

THE ALKALINE HYDROLYSIS DEGRADATION OF A WATER-BORNE STYRENE ACRYLIC COATING

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Abstract

The degradation of water-borne styrene acrylic coating during the immersion in the 20 % NaOH and saturated $\text{Ca}(\text{OH})_2$ solutions was quantitatively investigated by using a IR spectroscopy and by measuring the sample weight and adhesion losses. The obtained results showed that during the immersion, the functional groups of coating were changed. The alkane C-H, ester C=O, C-O- and C_6H_5 groups decreased. Of which, the C-O- stretching shows the largest decreased. The hydroxyl group (-OH) and carboxyl group (C=O) (in $-\text{COO}^-$) increased. The functional groups of the coating immersed in the 20 % NaOH solution changed more strongly than those of coating immersed in the saturated $\text{Ca}(\text{OH})_2$ solution. The formation of alkaline hydrolysis products (the OH and $-\text{COO}^-$ groups) in the coating immersed in the former was larger than in the coating immersed in the latter one. The alkane C-H, ester C=O, C-O- and C_6H_5 groups of the coating immersed in the saturated $\text{Ca}(\text{OH})_2$ solution significantly decreased while the formation of the OH and $-\text{COO}^-$ groups only slightly increased. These chemical changes caused the weight and adhesion losses of the coating. This information was useful to better understand about the major mechanisms that control of the alkaline hydrolysis degradation of water- borne styrene acrylic coating.

Keywords. Alkaline hydrolysis degradation, water-borne styrene acrylic coating, IR analysis, weight loss, adhesion.

1. INTRODUCTION

Due to the low manufacturing costs, suitable bulk properties, versatility and aesthetic attributes, organic coatings are nowadays widely used to protect and decorate various metallic surfaces and buildings. Acrylic resins have attracted special interest of scientists and producers because of its distinct advantages characteristics, including its weathering durability, its optical clarity, its good mechanical properties and its chemical stability. Although there are many advantages such but a common drawback of these coatings is to cause environmental pollution. In recent years, 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 environmental friendly solvent-free coatings such as UV-cured systems and water-borne coatings [1-8].

The styrene acrylic emulsions-based coatings are now commonly used for the alkali resistant primer wall paints of buildings (both exterior and interior). The main advantages of these systems consist in their solvent-free formulation.

However, outdoor coatings can be degraded during the weathering and the alkaline environment exposure which can deteriorate their bulk properties. The weathering aging properties of both solvent-borne and water-borne acrylic coatings have been widely investigated and the trends described, including photooxidative 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 [1-13] but there is a lack of information about the alkaline hydrolysis degradation of water-borne styrene acrylic coatings [14, 15].

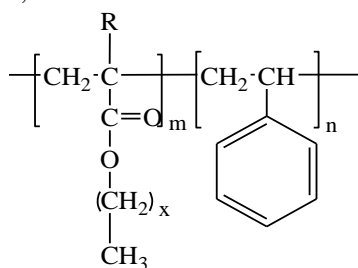
In this study, the degradation process of a water-borne styrene acrylic coating was quantitatively studied by monitoring the chemical modifications

occurring during exposure to 20 % NaOH and saturated $\text{Ca}(\text{OH})_2$ alkaline solutions. By using a IR spectroscopy and by measuring of sample weight and adhesion losses, it was possible to follow continuously the formation of alkaline hydrolysis products and the loss of the binder functional groups on the same sample undergoing during aging. This kind of study is considered to provide a reliable evaluation of the alkali resistance of a given polymer. It is hoped that the obtained results can provide some useful information about the mechanism for the alkaline hydrolysis degradation 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 % were obtained from The GreenPol, with chemical formula as below:



Where: $m, n: 0, 1, 2, \dots$; $x: 0, 1, 2, 3$.

