

Influence of Drying Temperature on Protective Properties of Waterborne and Solventborne Epoxy Coatings

Ivan Stojanović*, Ivan Juraga, Vesna Alar

University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture,
I. Lučića 5, 10000 Zagreb, Croatia

*E-mail: ivan.stojanovic@fsb.hr

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One of the major directions in the research of protective coatings is the development of environmentally-friendly waterborne coatings that contain a small amount of volatile organic compounds (VOCs) and protect metals from corrosion in different environments. In this paper, curing and corrosion protection properties of waterborne and solventborne epoxy coatings at three drying temperatures 5, 23 and 35 °C were studied. Curing of coatings was studied by measuring the König pendulum hardness during 21 day of drying at different temperatures as well as by testing the physical properties of coatings (Buchholz hardness, elasticity, impact resistance, adhesion, gloss) dried at room temperature. Corrosion protection properties of coatings were studied by conducting the Electrochemical Impedance Spectroscopy (EIS) in 3.5 % NaCl solution and salt chamber testing. The analysis of the test results has shown satisfactory corrosion protection properties of waterborne epoxy coatings dried at temperature of 35 °C, while at lower drying temperatures certain limitations in their application have been established. The solventborne epoxy coating show stable protective properties at all tested drying temperatures.

Keywords: waterborne coatings, solventborne coatings, drying temperature, pendulum hardness, corrosion protection properties, EIS study

1. INTRODUCTION

Nowadays, corrosion plays a key role in economic, safety and ecological terms, what results in a growing interest in these issues and viable solutions for reducing the corrosion damage by applying an appropriate corrosion protection method. Corrosion causes plant shutdowns, structure and equipment failures, waste of valuable resources, product contamination, loss of efficiency and high maintenance cost [1-3].

Organic coatings are the most commonly used method for combating corrosion by forming a barrier relatively impermeable to moisture and electrolytes necessary for corrosion. There are a lot of challenges ahead of coatings today, because apart from ensuring long-term protection and lower degree of maintenance, they have to meet safety, health and environment protection standards. Modern solutions are environmentally friendly waterborne coatings for corrosion protection, developed to replace organic solvents with water that is inflammable and non-toxic [4-7].

Due to statutory provisions limiting the VOC emissions into the environment, the development of waterborne coatings has been intensified over the last few years [4]. Contrary to solventborne coatings, waterborne coatings contain only a smaller quantity of co-solvents (<5%) necessary for final film forming, whereby the VOC emissions are reduced [6]. Using a waterborne coating system would lead to a 80-90% reduction in solvent emissions to the atmosphere. Among other advantages, it is worth stating their lower toxicity and degree of smell, increased safety of workers, use of conventional application methods and easy cleaning of tools [5, 8].

Waterborne coatings are used for protection of different steel structures, bridges, tanks, pipelines, railway wagons, transport containers, automotive parts, agricultural machines, metal furniture, etc. [8-13]. Nevertheless, their wider application is still absent primarily due to their protection properties which were much poorer in the past and are still insufficiently known today [9].

To implement and widely apply waterborne coatings, it is crucial to thoroughly understand their protection properties and limits to their application in order to ensure a corrosion protection without failures. Considering that in production and application of waterborne resins water is used as a solvent, it should be taken into account that physical properties of water and organic solvents are dissimilar. Water has a high dipole moment and high degree of association. This results in a high boiling point and high latent heat of evaporation, which leads to a longer drying period in cold and humid environments, i.e., significant energy consumption in the form of heat for drying is needed. Additionally, the evaporation rate depends on the vapour pressure difference between water in the coating and the air being circulated over the substrate. This reveals that it is crucial to better control temperature, relative humidity and ventilation during application and drying of waterborne coatings. Due to high dipole moment of water, improper wetting, unsatisfactory edge covering and crater formation on low surface energy substrates (plastic or oily metals) may occur [5, 10-15].

Although the new generation of high molecular weight solid epoxy dispersion, cured with polyamine adducts show equivalent corrosion protection properties with solvent-borne epoxies for most industrial purposes [9], the protection in heavy duty environments is still lagging behind in comparison to solventborne coatings [12, 16].

