Degradation of PVC Waterproofing Membrane containing Plasticizers

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Abstract. Durability and repairability are one of the basic conditions for the economically efficient use of building materials. The actual lifetime of PVC waterproofing membrane is not only affected by the ageing of the materials, but also by the ageing of the joints. Thus, a significant phenomenon in the evaluation of the lifetime of roof cladding is its realisation - welding. Plasticizers are used for the production of PVC waterproofing membrane. The migration of the plasticizers and the quantity of non-combustible residues (fillers) influence the service life (durability) and the possibility of subsequent repair. Methods used to determine the quantity of non-combustible residues and quantity of plasticizers are described in the paper. Samples were taken from roofs with degrading roofing layer. Based on the results, the lifetime of the PVC waterproofing membrane was determined in dependence on the plasticizers.

1. Introduction

The issue of ageing of the waterproofing membrane is currently very widespread. The most common materials of waterproofing membrane are bituminous waterproofing membrane and polymerized PVC waterproofing membrane (foils). The issue of material ageing and constructional details in asphalt strips were discussed [1-3]. Ageing of the material and constructional details of polymer foils are based on works [4-5].

In the framework of ageing of waterproofing materials [4], two basic phenomena have been identified which lead to premature destruction of the PVC waterproofing materials. There are plasticizers (plasticizers) and fillers (non-combustible residues). In the case of plasticizers, it is the migration (evaporation) of a substantial part of the plasticisers from the waterproofing membrane. In the case of fillers, this is an increase in the proportion, percentage of mineral fillers in the whole mass or on the surface of the foil materials.

The same destructive effect can be achieved by the correct ratio of the two components. In the case of synergy, very rapid destruction of the plasticized PVC waterproofing membrane occurs within a few years (See Figure 1). Materials of this type will fully survive the warranty provided by the manufacturer. If it is not possible to obtain a 10-year warranty from the manufacturer, it is clear that the materials will survive for a maximum of 5 years. Of course, these materials belong to the lowest price range, which is also the riskiest. The direct proportion applies, the lower the price, the shorter the service life.

For the reasons described above, the samples of plasticized PVC membrane were taken from the roof cladding. The samples were subjected to analysis to determine what was the dominant cause of the collapse of the softened PVC waterproofing membrane.

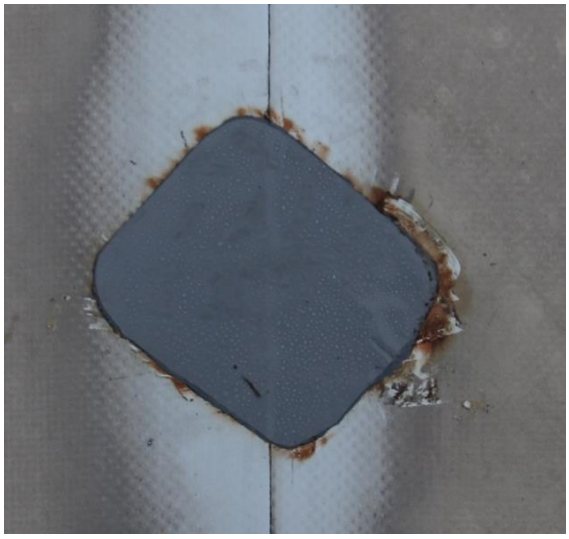

Figure 1. Patch applied to plasticized PVC waterproofing membrane that has already lost a significant amount of plasticizer [6].

2. Material and methodology

This paper is based on samples of the company A.W.A.L. [6]. Within the expert activity, many roofs with PVC waterproofing membrane were inspected and samples of polymeric membrane from softened (plasticizer) PVC were taken. These samples were subsequently analysed. Samples that had already spontaneous radial cracking were subject to inspection (See Figure 2).

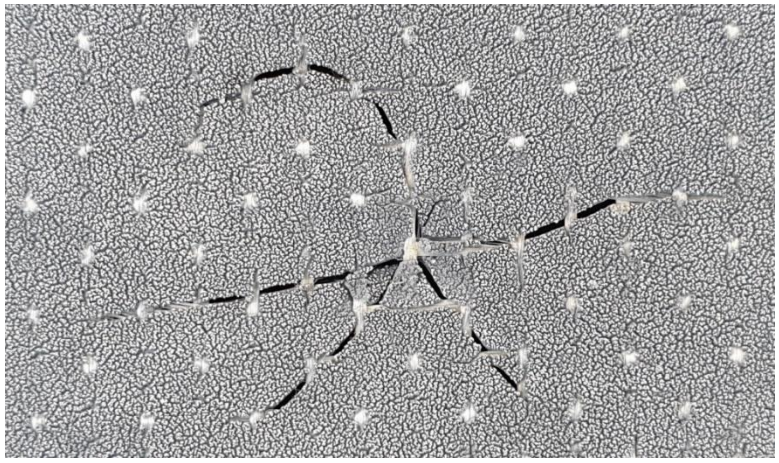

Figure 2. Exposed (uncovered) reinforcement insert on degraded softened PVC waterproofing membrane already showing the brittle fracture [7].