2.2. Sample preparation

Coating samples with about $25 \mu\text{m}$ thickness for IR analysis and for measurement of the weight loss during the immersion in the alkaline solutions were prepared on glass plates with the dimension of $100 \times 70 \times 2$ mm by using a quadruple film applicator (Erichsen model 360). After 7 days of atmospheric drying, the sample for IR analysis was removed from the glass plate and mounted over a window on a polypropylene holder for direct transmission measurements.

The samples for adhesion measurements were prepared on sheets of concretes reached mark 100 (according the TCVN 3121-11:2003) with the size of $150 \times 100 \times 10$ mm and fabricated from cement Portland PC 30 provided by Nghi Son Cement company and river sand with the size < 2 mm, the paint consumption of 120 g/m^2 (corresponding dry thickness of $45 \mu\text{m}$) by spraying at the 6 kg/cm^2 air pressure.

2.3. Alkali resistance test

Alkali resistance test was carried out by

immersing the films in the 20 % NaOH solution (according to the TC41-2005/ICI-Dulux weather shield alkaline resistance sealer) and in the saturated $\text{Ca}(\text{OH})_2$ solution (according to the TCVN 8653-3:2012). The samples before and after testing were washed with deionized water until the $\text{pH} = 7$ and dried in vacuum oven at $60 \text{ }^\circ\text{C}$ for 24 hours before the analysis.

2.4. Analysis

2.4.1. IR analysis

The chemical structural changes occurring upon the coating immersed in the alkaline solutions were analyzed by a FT-IR spectroscopy (NEXUS 670, 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 immersion 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 immersion duration (D_t) to the absorbance of the non-immersed sample (D_0) [8]:

$$\text{Remaining group (\%)} = (D_t/D_0) \times 100 \quad (\text{Eq.1})$$

The apparition of alkaline hydrolysis products (COO^- , OH) was quantified by characterising of its IR absorbance values, which were standardized for a $25 \mu\text{m}$ thickness to make a reliable comparison between immersed and non-immersed samples.

2.4.2. Weight loss of the coating

Weight loss of the coatings (Δm_t) after alkali resistance test was determined as the difference between the weights of the samples (dried in vacuum oven at $60 \text{ }^\circ\text{C}$ until the constant weight) before (m_0) and after (m_t) the immersion process by the following formula [8]:

$$\Delta m_t (\%) = [(m_0 - m_t)/m_0] \times 100 \quad (\text{Eq.2})$$

2.4.3. Adhesion

The adhesion strength of the non-immersed and 20-day immersed coatings to sheets of concrete was determined by using an adhesion tester PosiTest AT, according to ASTM D 4541 standard. The Defelsko Posi Test Pull-Off Adhesion Tester measures the force required to pull a specified test diameter (2 cm in this study) of coating away from its substrate using hydraulic pressure. It evaluates the adhesion (pull-off strength) of a coating by determining the

greatest tensile pull-off force that it can bear before detaching.

3. RESULTS AND DISCUSSION

3.1. Chemical changes of water-borne styrene acrylic coating

Infrared spectroscopy is a sensitive and reliable technique which is widely used to quantify the chemical changes of the degradation process. The alterations of the chemical structure of polymer materials can be determined spectroscopically well

before the observation of physical and optical properties changes [5-6, 8, 11-13]. Figure 1 showed the IR spectrum of a water-borne styrene acrylic coating before and after 20 days of immersion in the alkaline solutions. Some IR characteristic bands of functional groups of this coating were presented in table 1. A quantitative analysis of the IR characteristic bands for this material such as of O-H, alkane C-H, ester C=O, C=O (in -COO⁻), ester C-O- and C₆H₅ groups located at the wavenumbers of 3440, 2945, 1725, 1570, 1170 and 760 cm⁻¹, respectively was carried out and the results were shown in table 1 and figure 2.