Ongoing developments and a growing list of their advantages will surely bring waterborne coatings closer to solventborne in the years to come [4, 9, 12].

2. EXPERIMENTAL

In the experimental work two pack solvent and waterborne coating comparative testing were conducted aimed at studying the influence of different drying temperatures on curing time and

corrosion protective properties. The research consisted of periodical monitoring of coating hardness, measuring physical properties of coatings before and after corrosion testing, testing in salt chamber and EIS study. A 21 day drying was conducted at temperatures of 5, 23 and 35 °C in climatic chambers. Before testing, samples were held in room conditions for 24 hours (23±2 °C and RH 55±5%).

2.1 Materials

Table 1 shows the main characteristic of tested epoxy coatings in the study. The study was conducted on 1 solventborne (OT) and 2 waterborne (V1T and V2T) epoxy coatings used for corrosion protection in metal industry.

Table 1. Main characteristic of tested epoxy coatings

Sample mark	Type	Binder	Hardener	Mixing ratio (volume)	Pigment	Volume solids [%]	VOC [g/l]	DFT [μm]	Dry to recoat at 23 °C [h]
OT	solventborne	epoxy	polyamide/amine (for low temp.)	86:14	zinc-phosphate	54	465	60	2
V1T	waterborne	epoxy	polyamine	1:1.2	zinc-phosphate	46	60	60	1.5
V2T	waterborne	epoxy	polyamine	3.6:1	zinc-phosphate	47	40	50	4

For pendulum hardness testing at different drying temperatures according to König, coatings were applied to glass panels of dimensions 100x75 mm by cubic applicator BA45 in wet film thickness (WFT) of 225 μm .

For comparative testing of physical properties of coatings dried at room temperature, coatings were applied by airless spraying on pickled low-carbon steel plates (W. Nr. 1.0347), dimension 75x150x1 mm.

For EIS study and salt chamber testing, coatings were applied by airless spraying in dry film thickness (DFT) of ~150 μm on low-carbon steel plates (W. Nr. 1.0347), dimension 100x150x2.5 mm and \varnothing 16 mm, which were blast cleaned to Sa 2½ (ISO 8501-1) and fine to medium roughness grade (30-85 μm , Ry5) (ISO 8503-2).

Coating application was conducted at room temperature according to the paintmakers' recommendation, while the 21 day drying was conducted at 3 different temperatures 5, 23, 35 °C and constant relative humidity (RH) in climatic chambers.

2.2 Methods

Determination of dry film thickness on samples was conducted by non-destructive magnetic method according to ISO 2808 using Quanix 1500 instrument.

Monitoring of coating curing was conducted by measuring the König pendulum hardness according to ISO 1522. Hardness was measured every 24 hours during 21 days of drying to establish the influence of different drying temperatures (T_s) on the film curing time.

The curing of coatings was additionally studied by measuring the physical properties, i.e., Buchholz hardness (ISO 2815), impact resistance (ISO 6272), elasticity (ISO 1520) and adhesion (ISO 2409) after 24 hours and 7 days of drying at room conditions (23 ± 2 °C and RH $55\pm 5\%$). These tests simulate mechanical stress in the environment such as impacts caused by objects falling on the surface (impact test) or deformations caused by bending and by elongation (a bending test and a cupping test) [17]. The coating gloss was measured with a conventional BykGardner glossmeter with 60° geometry according to ISO 2813.

The characterization of the protective properties of coatings was conducted by electrochemical impedance spectroscopy [18, 19]. EIS measurements were carried out with a Potentiostat/Galvanostat EG&G PAR 378 electrochemical impedance measuring system. The measuring frequency range was 500 kHz to 100 mHz, and the impedance spectra were obtained at open circuit potential (OCP) with a 5mV sinusoidal perturbation. A three-electrode cell arrangement was used in the experiments. A coated metal panel was the working electrode, a saturated calomel electrode (SCE) was the reference electrode and graphite sticks served as counter electrodes. The tested area of working electrode was 1 cm². EIS measurement was carried out after the 1 hour and after 500 hours of immersion in 3.5 wt% NaCl solution, open to the air, at room temperature, (23 ± 2) °C. The data analysis was carried out by the Solartron Z-View 2.2 software.