Basic chemical tests were used for all analyses. Specifically, these were IR (infrared analysis), gas chromatography, glass transition temperature analysis and a quantity of non-combustible residues. The paper is further specified by gas chromatography and determination of non-combustible residues. The analyses were carried out in cooperation with the Technical University of Liberec.

IR analysis shows changes in the entire waterproofing mass spectrum relative to any reference sample. The sample is obtained from the overlap of waterproofing, which is not exposed to UV radiation and other climatic stresses. Neglects the natural ageing, i.e. temperature, which affects the acceleration of ageing processes.

Gas chromatography provides quantitative results of a decrease in the volume of plasticizers in the mass of a softened PVC waterproofing membrane. This value is probably the most important and should be monitored. The decline of these values for the standard PVC waterproofing materials is observed.

The samples for analysis were taken from the supplied PVC waterproofing membranes (Figure 3). Each sample was carefully described. One gram of sample, and also a duplicate, was taken from the covered and uncovered part of every waterproofing membrane (together 4 samples of each membrane). Analytical balances Kern ABT 220-4M were used for weighing. Individual samples were cut into strips approximately 1 cm long and 3 mm wide and placed in 10 ml test tubes. Methanol (99.9%) was used as the extraction solvent. The volume of solvent added to the extracted sample was 10 ml. The samples prepared in the test tubes were placed on a horizontal back and forth shaker GFL 3006 and shaken for 70 hours. Subsequently, all samples were filtered using a glass syringe and 45 µm CHS Filterpure Syring Filtres filters. Because of the high sensitivity of the analyzing machine, samples were diluted 1000-fold before analysis.

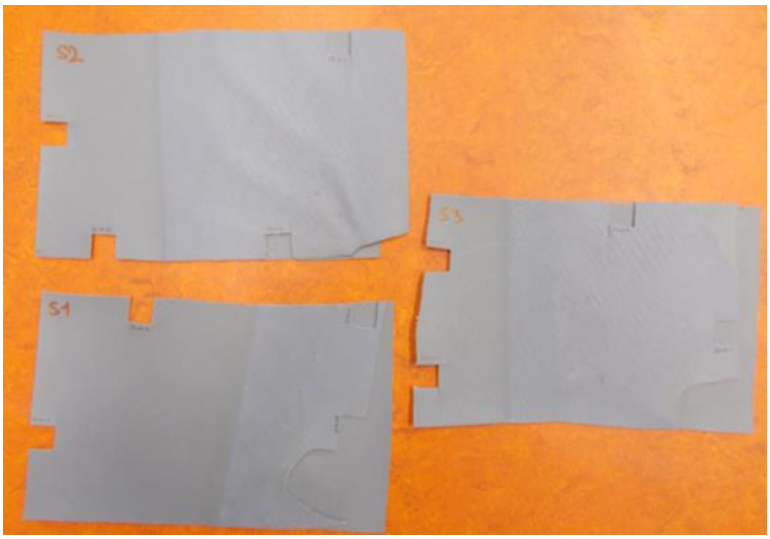

Figure 3. Analysed samples of waterproofing membrane from softened PVC [6].

Thermo Trace 1310 gas chromatograph with TSQ 8000 Triple quandrupole MS mass spectrometer was used to determine quantity of plasticizers. For separation, a chromatographic column DB-5MS was used with parameters: length 30 m, diameter 0.25 mm and a film thickness of 0.25 µm with a temperature limitation of 325°C/350°C. A liquid sample injection (1.0 µl) was injected by an autosampler PAL LHX-XT. The temperature mode of the gas chromatograph furnace was an initial temperature of 100°C, followed by a temperature gradient of 10°C per minute to 300°C, which has stabilized for 12 minutes. Minor oscillations of the MS system are removed by adding deuterated internal standard (ISTD - di-2-ethylhexyl phthalate D4) to all measured extracts.

The parameters of the measurement method were: ion source temperature 200°C, temperature transfer line 250°C, injection temperature 250°C and a carrier gas (helium) flow rate of 1 ml per minute. First, full-scale measurement of samples was performed, where all masses in the range of 35 to 500 m/z were scanned (m/z indicates the ratio between mass and charge and it is thus possible to identify

individual substances). Based on the measured spectra and comparison with the NIST library, it was determined that probably the majority of the extracted component was diisooctyl and diisodecyl phthalate in all of the tested waterproofing membranes. Subsequently, the measurement method was modified with a focus only on the phthalate-specific mass 149, and the prepared extracts were analyzed and the mass 153, which is specific for the added internal standard.