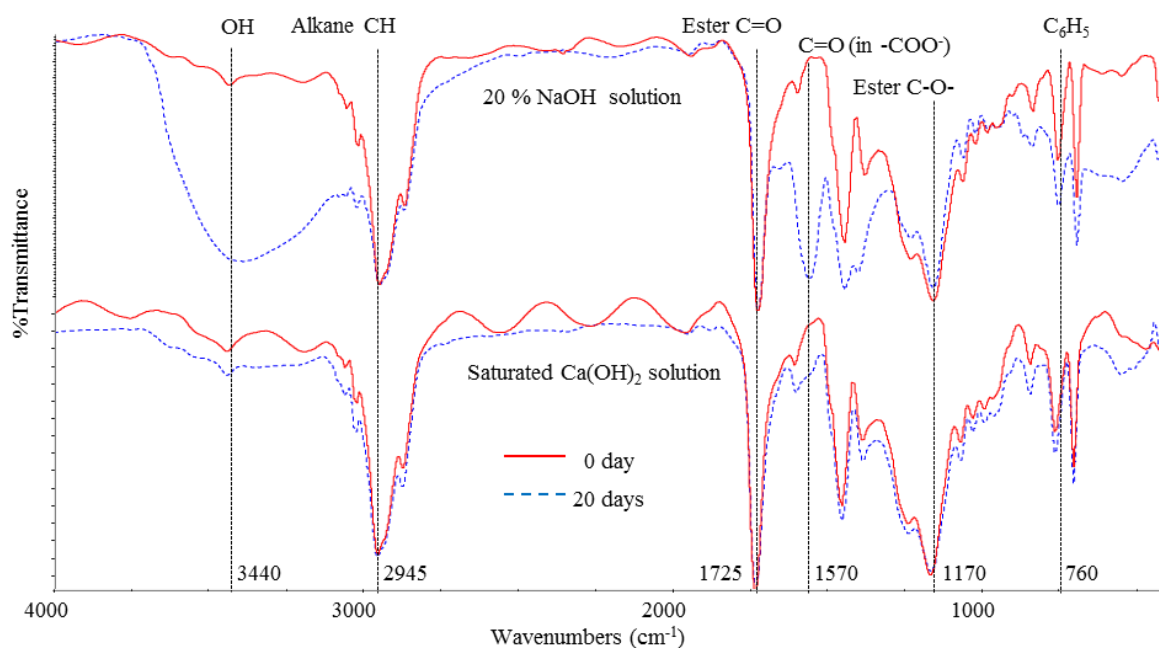


Figure 1: The IR spectrum of water-borne styrene acrylic coating before and after 20 days of immersion in the alkaline solutions

Table 1: Some characteristic infrared absorptions of the functional groups in the water-borne styrene acrylic coating before and after 20 days of immersion in the alkaline solutions

IR band (cm ⁻¹)	Functional group	Immersion in the 20 % NaOH solution			Immersion in the saturated Ca(OH) ₂ solution		
		0 day	20 days	Changes	0 day	20 days	Changes
3440	O-H	+	+	Strongly increased	+	+	Slightly increased
2945	C-H stretching in alkane	+	+	Significantly decreased	+	+	Significantly decreased
1725	C=O stretching in ester group	+	+	Significantly decreased	+	+	Significantly decreased
1570*	C=O stretching in -COO ⁻	-	+	Strongly increased	-	+	Slightly increased
1170	C-O- stretching in ester group	+	+	Significantly decreased	+	+	Significantly decreased
760, 700	C-H in benzene ring	+	+	Significantly decreased	+	+	Significantly decreased

Note: "+": absorption; "-": no absorption; "*": apparition during the immersion process.

