THE ACCELERATED WEATHERING AGING OF A WATER-BORNE STYRENE ACRYLIC COATING

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Abstract

The aging of a water-borne styrene acrylic coating in the artificial weathering environment of a QUV/condensation weathering chamber equipped with UVB-313 fluorescent lamps has been investigated by using both chemical structure analyses (IR, UV-Vis) and measuring weigh loss and discoloration. The obtained results indicated that under the effects of UV radiation, oxygen, heat and moisture, the coating exhibited various chemical structure changes. These modifications can be linked to several mechanisms including the photolysis, photo-oxidative and hydrolysis reactions that caused a reduction of characteristic IR absorption bands for the alkane C-H, ester C-O- and C_6H_5 groups and the generation of photo-oxidative products (hydroperoxide, carboxylic acid and conjugated double bonds). These chemical changes result in the weight loss and yellowing of the coating. The obtained information was useful to better understand the degradation mechanisms of the coating during accelerated weathering.

Keywords. Accelerated weathering, aging, styrene acrylic emulsion, FTIR, UV-Vis, weight loss, discoloration.

1. INTRODUCTION

Organic coatings are used in a large variety of applications to improve the surface properties of all kinds of materials. Acrylic binders have attracted special interest of scientists and manufactures due to the distinctly advanced characteristics, including the weathering durability, optical clarity, mechanical properties and chemical stability. However, a common drawback of these solvent-based coatings is to cause environmental pollution. In recent decades, with the increasing social and political awareness, coupled with the tightening of worldwide environmental legislation, coating industries are obliged to propose new solutions to minimize the levels of polluting substances released into the atmosphere. For this reason, end-users have tried to develop environmentally friendly solvent-free coatings such as UV-cured systems and water-borne coatings [1-6]. The styrene acrylic emulsions-based coatings are now commonly used for the alkali resistance wall paints of buildings (both exterior and interior). The main advantages of these systems consist of their solvent-free formulation.

However, outdoor coatings can be degraded under the effect of weathering environmental factors such as UV-light, oxygen, temperature, water and pollutants, which can deteriorate their bulk properties. Among these factors, UV irradiation is a major contributor to the degradation of the material. The aging properties of solvent-borne acrylics have been widely investigated and the trends described, including photo-oxidative degradation of these resins (chain scission of side ester groups, cross-linking of the polymer backbone, oxidation processes leading to new hydroxyl and carbonyl functionalities) having been confirmed to affect water-borne products [1, 6-9].

At present, there have been only a few of studies concerning of weathering degradation of water-borne styrene acrylic coatings, in particular, in Vietnam there is a lack of information about the degradation of these coatings [10-13].

In this study, the weathering degradation process of a water-borne styrene acrylic coating was quantitatively studied by monitoring the chemical modifications occurring upon UV-B/condensation artificial weathering. By using non-destructive analytical methods, such as IR, UV-Vis spectroscopies and by measuring of sample weight loss and discoloration, it was possible to follow continuously the formation of photo-oxidative products and the loss of the binder functional groups on the same sample undergoing during weathering-

aging. It is expected that the obtained results can help to better understand the aging mechanism of a water-born styrene acrylic coating.

2. EXPERIMENTAL

2.1. Materials

GP 1106 Styrene Acrylic Emulsion having a solid content of 50 ± 1 wt % was obtained from The GreenPol, with chemical formula as below:
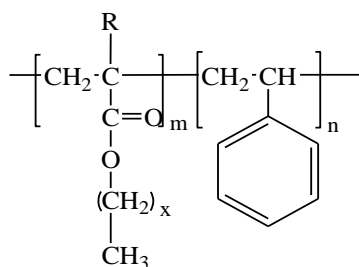
Where: m, n: 0, 1, 2, …; x: 0, 1, 2, 3.