Coating resistance in salt environment was established by 500-hour salt chamber testing (Ascott cabinet, model 5250) according to ISO 9227. A 5 % neutral NaCl solution that spread in the form of salt fog on samples was used. The temperature inside the cabinet amounted to (35 ± 0.1) °C. During testing, the samples were periodically assessed according to ISO 4628. Cross-cut adhesion was evaluated according to ISO 2409. The salt spray chamber test is used as an accelerated laboratory test for predicting corrosion performance of coatings [10, 20, 21].

3. RESULTS AND DISCUSSION

From comparative results of hardness measurement through 21 days of drying it has been established that waterborne coatings dry slower and have a lower final hardness compared to solventborne coating at drying temperatures of 5 and 23 °C, whereas drying at 35 °C results in equal

curing of both waterborne and solventborne coatings, Figures 1-3. Tested waterborne coatings have equal hardness after 8 days of drying at 5 °C and 1 day of drying at 23 °C. The results of physical properties of epoxy coatings testing at room temperature of 23±2 °C show that a solvent based coating (OT) has a greater hardness after 24 hours of drying compared to the tested waterborne coatings V1T and V2T, whereas with regard to elasticity and impact resistance it is rated in-between coatings V1T and V2T, Figure 4. After 7 days of drying, the hardness of solvent based coatings rises, whereas the elasticity and impact resistance significantly fall. Waterborne epoxy coatings retain their initial properties, Figure 5.

