

Influence of weathering factors on durability of polymeric coatings used for concrete protection

1. Introduction

Reinforced concrete structures are used under different environmental conditions and are subjected to an action of aggressive gaseous and liquid media. It leads to their gradual degradation and in consequence to the condition under which further use of the structures is endangered. Even though most structures are well designed and a special material protection has been given, after some time it turns out that this protection is not enough. Carbonation is one of the processes that significantly influences durability of reinforced concrete structures and causes loss of protective properties of concrete for steel. In order to prolong service life of the structures, different types of polymeric protective coatings are commonly used. The most popular are epoxy, acrylic and polyurethane ones.

Such materials must fulfil the following requirements:

- high resistance to carbon dioxide;
- good permeability to water vapour,
- resistance to alkaline influence of concrete substrate;
- good adherence to substrate;
- crack-bridging ability,
- good resistance to colour retention;
- good resistance to impact of oxygen, ultra violet light and variable temperature (weathering);
- appropriate durability (1-3).

Polymeric coatings for protection of the structures should both “breathe” in order to enable water vapour to escape from concrete and make a barrier against aggressive gases, mainly CO_2 , from outdoor environment. Moreover, the materials must be durable in exterior applications.

Environmental factors such as ultraviolet light, moisture, variable temperature, microorganisms and ozone as well as sulphur and nitrogen oxides reduce service life of the coatings. Organic coatings after depositing on well-prepared concrete surface and seasoning usually fulfil requirements concerning so-called barrier properties. These properties include diffusion coefficient D [m^2/s], diffusion resistance R [s/m] and equivalent air layer thickness R_{air} [m] that is

equal to diffusion resistance of coating. It is generally accepted that for proper action of coating value of diffusion resistance for carbon dioxide measured with a R_{air} value should be at least 50 m, while “breathing” coating should have R_{air} value for water vapour less than 5 m (2-5). Unfortunately, even after one year of the service life, some cracks of the coatings applied on concrete can appear.

Apart from meeting the barrier properties mentioned above, the coats must show appropriate adherence to concrete substrate. According to PN EN 1504-9 standard, the minimal values of the adherence depend on type of the coatings. In case of elastic coatings the value should not be less than 0.8 MPa and in case of non-elastic materials, the value ought to be higher than 1.0 MPa, respectively (5).

Polymeric coatings degrade because of different weathering factors. These factors include: solar radiation, presence of oxygen, ozone and moisture, contamination of the atmosphere, elevated temperature, mechanical load and action of microorganisms. The most significant factor is sunlight, whose radiation is high enough to cause cleavage of chemical bonds present in polymers. Nevertheless, other factors play also very important role in the degradation process. Elevated temperature accelerates photochemical processes. The presence of oxygen and ozone induces oxidation processes. The contamination of the atmosphere (acid rains) leads to chemical reactions between polymeric materials and aggressive chemicals. Mechanical factors such as heavy rain, hail etc. also have considerable influence on durability of the coatings (4). Currently more and more attention is drawn to biological factors. Different microorganisms (fungi, bacteria) use polymeric materials as a source of food. Presence of carbonyl groups is beneficial to them, because it is the source of carbon (4, 6). Unfortunately, the action of different factors can take place simultaneously; hence the degradation process is synergistic.

In order to assess properties of the coatings before and after the action of weathering factors, one should choose appropriate diagnostic features. They should include both checking barrier properties and mechanical ones.

2. Experimental part

Two different materials were tested: plasticized epoxy (EP) and polyurethane (PU) coatings. Materials were weathered both under natural and artificial conditions. The specimens were divided into three groups. One series of samples was exposed in Cracow University camp to check durability of coatings under municipal-industrial conditions. Another series was weathered in a mountain weather station in Tatranska Strba (Slovakia). The third series of samples was weathered in a weathering chamber according to ASTM G 154a (7) for 252 cycles. One weathering cycle consisted of 6h of irradiating by UV lamps at $60\pm 3^{\circ}\text{C}$, and then 2 h of sprinkling with distilled water at $40\pm 3^{\circ}\text{C}$. Time of accelerated weathering was 2160 h (3 months). Radiation range was between 295 to 400 nm, which corresponded to UVA+B. Value of radiation was $40\pm 2 \text{ W/m}^2$ and it was also the highest radiation intensity of UVA+B measured during summer in Cracow in 2006.

Coatings tested were either deposited on mineral substrate (concrete) or studied in the form of foils. The following diagnostic features were determined: adherence to concrete, changes in elongation and barrier properties. Moreover, studies of their structure were performed using XRD and FTIR spectroscopy.