2.2. Samples preparation

Coating sample with about 25 μm thickness for IR, UV-Vis analyses and the weight los measurement during the artificial weathering was prepared on glass plates with the dimension of 100 × 70×2 mm by using a quadruple film applicator (Erichsen model 360). After 7 days of atmospheric drying, the sample for IR and UV-Vis analyses was removed from the glass plate and mounted over a window on an aluminum holder for direct transmission measurements.

The sample for color measurement was prepared on the sheet of the concrete with the size of 150 × 75 × 10 mm and fabricated at the volume ratio of cement/sand = 1/5, the paint consumption of 120 g/m^2 (corresponding dry thickness was 45 μm) by spray at the air pressure of 6 kg/cm^2.

2.3. Artificial weathering test

Artificial weathering test was performed in a QUV/condensation weathering chamber Atlas UVCON UC – 327 – 2 (USA) equipped with UVB-313 fluorescent lamps and operated under wet-cycle conditions of 8 h UV irradiation at 60°C followed by 4 h of dark water condensation (CON) at 50°C (1 cycle consists 8 h UV and 4 h CON).

The samples before and after testing were dried in vacuum oven at 50 °C for 24 hours before the analysis.

2.4. Analysis

2.4.1. IR analysis

The chemical changes occurring upon the QUV-B/condensation artificial weathering in aged coating were analyzed by FTIR spectroscopy (NEXUS 670 from Nicolet). The variation of the following IR bands was monitored quantitatively through discrete measurements made on exactly the same spot of each sample, after various exposure times. From the decrease of the binder structural bands, the relative amount of remaining functional groups was determined by making the ratio of the IR absorbance at the corresponding wavenumber after a given exposure time (D_t) to the absorbance of the unexposed sample (D_0) [5]:

Remaining group (%) = (D_t/D_0) × 100   (Eq.1)

The generation of oxidation products (COOH, OH and conjugated C=C group) was quantified by measuring the changes of their corresponding IR absorbance values, which were standardized for a 25 μm thickness film to make a reliable comparison between aged and unaged sample.

2.4.2. UV-Vis analysis

An UV–Vis spectrophotometer (GBC, CINTRA 40, USA) was also employed to monitor the absorbance of the chromophores and functional groups before and after artificial weathering exposure. The sample used for UV-Vis analysis was similar to that for FI-IR analysis.

2.4.3. Weight loss of coating

The sample to analyze the weight loss was prepared on glass plates with dimension of 100 × 70×2 mm. The weight loss (Δm_t) of the coating after artificial weathering test was determined by the difference between the weights of the sample (dried in vacuum oven at 60 °C until the constant weight) before (m_0) and after (m_t) the aging testing by the formula [6]:

$$\Delta m_t \ (\%) = [(m_0 - m_t)/m_0] \times 100$$

3.4.4. Color measurement

Color measuring of coating sample was carried out according to ASTM D2244. A Color-Tec PCM+ measured the color in coordinates of L*, a* and b* at three locations on each sample using the Commission Internationale d'Eclairage (CIELAB 1976 color space) three-dimension color space system. In this system, L*axis (+L* for light, - L* for dark) represents the lightness, a*(+ a* for red, -

a* for green), and b*(+ b* for yellow, and - b* for blue) symbolize the chromaticity coordinates. At least four replicates were measured for each formulation to obtain the average values of color. Calculations incorporated the values of lightness and chromaticity coordinates before and after weathering tests to determine the discoloration (ΔE*) of the weathering exposed samples by using the following equation: $\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$ with ΔL*, Δa*, and Δb* as the difference of initial and final values of L*, a*, and b*.

3. RESULTS AND DISCUSSION

3.1. Chemical changes of water-borne styrene-acrylic coating

3.1.1. IR analysis

Infrared spectroscopy is a sensitive and reliable technique permitting to quantify the chemical changes of the photodegradation process. Modifications of the chemical structure of polymer materials can be determined spectroscopically well before the observation of physical and optical property changes [5]. Figure 1 showed the infrared spectra of a water-borne styrene acrylic coating before and after 60 cycles of artificial weathering test. Some IR characteristic bands of functional groups of this coating were presented in table 1. A quantitative analysis of the IR characterictic bands for this material such as of O-H, alkane C-H, carboxylic acid C=O, conjugated C=C, ester C-O- and C_6H_5 stretchings located at the wavenumbers of 3440, 2945, 1775, 1620, 1170 and 760 cm^{-1}, respectively, was carried out and the results were shown in table 1 and figure 2.