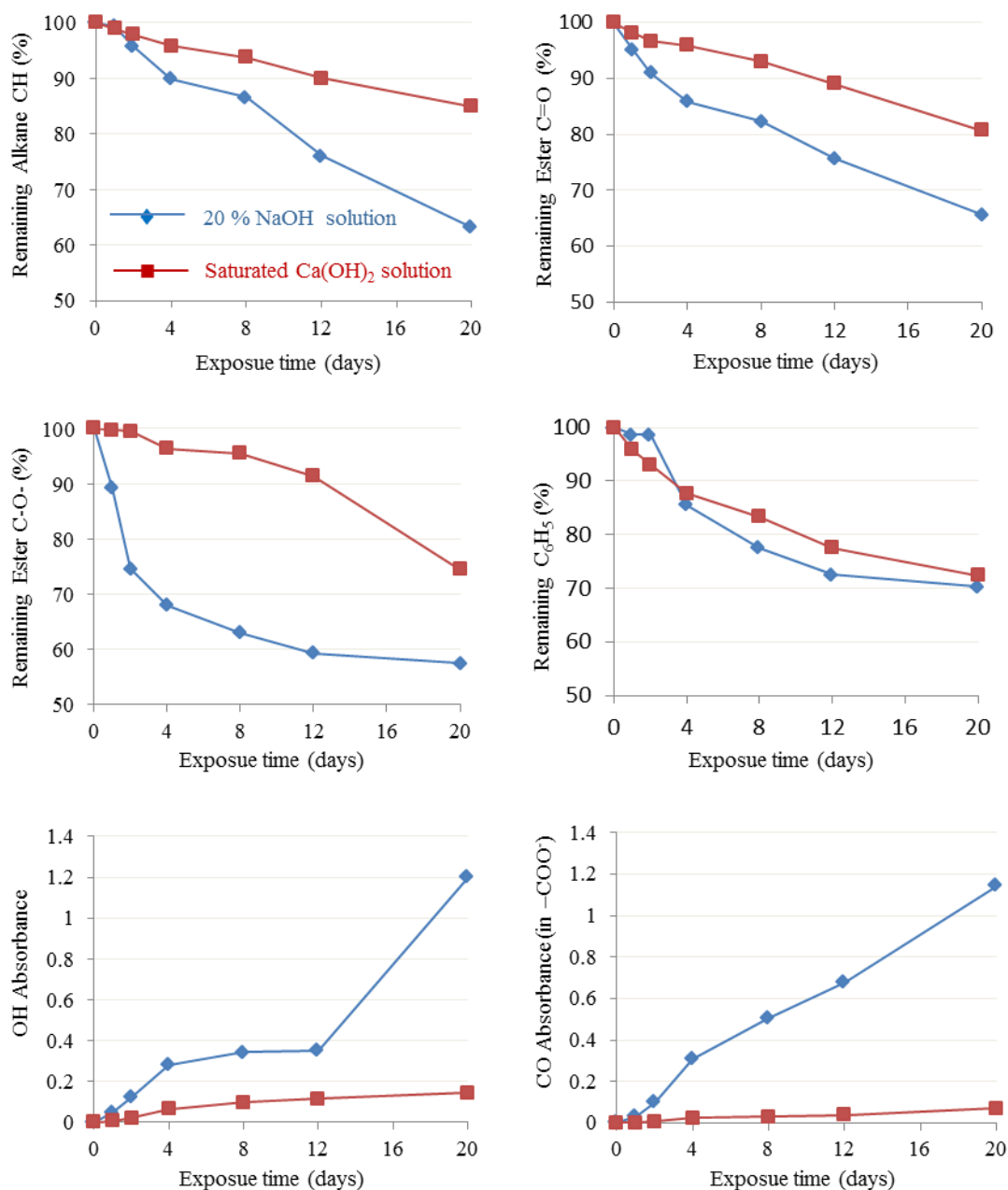


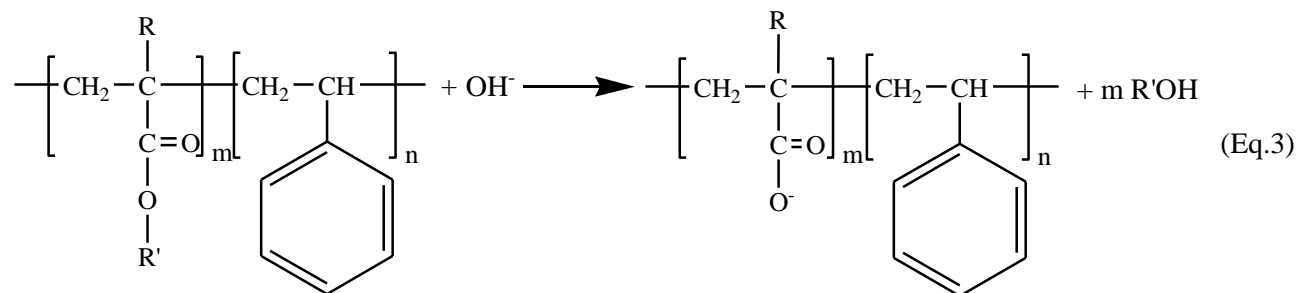
Figure 2: Variation of functional groups of water-borne styrene acrylic coating as a function of immersion time

It can be seen that the intensity bands assigning to the alkane C-H, ester C=O, C-O- and C₆H₅ groups decreased during the test process (figure 2) while the IR bands corresponding to the hydroxyl group (-OH) and carboxyl group (C=O) (in -COO⁻) increased. This figure demonstrates that the C-O- stretching seemed to be largest decreased. The results also showed that the chemical structural groups of coating immersed in the 20 % NaOH solution changed more strongly than that of coating immersed in the saturated Ca(OH)₂ solution. After 20 days of immersion in the 20 % NaOH solution, the alkane C-H, ester C=O, C-O- and C₆H₅ groups

remained 63, 65, 57 and 70 %, respectively while these groups of coating immersed in the saturated Ca(OH)₂ solution remained 85, 81, 74 and 73 %, respectively. The formation of alkaline hydrolysis products (the OH and -COO⁻ groups) in the coating immersed in the former was larger than in the coating immersed in the latter one. The alkane C-H, ester C=O, C-O- and C₆H₅ groups of the coating immersed in the saturated Ca(OH)₂ solution were significantly decreased while the formation of the OH and -COO⁻ groups only slightly increased.

The decrease of ester C=O and C-O- stretchings could be explained due to the occurrence of the

scission of C-O- bond by the hydrolysis reaction of ester groups occurred during the acrylic coating