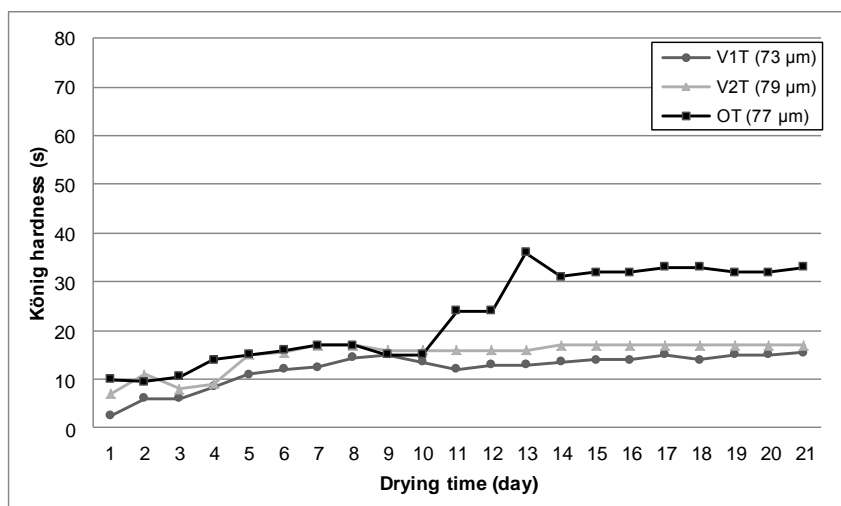


Figure 1. Epoxy coatings curing at 5 °C

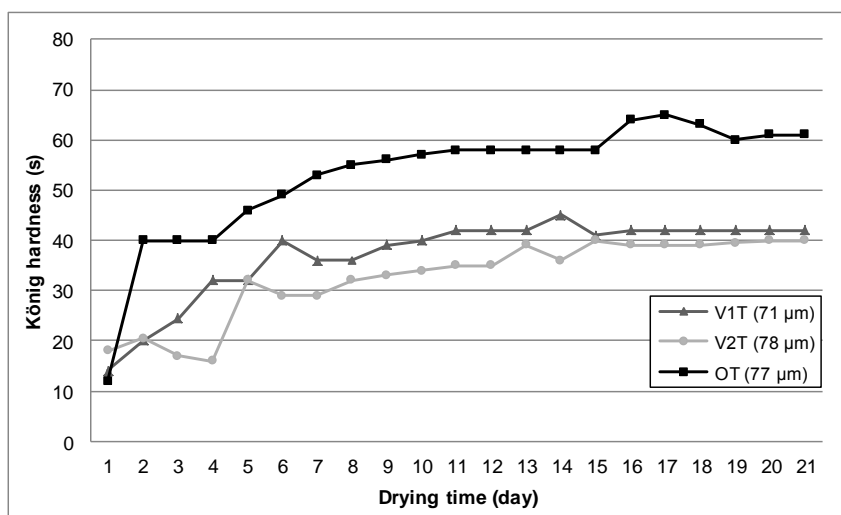


Figure 2. Epoxy coatings curing at 23 °C

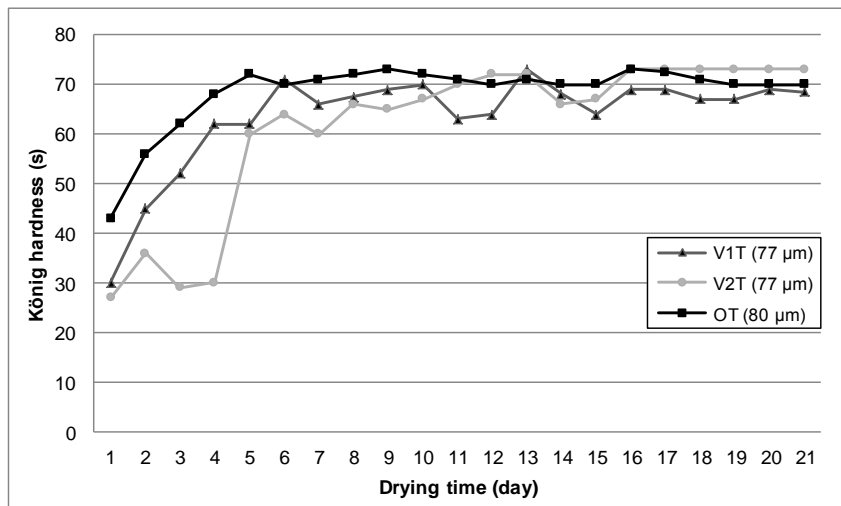


Figure 3. Epoxy coatings curing at 35 °C

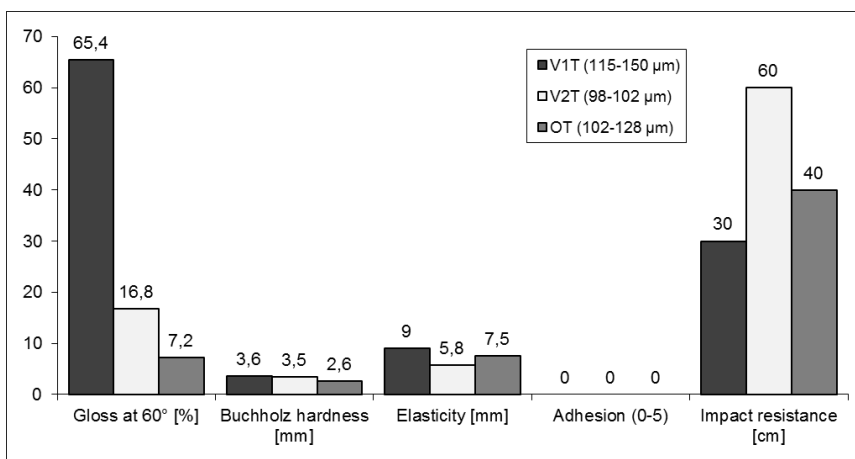


Figure 4. Epoxy coatings physical properties after 24 hours drying at room temperature

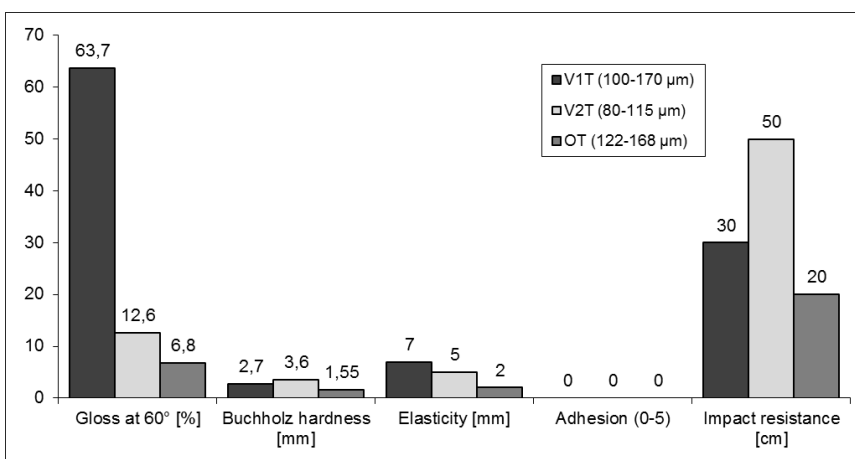


Figure 5. Epoxy coatings physical properties after 7 days drying at room temperature