Adherence to concrete was checked by means of Dyna 715 device. The tests were performed according to EN 1542:1999 standard (8). The coatings tested were deposited on concrete substrate and seasoned according to guidelines and after 24 hours the tests were done. Fig. 1 shows the apparatus used for adherence tests.



Fig. 1. Apparatus used for adherence tests.

Studies of changes in elongation of coating foils as a result of weathering were done using ZWICK 1445 universal machine according to PN-81/C-89092 standard (9). The coatings were prepared in the form of foils and their thickness was around 140 nm. Then the samples have been prepared using the special device for cutting out samples from polymeric foils as shown on Fig. 2.

Permeability to carbon dioxide was determined in accordance with the RILEM-Cembureau method. The measurements were carried out using the apparatus shown in Fig. 3. Cylindrical concrete samples were used in all tests. The specimens were 150 mm in diameter with the thickness of 50mm. The coatings were deposited on these concrete substrates and seasoned for one week.



Fig. 2. Machine used for cutting out the samples and the picture of sample obtained

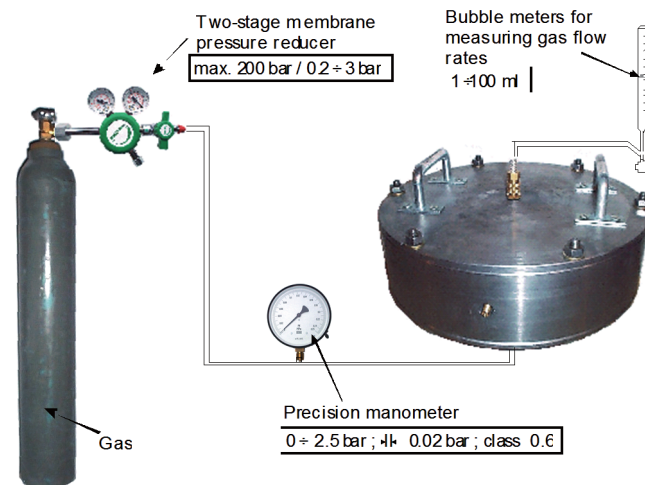


Fig. 3. Scheme of the apparatus for testing the permeability by means of Cembureau method (10)

The XRD tests were performed using Philips PW 1830 device. The study dealt with analysis of EP and PU coatings before and after 252 cycles of artificial weathering. The aim of the study was to check whether, after weathering, any new crystalline phases were formed in the structure of the materials. Moreover, by means of XRD, it was possible to identify different inorganic compounds such as fillers and pigments commonly added to coatings.

FTIR measurements were performed using BIO-RAD FTS 175C device. Spectra of samples were recorded using KBr pastille technique. Initial spectra were compared with spectra of specimens after weathering and then, comparing characteristic functional groups of given coating, an attempt was made to explain changes in the structure of the coats.

2.1. Tests results

2.1.1. Mechanical properties

In case of EP coatings, their adherence to concrete before and after weathering was in the range from 5.0 to 6.5 MPa. PU coatings had also very good adherence, their values varied between 4.8 and 6.5 MPa. No changes of the adherence of coatings tested were

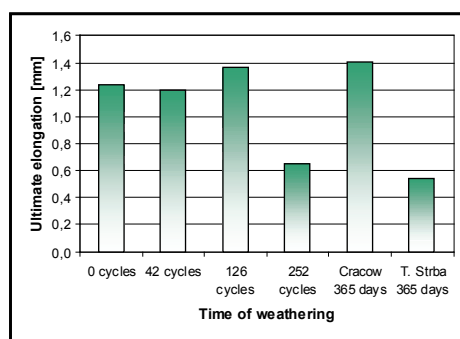


Fig. 4. Ultimate elongation of EP coating before and after weathering

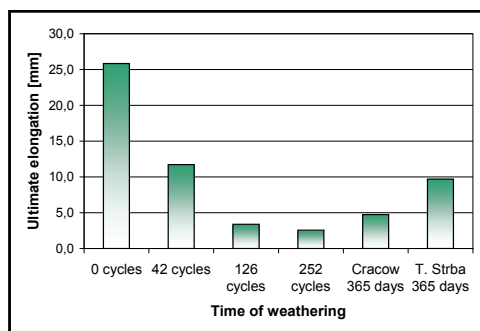


Fig. 5. Ultimate elongation of PU coating before and after weathering

observed during both natural and artificial changes. Adherence of both coatings was much higher than required (5). Deformability was determined during tensile strength tests. Fig. 4 and 5 present test results (mean values).