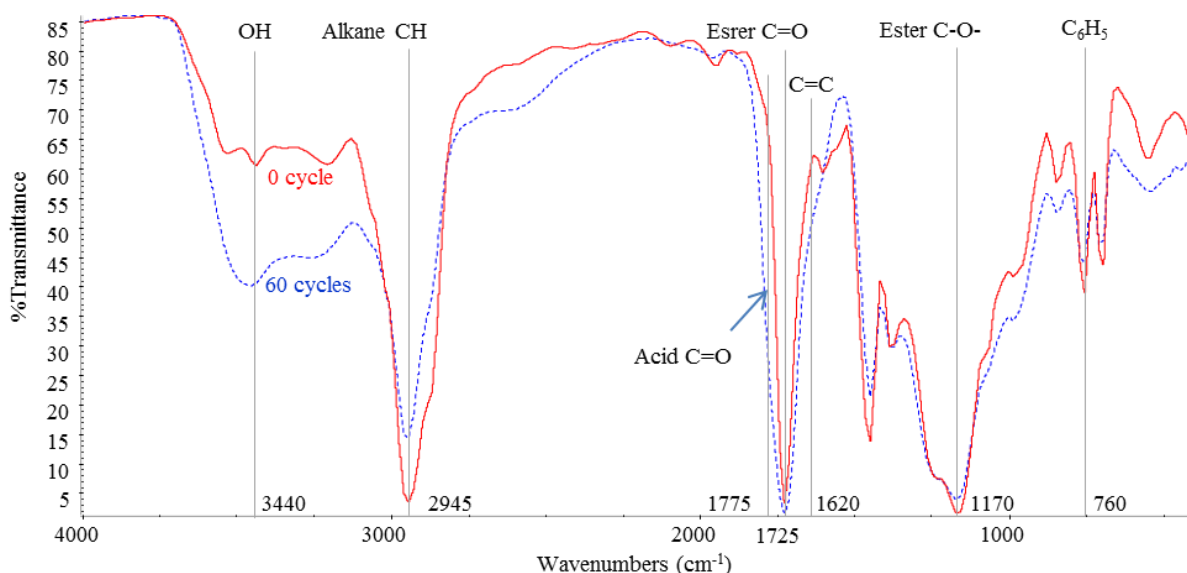By comparison of the intensity of characteristic

Figure 1: The IR spectra of the water-borne styrene acrylic coating before and after 60 cycles of artificial weathering exposure

bands of aged and unaged coating sample, it can be seen that the intensity bands assigned to the alkane C-H and ester C-O- groups are decreased during the aging process. However, IR bands corresponding to the hydroxyl group (-OH), carboxyl in carboxylic acid and conjugated double bonds (C=C) were increased. After 60 cycles of aging, the alkane C-H, ester C-O- and C_6H_5 groups remained about 52, 55 and 51%, respectively.

During the artificial weathering test, the coating was simultaneously affected by various factors such as ultraviolet radiations, heat, moisture and oxygen. The ultraviolet radiations caused the polymer chain scission, and in the presence of oxygen, led to the

photo-oxidation of polymer. In addition the properties of coating may be also deteriorated by moisture and water through the hydrolysis reaction of the hydrophilic ester groups in the polymer chain. Increasing of the temperature has accelerated this process. These degradation mechanisms could be attributed to the modifications of IR bands corresponding to the alkane C-H, ester C-O- and C_6H_5 groups previously observed [2-3, 11-13].

3.1.2. UV-Vis analysis

UV-Vis spectroscopy was employed to monitor the changes of the absorbance of chromophores [2].