All tested coatings showed an excellent adhesion ($G_t = 0$ according to ISO 2409) on the first day and after 7 days of drying. Compared to solventborne coatings, waterborne coatings showed a higher gloss measured at 60° according to ISO 2813. In general, all coatings show good appearance before corrosion testing.

The results of EIS analysis after 500 hours of exposure to a 3.5 % NaCl solution (Table 2) show that the V1T waterborne coating has the weakest protective properties at all drying temperatures, visible through a decrease of coating resistance to approximately $10^4 \Omega$, which is below the generally accepted value ($10^6 \Omega\text{cm}^2$) for protective coatings [22]. The coating resistance reflects the ability to resist electrolyte penetration, and may be used to evaluate the protective performance of the coatings [23]. After immersion of 500 hours, the Nyquist spectrum showed a small capacitance arc in high frequency region and a large capacitance arc in low frequency region (two time constant spectrum), Figure 6. The results indicate to porous coating V1T, where the corrosive medium has reached the metal/coating interface [24].

Table 2. The results of EIS measurement after 1 hour and after 500 hours immersion in 3.5 % NaCl solution

Sample	T_s [°C]	t [h]	R_c [Ω]	DFT [μm]
V1T	5	1	$2.2 \cdot 10^8$	150
		500	33000	
	23	1	$2.147 \cdot 10^6$	132
		500	76000	
	35	1	$5.985 \cdot 10^8$	130
		500	49690	
V2T	5	1	$2.0568 \cdot 10^6$	176
		500	996270	
	23	1	427020	254
		500	$2.4462 \cdot 10^7$	
	35	1	$2.9194 \cdot 10^6$	251
		500	$8.8944 \cdot 10^6$	
OT	5	1	$1.5340 \cdot 10^6$	184
		500	$3.2342 \cdot 10^6$	
	23	1	$0.8270 \cdot 10^6$	156
		500	$1.6317 \cdot 10^6$	
	35	1	$2.7605 \cdot 10^6$	167
		500	$3.4862 \cdot 10^6$	

The EIS spectrum of coatings OT and V2T shows the existence of one time constant during the initial and 500 hour exposure to a 3.5 % NaCl solution (Figure 6), which can be related to very good adhesion properties to the substrate [25] and good barrier properties [26]. The V2T waterborne coating dried at 23°C has the greatest coating resistance ($\sim 10^7 \Omega$), but also a greater thickness compared to V1T and OT tested coatings, Table 2.

The OT solventborne coating, at all drying temperatures, shows an increase of coating resistance after 500 hour immersion in the testing solution. Jianguo et al. [24] associate this property with the accumulation of indissoluble corrosion products in coating/composite system which leads to pores closure in the coating, thus preventing further penetration of the corrosive solution to the substrate. The observation of coating resistance increasing trend with the immersion in the 3.5 % NaCl solution was also established by Shao et al. [27] when studying epoxy coating with zinc phosphate pigment. They concluded that zinc phosphate inhibits the corrosion of steel beneath the coating. This finding can be adopted for the epoxy coatings behaviour in this experiment.