Non-combustible residues, this test determines the quantity of the fillers in the tested material. A certain amount of mineral filler is in each film material, there they stabilize and improve technological and some technical properties, i.e. they are necessary. However, the amount depends on the entire composition of the waterproofing material. For plasticized PVC waterproofing membrane, the quantity of the fillers should not exceed 10%, which is a limit value where good quality waterproofing membrane can function properly in the long term [4-6]. The larger amount of fillers has a negative impact on the service life, but mainly on welding. The more filler in the surface layers, the worse the membranes are to weld. Above 10% this welding is already very risky [7].

The analytical balances Santorius BP110s were used to measure the sample weight. For each sample of welded foils, the content of non-combustible residues was monitored from two sampling - in the covered and uncovered parts of the bottom membrane material. The necessary parts of the membrane materials were separated from the tested waterproofing membrane. These were placed in pre-annealed ceramic crucibles (750°C), where the waterproofing membrane weights were in the range of 0.5 - 0.8 g. This weight corresponded approximately to a 20 x 20 mm area of the waterproofing membrane. The samples were then burned in an electric furnace (Nabertherm B180, Nabertherm, Germany) at 700°C/1.5 hours with air inlet. Ceramic crucibles, along with non-combustible residues, were left in the desiccator to cool freely to room temperature. The content of non-combustible residues was determined from the weights.

3. Results

The quantity of non-combustible residues is higher for the uncovered sides of the membranes than for the covered sides. The quantity of non-combustible residues on the covered sides was approximately 10.6%. The quantity of non-combustible residues on the exposed (uncovered) sides was approximately 12.1% (see Table 1).

Table 1. The quantity of non-combustible residues [6].

Sample	Sampling	Sample weight [g]	Weight of non-combustible residues [g]	Non-combustible residues [%]	Mean non-combustible residues [%]
S1 covered	1	0.7203	0.0769	10.68	10.75±0.140
	2	0.7119	0.0770	10.82	
S1 uncovered	1	0.5933	0.0702	11.83	11.94±0.223
	2	0.613	0.0739	12.06	
S2 covered	1	0.7659	0.0825	10.77	10.73±0.082
	2	0.7596	0.0812	10.69	
S2 uncovered	1	0.5968	0.0722	12.10	12.22±0.254
	2	0.5829	0.0720	12.35	
S3 covered	1	0.7581	0.0811	10.70	10.25±0.896
	2	0.7621	0.0747	9.80	
S3 uncovered	1	0.5853	0.0701	11.98	11.98±0.007
	2	0.5958	0.0714	11.98	

Calibration was not necessary for the relative comparison of the plasticizer (phthalate) content. The results are represented by the ratio between the measured area of the analytes on mass 149 and the area of the internal standard measured on mass 153, see Table 2. Table 3 shows the calculated percentage decreases in the content of diisooctyl phthalate and diisodecyl phthalate in the uncovered parts of the membrane versus the covered parts. The ratio of the area of the analytes to internal standard express the measured concentration. The higher the ratio, the greater the concentration in the sample.

Table 2. Calculated mean ratios of measured surfaces of analytes vs. ISTD [6].

Sample	The ratio of diisooctyl phthalate/ISTD	Measured area of diisodecyl phthalate/ISTD
S1- uncovered	6.7	35.9
S1-covered	11.2	90.7
S2- uncovered	6.3	43.4
S2-covered	12.2	116.9
S3- uncovered	7.0	60.6
S3-covered	12.7	118.6

Table 3. Calculated decrease [%] of plasticizers in the exposed (uncovered) parts of the membrane vs the covered parts [6].

Sample	Decrease of diisooctyl phthalate	Decrease of diisodecyl phthalate
S1	40.7	60.4
S2	48.0	62.8
S3	45.3	48.9

The presence of plasticisers was detected using the gas chromatograph Thermo Trace 1310 with TSQ 8000 Triple quandrupole MS mass spectrometer. Based on the measured spectra and comparison with the NIST library, it was determined that these were plasticizers diisooctyl phthalate and diisodecyl phthalate. Both plasticizers were included in all supplied samples of waterproofing membranes S1, S2 and S3. The decrease in the diisoocyl phthalate content ranged from 41 to 48% in the covered parts of the membrane compared to the uncovered parts of the membrane. The lowest decrease was observed in PVC waterproofing membrane S1 and the greatest decrease was observed for PVC waterproofing membrane S2. The loss of diisodecyl phthalate ranged from 49% to 63% in the covered parts versus the uncovered parts of the waterproofing membrane. The lowest decrease was found in membrane S3 and the largest decrease was found in membrane S2. The greatest decrease of both plasticizers was measured in PVC waterproofing membrane S2 (48 and 63%).