Figure 3 showed the UV-Vis spectra of a water-borne styrene acrylic coating before and after 60 cycles of aging.

It can be seen that the characteristic absorbances of ester C=O group at 235 nm and of benzene ring at 260 nm decreased after 60 cycles of ageing and the absorbance of the characteristic chromophores for conjugated double bonds was expanded during artificial weathering exposure. These results have confirmed a decrease of main functional groups such as ester C=O group and benzene ring as well as the generation of the pho-oxidative products

Table 1: Some characteristic infrared absorptions of the functional groups in the water-borne styrene acrylic coating before and after 60 cycles of ageing.

IR band (cm^{-1})	Functional group	0 cycle	After 60 cycles	Observations	
				Intensity	Changes
3440	O-H	+	+	Weak	Strongly increased
2945	C-H stretching in alkane	+	+	Strong	Significantly decreased
1780	C=O stretching in carboxylic acid	-	+	*	Increased
1725	C=O stretching in ester group	+	+	Very strong	Unclearly changes
1620	Conjugated C=C stretching	-	+	*	Increased
1170	C-O- stretching in ester group	+	+	Strong	Significantly decreased
760, 700	C-H in benzene ring	+	+	Weak	Significantly decreased

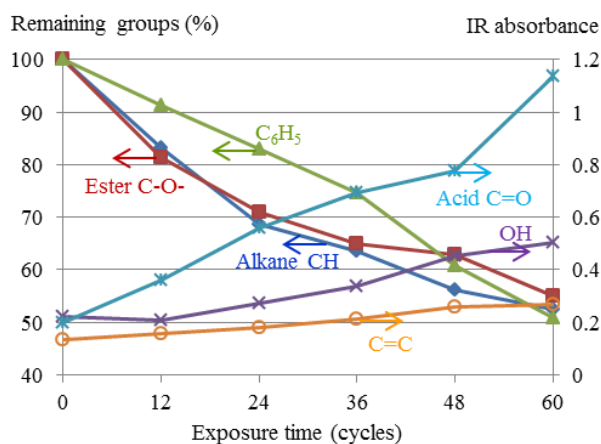Note: "+": absorption; "-": no absorption; "*": generation during the ageing process.

Figure 2: Variation of functional groups of a water-borne styrene acrylic coating as a function of aging exposure time

3.2. Weight loss of coating

The degradation of the coating upon weathering test can be followed by various methods, including discoloration, loss of gloss, chalking, cracking, thickness decrease and weight loss resulting from the light-induced chemical changes. Previous investigations have found that an average
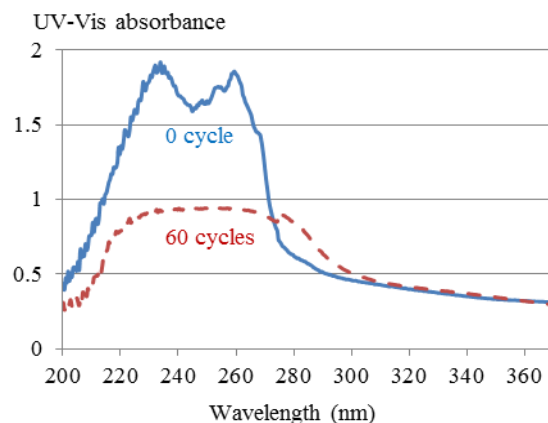

Figure 3: UV-Vis spectrum of a water-borne styrene acrylic coating before and after 60 cycles of aging

decrease in thickness of 5 to 25 μm can be observed in the dry film after one year weathering [1]. In this work, besides the use of chemical structure analyses, the degradation of the coating was also followed by measuring the weight loss of the coating exposed to QUV-B weathering. The weight loss of coating upon

containing conjugated double bonds during the artificial weathering [5, 12].