As a result of weathering of EP coatings, their ultimate elongation did not change significantly in comparison with initial samples apart from the ones weathered for one year in Tatranska Strba and for 252 cycles in the chamber. The reduction of ultimate elongation of the specimens can be explained by the fact that they have been exposed to UV for a long time and epoxy resins are known to be rather poorly resistant to the action of ultraviolet light. In general, the material showed low deformability and weathering caused the significant increase in its brittleness and fragility. These results are confirmed by the pictures presented below, showing numerous micro-scratches after 252 cycles (Fig. 6).

Weathering of PU coatings caused progressing decrease in ultimate elongation regardless of the place of aging. The longer the time of weathering in the chamber, the higher the decrease in the

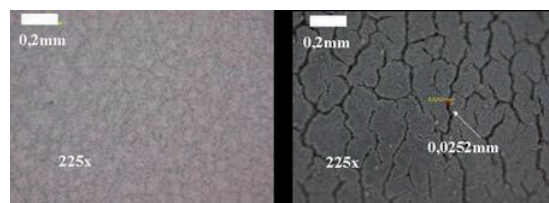


Fig. 6. a) initial EP coating, b) EP coating after 252 cycles

elongation of samples was observed. In the case of weathering under natural environment, more significant reduction of the elongation was noticed for the samples from Cracow than the ones from Tatranska Strba.

The coefficients of variation for EP coatings varied from 11% to 39% and in case of PU coatings the values were 12% and 56%, respectively. The average coefficients of variation for EP and PU sets of samples were 26% and 27%, respectively. Such value can be explained by the fact that the materials tested were very thin. Moreover, EP coatings were very difficult to examine, since they became very brittle as a result of weathering.

2.1.2. Barrier properties

In the case of EP coatings, initial coatings were impermeable to carbon dioxide under conditions tested. The specimen in Slovakia, after one year of aging, did not show any gas flow, either.

The samples weathered in Cracow showed different permeability. Some of them were completely tight, some were permeable to CO₂. It could have been caused by mechanical actions, for instance hail. The Table 1 presents permeability of EP coatings after weathering for one year in Cracow.

Test results of the samples weathered in the chamber are presented in the Table 2.

Accelerated weathering of EP samples caused dramatic increase in their permeability after 126 and 252 cycles. Such a long process led to the total lack of resistance to CO₂ ingress of the material. The samples became very brittle after weathering. The tests results confirm that epoxy coatings are very susceptible to UV action.

Initial samples of PU coatings were also impermeable to CO₂ under conditions tested. The specimen in Slovakia, after one year of weathering, also did not exhibit any gas flow. In the case of samples from Cracow, 4 out of 6 specimens were completely

Table 1

PERMEABILITY OF EP COATINGS AFTER WEATHERING FOR ONE YEAR IN CRACOW

Type of the coating	No.	Permeability	Flux density	Diffusion coefficient	Diffusion resistance	S _d
		m ²	kg/m ² s	m ² /s	s/m	m
1	2	3	4	5	6	7
substrate +EP/Cracow	1,3-5	lack	-	-	-	-
	2	1.55E-21	2.83E-07	3.60E-11	6394442	95.3
	6	2.42E-20	1.92E-06	2.44E-10	942091	14.0

Table 2

PERMEABILITY OF EP COATINGS AFTER WEATHERING IN THE CHAMBER

Type of the coating	No.	Permeability	Flux density	Diffusion coefficient	Diffusion resistance	S_d
		m ²	kg/m ² s	m ² /s	s/m	m
1	2	3	4	5	6	7
substrate + EP/42 cycles	1,2,4-6	lack	-	-	-	-
	3	6.31E-21	5.00E-07	6.35E-11	3621162	53.96
substrate + EP/126 cycles	1	1.47E-20	1.17E-06	1.48E-10	1554450	23.16
	2	2.02E-19	1.60E-05	2.03E-09	113051	1.68
	3	6.46E-20	5.13E-06	6.51E-10	353284	5.26
	4	4.31E-20	3.42E-06	4.34E-10	529926	7.90
	5	2.99E-19	2.37E-05	3.01E-09	76486	1.1
	6	3.66E-20	2.90E-06	3.69E-10	624135	9.30
substrate + EP/252 cycles	1	3.92E-20	3.11E-06	3.95E-10	582919	8.7
	2	3.99E-18	3.64E-04	4.63E-08	4972	0.07
	3	3.81E-18	3.48E-04	4.41E-08	5211	0.08
	4	2.83E-18	2.25E-04	2.85E-08	8067	0.1
	5	1.41E-17	1.28E-03	1.63E-07	1413	0.02
	6	2.85E-19	2.26E-05	2.87E-09	80019	1.2