The hydrolysis process also created the lower molecular compounds such as organic salts ($\text{RCOO}^- \text{Na}^+$ or $(\text{RCOO}^-)_2\text{Ca}^{2+}$), such as alcohols ($\text{R}'\text{OH}$) which can either be washed or evaporate away during the immersion and clearing of the samples. This can be the reason for the decrease of alkane C-H and C_6H_5 groups. It could clearly see that the coating immersed in the 20 % NaOH solution was more strongly hydrolyzed than that immersed in the saturated $\text{Ca}(\text{OH})_2$ solution. The decrease of chemical structural groups of coating immersed in the saturated $\text{Ca}(\text{OH})_2$ solution was mainly caused by coating materials washed away during the immersion process and cleaning of the samples.

3.2. Weight loss of the coating

The degradation of the coating immersed in the alkaline solutions can be investigated by various physical methods, such as discoloration, loss of gloss, cracking, thickness decrease and weight loss resulting from the alkali-induced chemical changes. In this work, besides evaluating the chemical structural changes by IR spectroscopy, the degradation of coating was also assessed by measuring the weight loss of the coating during exposure to alkaline solutions. The weight loss of the coating during their immersion in the alkaline solutions were displayed in the figure 3.

As can be seen from figure 3, the weight of coating decreased with the immersion time. The weight loss of the coating immersed in the 20 % NaOH solution was larger than that of the coating immersed in the saturated $\text{Ca}(\text{OH})_2$ solution. After 20 days of the immersion, the coating lost about 33 and 26 % when it was immersed in the 20 % NaOH and saturated $\text{Ca}(\text{OH})_2$ solutions, respectively. It was not exaggerating to say that this result was

immersed in the alkaline solutions (Eq.3).

compatible with the chemical changes of coating as discussed above and the coating materials were washed away during the immersion and cleaning of the samples were the main cause of the weight loss.