weathering was presented in figure 4. It can be seen that the coating was gradually losing its weight under artificial weathering exposure. Indeed, after 60 cycles (720 h), the weight loss of coating of 19 % was recorded.
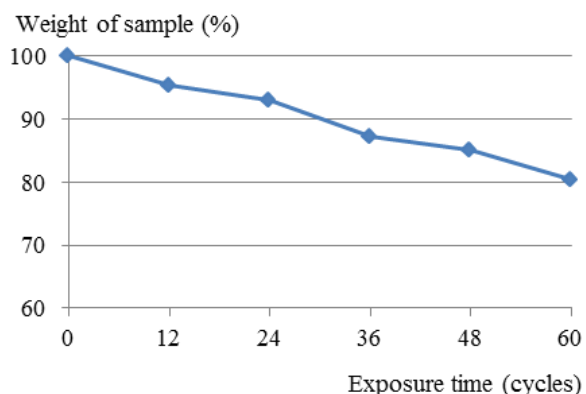

Figure 4: Weight loss of coating as a function of artificial weathering exposure time

Two mechanisms, in competition, relating to the weight loss had possibly occurred during artificial weathering exposure: (I) the photo-oxidation: oxygen atoms immigrated into the polymer matrix and conduced thus an increasing of the sample weight; (II) the chain scission of the polymer molecules might be occurred by photolysis and hydrolysis that produced the oxidative products with low molecular weight such as CO_2, CH_3, aldehydes, or acids. These degradation products then could either evaporate or was washed away by moisture and led to a loss of coating materials [1, 9]. In our case, it seems that the mechanism (II) was dominant.

3.3. Color change of coating

Photographic images of water-borne styrene acrylic coating before and after 60 cycles of artificial weathering were presented in figure 5. The changes of the lightness (L*), red-green (a*), yellow-blue (b*) and the discoloration (ΔE*) values of the coating during artificial weathering exposure were illustrated in table 2.

It can be seen that the coating was yellowed after 60 cycles of aging. The b* and ΔE* values of the coating significantly increased while the L* and a* values only slightly changed. The cause of this

yellowing was explained due to the appearance of polyene conjugated systems in the coating because of photochemical reactions involving photo-oxidized styrene phases under effect of the UV-light [12].
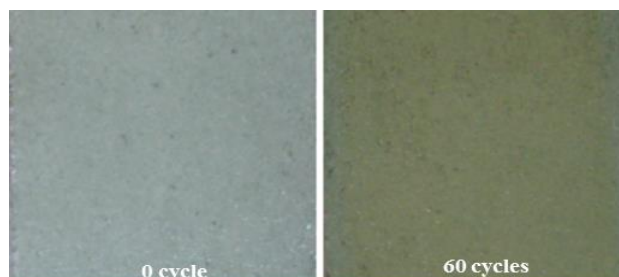

Figure 5: Photographic images of water-borne styrene acrylic coating before and after 60 cycles of artificial weathering exposure

Table 2: Color change of water-borne styrene acrylic coating during the ageing process.

Exposure time (cycles)	L*	a*	b*	ΔE*
0	59.25	2.12	5.87	-
12	58.47	2.04	8.82	3.05
24	58.82	1.96	10.34	4.49
36	57.81	1.92	12.17	6.46
48	57.46	1.93	12.72	7.08
60	57.30	1.97	14.53	8.88

4. CONCLUSIONS

The aging of a water-borne styrene acrylic coating was investigated in artificial weathering environment by using both chemical structure analyses (IR, UV-Vis) and weigh loss and discoloration measurements.

Under the effects of UV radiation, oxygen, heat and moisture, the coating exhibited various chemical structure changes. These modifications can be linked to several mechanisms including the photolysis, photo-oxidative and hydrolysis reactions that caused a reduction of characteristic IR absorption bands for the alkane C-H, ester C-O- and C_6H_5 groups and the generation of photo-oxidative products (hydroperoxide, carboxylic acid and conjugated double bonds). These chemical changes results in the weight loss and yellowing of the coating. The obtained information was useful to better understand

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