tinuvin 292 on thermal oxidation resistance of coating

To study the effect of Tinuvin 292 on thermal oxidation resistance of AC-ML varnish, TGA was carried out on M0 and M3

before and after testing with 100 cycles of accelerated exposure. Results are shown in Table 5 and Fig. 3.

Table 5. Effect of Tinuvin 292 on thermal oxidation resistance of AC-ML varnish.

Samples	Weight loss (%)		
	300°C	400°C	500°C
M0 (initial)	6.81	56.05	85.25
M0 (aged)	9.53	59.58	90.68
M3 (initial)	3.56	41.35	85.06
M3 (aged)	8.05	53.18	87.82

Table 5 and Fig. 3 showed that the samples had different curve slopes. At different temperatures, weight loss of samples was different, too. The TGA curve slope of aged M0 was the highest. The results also showed that Tinuvin 292 had remarkably enhanced thermostability of the coating [5, 19-21]. This can be explained that under 200°C, decomposition occurred with low molecular substances and residual solvents with a decomposition volume of about 2-4%. Up to 400°C, decomposition occurred with residual functional groups in polymer branches, which are low molecular substances. The decomposition of M0 and M3 was the

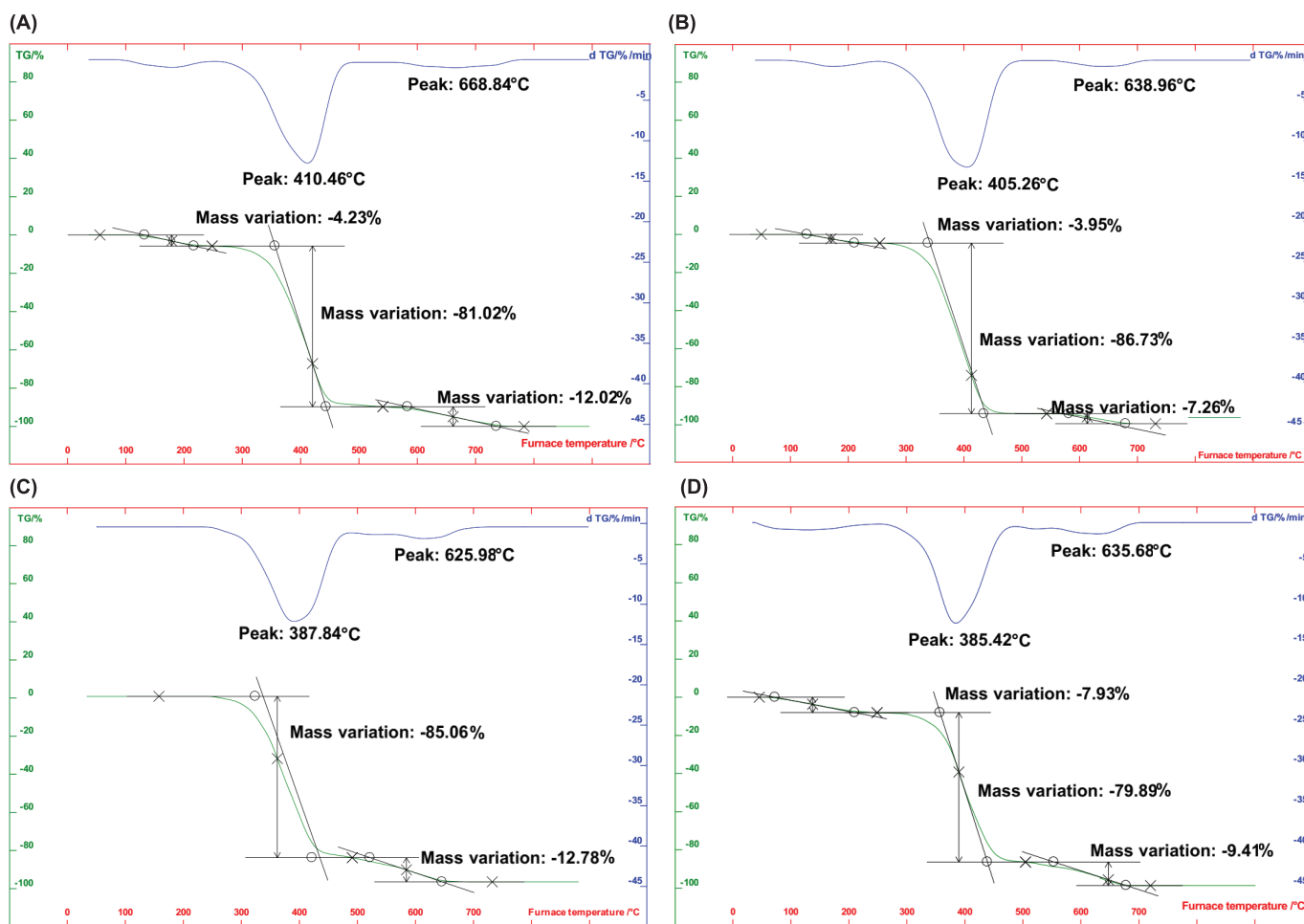


Fig. 3. TGA diagrams of (A) before and (B) after accelerated exposure testing and M3 (C) before and (D) after accelerated exposure testing.

same. Meanwhile, aged M0 decomposed more than aged M3 and was the strongest of all. This can be explained that after aging, polymer chains of M0 had been broken and while the Tinuvin 292 in sample M3 had prevented polymer chains from breaking, lowering its decomposition [20, 21]. By Tinuvin 292 preventing chemical bonds of the polymers from breaking, slits in the material structure were reduced thereby reducing oxygen permeation in the material and increasing thermal oxidation resistance of the coating. Up to 500°C and above, the decomposition of the two samples were similar because at high temperatures all organic components were burnt or decomposed and inorganic parts of samples remained the same [26-28].

4. Conclusions

Investigations indicated that the presence of Tinuvin 292 improved adhesion, flexibility, impact resistance, relative hardness, and gloss loss of AC-ML varnish after 100 cycles of accelerated exposure testing. The suitable content of Tinuvin 292 for this varnish was determined to be 2.5 wt.%. Under UV irradiation, bonds of $\sim\text{CH}_2$ and ester groups of the samples without Tinuvin 292 strongly decreased. Meanwhile, the sample with Tinuvin 292 found the breakage of those groups to be limited. AC-

ML varnish with 2.5 wt.% of Tinuvin 292 could withstand 100 UV-thermo-humidity complex cycles without cracks, blisters, or visible surface changes. Thus, Tinuvin 292 improved the thermal oxidation resistance of AC-ML varnish. From room temperature to 400°C, with Tinuvin 292, the decomposition of the sample was 53.18 compared to a value of 59.58 from the sample without Tinuvin 292.

COMPETING INTERESTS

The author declares that there is no conflict of interest regarding the publication of this article.

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