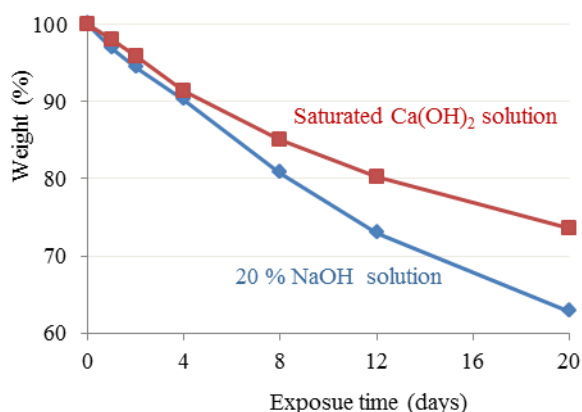


Figure 3: Weight loss of coating as a function of immersion time

3.3. Adhesion changes of coating

Besides monitoring the weight loss of coating, the alkaline hydrolysis degradation of coating was also evaluated through the change of its adhesion to the concrete substrate. Adhesion of water-borne styrene acrylic coating before and after 20 days of the immersion in the alkaline solutions was presented in figure 4.

As can be seen from figure 4, the adhesion of coating decreased after 20 days of immersion. For the sample immersed in the 20 % NaOH solution, the adhesion of the coating reduced from its initial value of 2.8 to the value of 2.1 N/mm^2 after 20 days, which was more than that of the coating immersed in the saturated $\text{Ca}(\text{OH})_2$ solution, reduced from 2.8 to 2.5 N/mm^2 . It is logically expected that the alkaline hydrolysis reaction should be responsible for the above adhesion loss. This reaction occurred in the

coating immersed in the 20 % NaOH solution more strongly than in the coating immersed in the saturated Ca(OH)₂ solution.

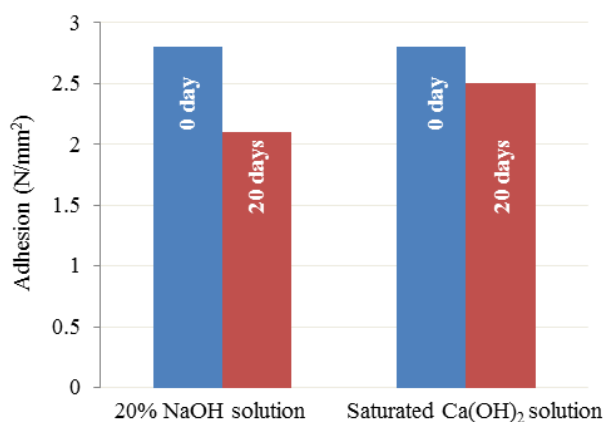


Figure 4: Adhesion of water-borne styrene acrylic coating before and after 20 days of immersion in the alkaline solutions

4. CONCLUSION

The degradation of water-borne styrene acrylic coatings during the immersion in the 20 % NaOH and saturated Ca(OH)₂ solutions was quantitatively investigated by using a IR spectroscopy and by measuring the sample weight and adhesion losses. During the immersion, the functional groups of coating were changed. The alkane C-H, ester C=O, C-O- and C₆H₅ groups decreased. Of which, the C-O- stretching shows the largest decreased. The hydroxyl group (-OH) and carboxyl group (C=O) (in -COO⁻) increased. The functional groups of the coating immersed in the 20 % NaOH solution changed more strongly than those of coating immersed in the saturated Ca(OH)₂ solution. The formation of alkaline hydrolysis products (the OH and -COO⁻ groups) in the coating immersed in the former was larger than in the coating immersed in the latter one. The alkane C-H, ester C=O, C-O- and C₆H₅ groups of the coating immersed in the saturated Ca(OH)₂ solution significantly decreased while the formation of the OH and -COO⁻ groups only slightly increased. These chemical changes results in the weight and adhesion losses of the coating. This work provides some useful information to better understanding on the major mechanisms that control of the alkaline hydrolysis degradation of water-borne styrene acrylic coating.

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