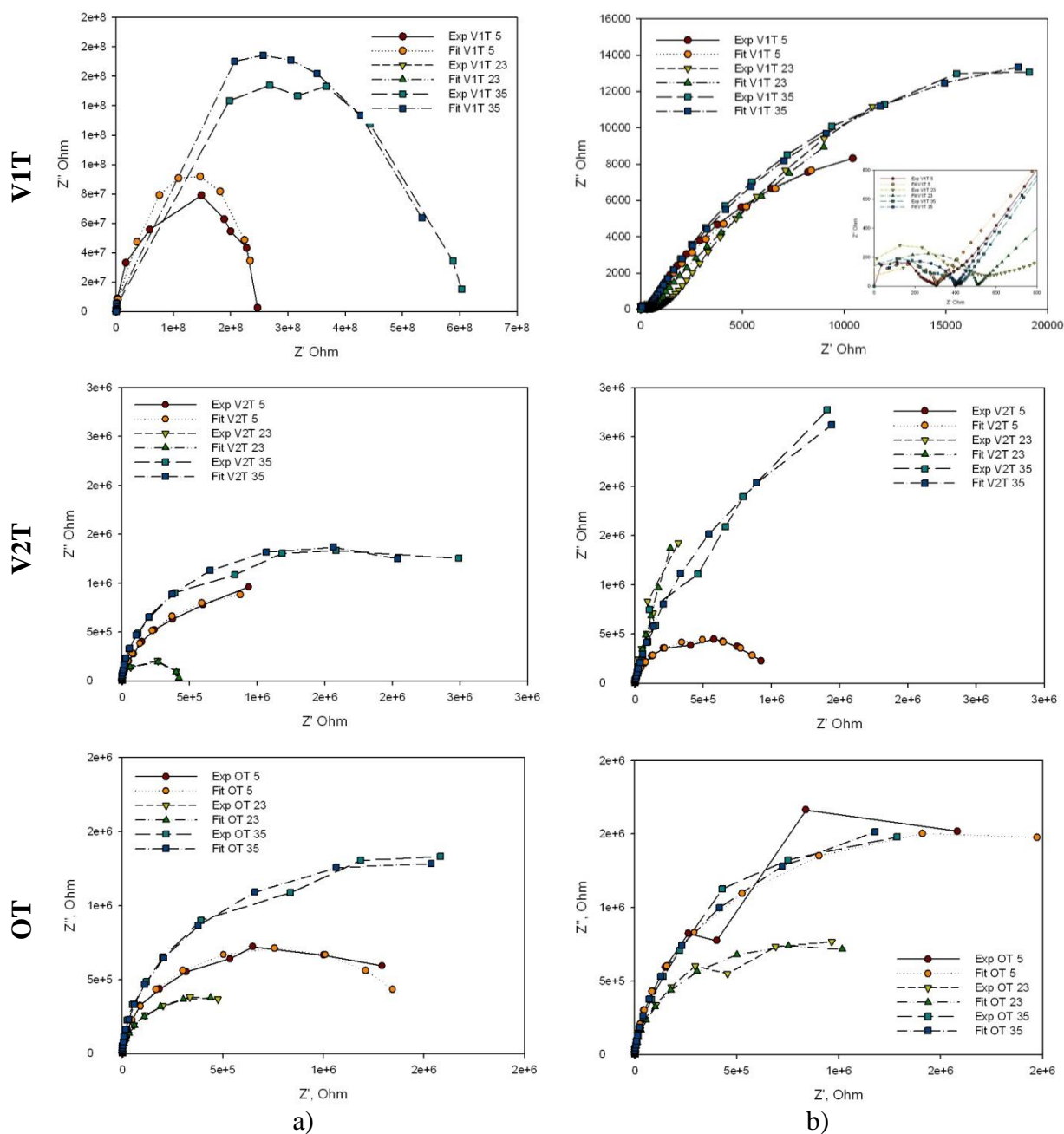


Figure 6. The Nyquist plots of epoxy coatings: a) after 1 hour, b) after 500 hours immersion in 3.5 % NaCl solution

The impedance data of tested coatings were fitted by the equivalent electric circuits shown in Figure 7. The equivalent circuits consist of the solution resistance, R_s , the coating pore resistance, R_c , the charge-transfer resistance, R_{ct} , the coating capacitance, C_c , and double-layer capacitance, C_{dl} .