Table 3

PERMEABILITY OF PU COATINGS AFTER WEATHERING IN THE CHAMBER

Type of the coating	No.	Permeability	Flux density	Diffusion coefficient	Diffusion resistance	S_d
		m ²	kg/m ² s	m ² /s	s/m	m
1	2	3	4	5	6	7
substrate + PU/42 cycles	1-6	lack	-	-	-	-
substrate + PU/126 cycles	1-6	lack	-	-	-	-
substrate + PU/252 cycles	1	1.67E-20	1.52E-06	1.93E-10	1192334	17.8
	2	4.31E-21	3.42E-07	4.34E-11	5299262	79.0
	3	2.44E-20	2.23E-06	2.83E-10	812553	12.1
	4	3.42E-21	2.71E-07	3.44E-11	6677070	99.5
	5	2.47E-21	1.96E-07	2.49E-11	9238380	137.7
	6	1.94E-20	1.77E-06	2.24E-10	1024524	15.3

tight. Two samples showed very small permeability expressed by equivalent air layer thickness equal to 120 and 271m. Test results of carbon dioxide permeability of the samples weathered in the chamber are shown in Table 3.

2.1.3. X-ray diffraction

Diffraction patterns of the coatings are shown below. Fig. 7 and 8 present diffraction patterns of EP and PU coatings respectively, before and after weathering.

XRD analysis of the initial sample showed the presence of BaSO₄ used as filler and TiO₂ which was pigment. No significant difference was observed between the two diffraction patterns above, which indicated that no crystalline phases were formed during weathering.

In the case of PU coatings, Fig. 8, XRD showed the presence of SiO₂, which played a role of filler and TiO₂. Again, there is no difference in shape of diffraction pattern between the initial and weathered samples.

2.1.4. Infra-red spectroscopy

Fig. 9 and 10 present spectra of initial samples and specimens after weathering.

Analysing spectra of the EP coatings one can observe broadening of band ~ 1700 cm⁻¹, which is characteristic for carbonyl groups. Oxidation process leads to the formation of additional carbonyl groups. Moreover, broadening the region may be prescribed to -C=N groups if hardener of the coating was amine.

After weathering of PU coatings, the increase of intensity of band at 1670-1750 cm⁻¹ was observed, which can be connected with both carbonyl group as well as NH-(C=O)-NH present in polyurethanes. Especially the growth of the band was observed for the samples aged in Tatranska Strba, which can be explained by very high UV radiation. As a result of the oxidation process of coatings, one can expect the presence of peroxides that undergo further conversion to aldehydes, acids and amines. Broadening a band at about 1700

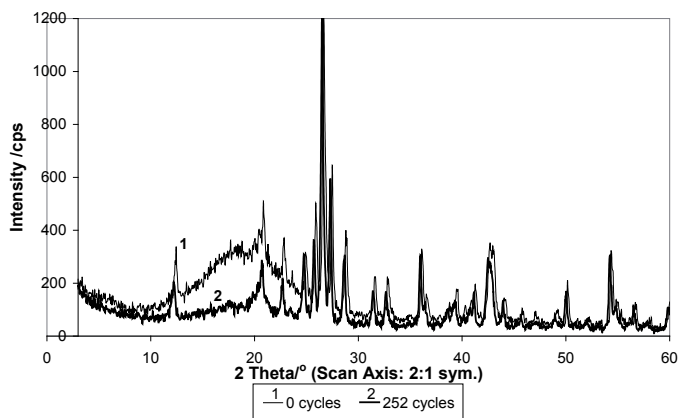


Fig. 7. Diffraction pattern of EP coating before and after 252 cycles of artificial weathering