4. Discussion

Dependence of durability (functionality) of synthetic membranes on the loss of plasticizers can be determined in the evaluation of the statistics that are currently available. However, the condition is that the amount of fillers remains below 10%. In the case of a significant increase in the percentage of plasticizers, the durability will also be reduced below the limits stated here.

Figure 4 shows the results of dozens of laboratory tests of waterproofing membranes made of softened PVC. The tests were aimed at decreasing the percentage of plasticizers in the mass of the waterproofing membrane itself and the occurrence of cracks (spontaneous) or hail damage. Based on the analysis of the results, the risk of a decrease plasticizers between 20 - 30% (yellow rectangle) is assumed. In the case of a higher decrease of plasticizers, the cracks of the investigated waterproofing membrane materials have always been identified. The lifetime (durability) of a particular waterproofing membrane can be estimated depending on the decrease of quantity plasticizers. Red-coloured area shows

safe behaviour of membranes during aging. The blue area shows the risk (very dangerous) behaviour of the membranes during aging.

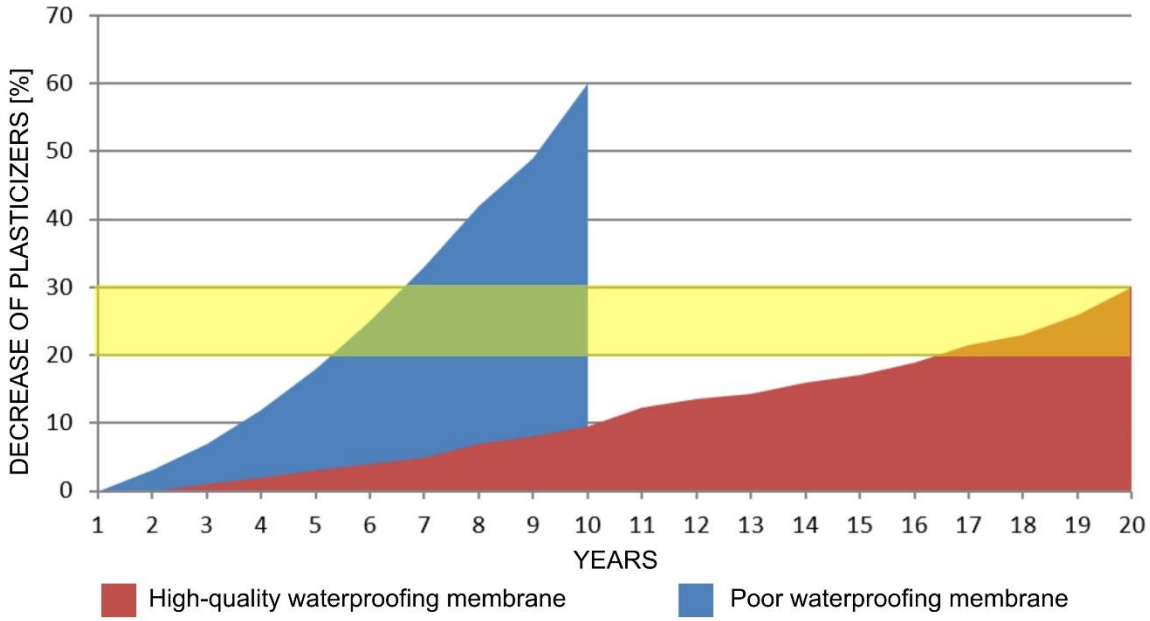

Figure 4. The lifetime of synthetic mPVC waterproofing membrane depending on the decrease of plasticizers [6].

5. Conclusions

The decrease quantity of plasticizers (compared to the overlapped material) can be observed in units of percent in the case of high-quality waterproofing membranes made of softened PVC, which will survive without problems for 20 - 25 years. On the other hand, in the case of defective waterproofing membrane materials, it is possible to observe a decrease of plasticizers by up to 60% in 10 years. This was always a collapse condition and the waterproofing material was plank and very brittle. Manipulating such material was impossible because it immediately cracked. The limit of quantity of fillers in softened PVC waterproofing membranes was confirmed. The quantity of the fillers should not exceed 10% if the service life is assumed. These underlying causes are the loss of sufficient technical properties to withstand the usual climatic stress and impossibility of repairs (i.e., the inability of the waterproofing membranes for further welding).

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