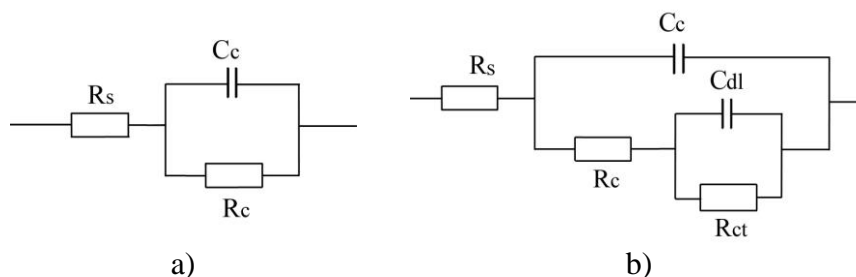


Figure 7. Electrical equivalent circuits for spectrum with: a) one time constant, b) two time constants [24-28]

The influence of drying temperatures of epoxy coatings on their corrosion resistance in the salt chamber during 500 hours of testing is shown in Table 3. At drying temperature of 23 °C, an early surface blistering of V1T waterborne coating appeared indicating a weaker resistance compared to the tested OT solventborne coating. At low drying temperature of 5 °C, the V1T waterborne coating has not shown any defects during salt chamber testing. The temperature below 5 °C presents a limitation to waterborne coatings application [5].

Table 3. Coatings protection properties assessment after 500 h salt spray chamber test

T_s [°C]	Sample	DFT [μm] ISO 2808	Blistering ISO 4628-2			Ri ISO 4628-3	Adhesion ISO 2409
			120 h	240 h	500 h		
5	V1T 12	132	0	0	0	0	0
	V2T 12	47,7	D3S2	D3S2	D3S2	3	2
	OT 11	125	0	0	0	0	1
23	V1T 2	103	0	D1S2	D2S2	1	1
	V2T 3	71,9	D1S2	D2S2	D3S3	2	1
	OT 4	108	0	0	D1S3	0	1
35	V1T 7	142	0	0	0	0	1
	V2T 12	74	0	D1S1	D3S3	1	1
	OT 9	153	0	0	0	0	0

The V2T waterborne coating showed the worst protective properties in salt environment, visible through early surface blistering and rusting (ISO 4628), due to insufficient dry film thickness, $DFT_{\text{min}} = 47.7 \mu\text{m}$. At drying temperature of 35 °C, the V2T waterborne coating showed slightly better protective properties compared to properties obtained at drying temperatures of 5 and 23 °C, which resulted in latter appearance of blistering (after 120 hours) and lower intensity of surface rusting

($R_i=1$). It can be concluded that drying temperature has a strong effect on corrosion resistance of waterborne epoxy coatings.

The OT solventborne coating showed equal resistance stability in salt solution at all drying temperatures. After 500 hours of testing, the coating showed no rusting ($R_i=0$) while blistering was noticed only locally in the form of a single blister on the coating dried at 23 °C.

4. CONCLUSIONS

The study analysis of epoxy coatings curing properties showed that drying temperature has a significant influence on drying time and final hardness. The obtained results of epoxy coatings drying show that there is a need to work with waterborne coatings at elevated temperatures in order to achieve the drying time of solventborne coatings, whereas during winter it is advisable to carry out the first 24 hours of drying at room temperature (workshop or paint shop) and then to expose the structure to outdoor environment in order to enable the waterborne coatings to sufficiently dry for manipulation.

With reference to physical properties analysis the difference in elasticity and impact resistance properties of waterborne and solventborne epoxy coatings indicates a need for longer drying time at room temperature in case of waterborne coatings, what has also been confirmed by hardness monitoring according to König.

The EIS study results show that OT solventborne epoxy coating is stable when exposed to a 3.5 % NaCl solution at all drying temperatures. The V1T and V2T waterborne coatings show greater corrosion resistance at higher drying temperatures. It has been established that the increase of coating thickness leads to better protective properties, in particular in the case of V2T waterborne coating.

The testing results of coatings in salt chamber show better protective properties of solventborne epoxy coating compared to waterborne coatings at drying temperature of 23 °C, whereas at drying temperatures of 5 and 35 °C, waterborne and solventborne coatings, applied in equal thickness, show identical corrosion resistance. It has been established that the tested V2T waterborne coatings applied in an insufficiently thick film layer show poor corrosion resistance.

In all samples an influence of coating thickness on their protective properties in salt environment has been established, where coatings with higher thickness show better corrosion resistance.

This study shows that by increasing the film thickness and by curing at elevated temperatures a higher performance of waterborne coatings can be achieved. However, making the film thicker is in practice of limited value, because possible insufficient evaporation of water and longer drying time may occur.

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