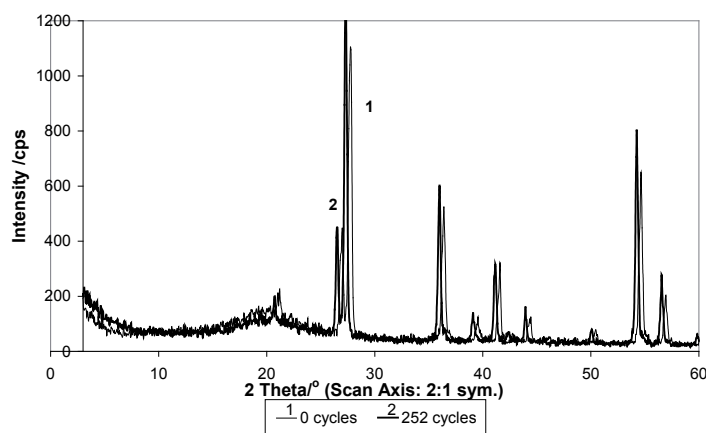


Fig. 8. Diffraction pattern of PU before and after 252 cycles of artificial weathering

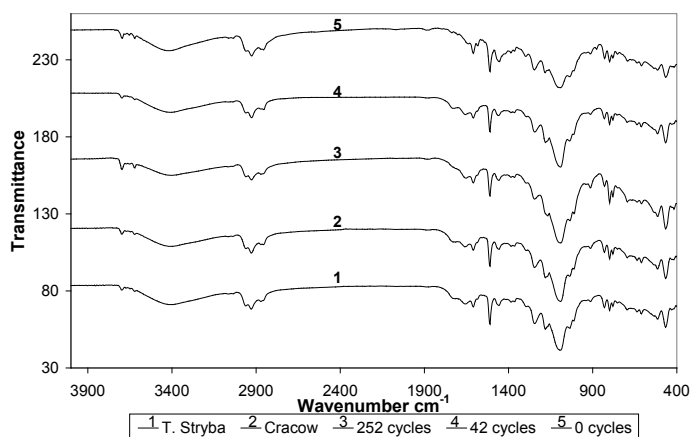


Fig. 9. Spectra of EP coatings before and after weathering

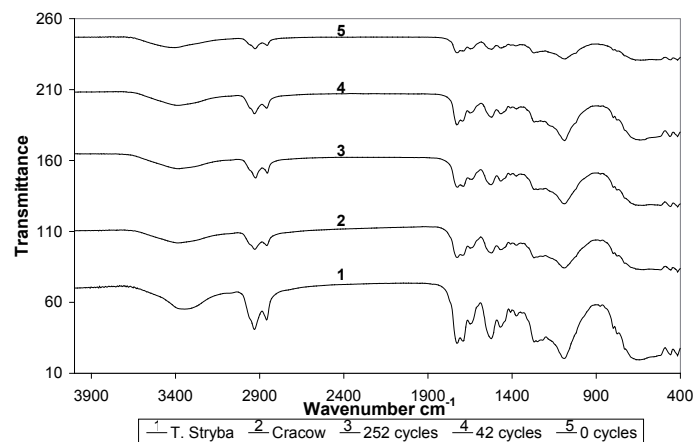


Fig. 10. Spectra of PU coatings before and after weathering

cm^{-1} confirms such suggestion. The length of hydrocarbon chain is connected with elasticity of coating. The longer the chain, the higher the elasticity is. Degradation of the chain causes higher stiffness of structure, which was confirmed in mechanical experiments. Changes in intensity of the band at around 3400 cm^{-1} can be connected with the presence of OH groups connected with alcohols. Changes in $2850\text{-}3000 \text{ cm}^{-1}$ region can be prescribed to CH_3 , CH_2 and CH groups formed as a result of degradation.

3. Conclusions

On the basis of the test results obtained the following conclusions have been drawn:

1. Weathering of elastic PU coatings led to a significant decrease in deformability of the materials. Reduction of elongation was noticed both for samples after natural and artificial aging.
2. Weathering processes did not cause changes in adherence of PU and EP coatings to mineral substrate regardless of the place where weathering occurred.
3. As diagnostic features of weathered coatings, barrier properties determined by manufactures of coatings cannot be the only given parameters and mechanical properties responsible for co-operation among coatings, and protected substrate should also be presented.

4. Both natural and artificial weathering lead to an increase in permeability of coatings tested. Nevertheless, the increase can be caused by higher stiffness of coatings after weathering and formation of micro-cracks.
5. XRD analysis showed that no new crystalline phases formed during weathering.
6. FTIR analysis allowed determining cause of changes of mechanical properties of coatings. It seems that a decrease in deformability was connected with stiffening of structure as a result of oxidation processes and formation of extra carbonyl groups.
7. The test results showed that weathering had much higher influence on the barrier properties of EP coating than on the properties of PU coat. Especially the artificial weathering caused dramatic loss of required properties of EP coating.

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