IPaintS - Intelligent coatings for concrete structures: immobilization of pH indicators on coating membranes

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Abstract. In Portugal and over the world, a significant number of concrete structures face challenges due to expansive chemical reactions, such as the alkali-silica reaction (ASR). These reactions have been shown to cause various types of damage, with microcracking being the most common, resulting from internal stresses created by the expansion of reaction products. It is well-documented that, over time, these microcracks can develop into significant fissures due to the hygroscopic nature of these products, which accelerates concrete degradation and potentially compromises structural integrity. One key aspect of ASR products is the presence of alkaline hydroxides in the gel formation process, resulting in elevated pH levels. When this gel reaches the concrete carbonated surface, a change in pH occurs. Based on this premises, the project IPaintS was undertaken to develop a coating that could detect the formation of ASR products on concrete surfaces by identifying variations in pH. This paper presents the results of the preliminary tests conducted, specifically the tests performed to confirm the possibility of immobilising pH indicators in a coating membrane and assess performance characteristics of the functionalised coating. Results show the effective immobilization of a pH indicator on a coating membrane without the loss of some fundamental properties of both the indicator and the coating membrane.

1 Introduction

Concrete is made of compounds that interact in complex ways, such as aggregates, water, additives and a binding agent (cement and other cementitious materials). Considering that aggregates make up the largest portion of concrete (about 75%), it must be chemically neutral and have adequate properties. The presence of amorphous or reactive silica, which reacts with alkalis present in cementitious materials, such as Na and K, promotes a destructive reaction of the concrete structure. This reaction is widely known as alkali-silica reaction (ASR), and it is the most recurrent and rapidly developing type of alkali-aggregate reaction (AAR) [1].

The degradation of concrete due to ASR represents a significant global challenge, as it diminishes its strength and stiffness and disturbs its internal forces [1, 2]. As the reaction proceeds, a gel is formed, which undergoes an expansion process as it adsorbs water from the concrete pore solution. Thus, its volume increases and its diffusion through the concrete occurs, until the gel reaches the surface of the structure [3].

Concrete typically exhibits a highly basic pH of approximately 13 during its initial phase. However, reactions between atmospheric carbon dioxide (CO_2) and alkalis in concrete rapidly reduce pH values on exposed surfaces to close to 8.5, in a process known as carbonation [4-5]. In the research conducted by Sutter et al. [6], a protocol for identifying possible causes of materials-related distress (MRD) was developed. This protocol involved the use of phenolphthalein in a staining test in which non-carbonated cement pastes were stained magenta, while carbonated pastes were not stained.

The presence of alkaline hydroxides in the gel formation by ASR results in a high pH, which can vary between about 10.9 and 12.7 depending on its composition [7]. Therefore, as the gel reaches the carbonated surface, there is a change in the pH of this surface.

Despite the availability of many pH indicators, such as phenolphthalein, for utilisation in pH sensors, there are recognised difficulties in this application, including a restricted range of pH indication and the instability of indicators. Thus, the development of an optical sensor based on pH-sensitive reagents requires a suitable substrate on which the indicator will be immobilised, avoiding such problems [8-10].

Several studies obtained favourable results for the immobilisation of acid-base indicators, including phenolphthalein [8-15].

Islam and Alshoaibi [15], evaluated the immobilisation of phenolphthalein in zincite-supported silica-anatase nanocomposite (ZSAC) synthesised by

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the sol-gel method. They verified a fast colour response of the indicator, a result also obtained by Liu, Luo & Chen [9] and Zhang et al. [13]. In the study by Liu, Luo & Chen [9], the covalent immobilisation of phenolphthalein in a cellulose membrane was investigated. It was found that this process resulted in a change in the behaviour of the indicators, as evidence by an expansion in its pH range to higher values. Zhang et al. [13] also observed the same phenomenon in the covalent immobilisation of phenolphthalein through a Mannich reaction.

This phenomenon was also identified by Sukhanov et al. [10] and Bacci et al. [8] in the immobilisation of other acid-base indicators. Sukhanov et al. [10] conducted a study to evaluate the adsorption of azo indicators, single base sulfonephthalein indicators and double base sulfonephthalein indicators in a polymethacrylate matrix. Bacci et al. [8], who studied the immobilisation in a polymeric matrix of the indicators bromothymol blue (BTB), phenol red, chlorophenol red (CPR) and alizarin, explained such behaviour by the multilayer adsorption of some indicators.

El-Nahhal et al.[12], immobilised phenolphthalein in transparent monolithic silica by means of sol-gel reactions catalysed by tetraethylorthosilicate acid. This process was verified by UV=Vis spectra, which demonstrated that phenolphthalein retained its structure during the reactions in terms of response to pH.

Based on the above, the project IPaintS was undertaken to develop a coating that could detect the formation of ASR products on concrete surfaces by identifying variations in pH. In this paper, preliminary results are presented for the immobilisation of an acid-base indicator (phenolphthalein) within a membrane, aiming to assess whether the indicator retains its activity and if the membrane preserves its original properties.

2 Materials and methods

2.1 Materials

Phenolphthalein (CAS 77-09-8, Acros Organics, ACS Reagent) was used as an acid-base indicator to be immobilised. Three solutions were prepared in different solvents: cyclohexanone (C6H10O, ≥98%, CAS 108-94-1, Fisher Chemical), 2-methyltetrahydrofuran (C5H10O, ≥99%, CAS 96-47-9, anhydrous, stabilized, Thermo Scientific Chemicals) and 2-butanone (≥99.5%, CAS 78-93-3, AnalaR NORMAPUR® ACS Reagent). The selection of such solvents was made after the testing of the solubility of phenolphthalein, with the objective of avoiding nitrogenous compounds or compounds that contained hydroxyl groups, which have been shown to interfere with the immobilisation reaction due to their high reactivity with the immobiliser. The solutions were prepared with the aim to achieve the highest saturation levels, and, thus, the mass percentages that were attained were 23.46% for cyclohexanone, 15.68% for 2-methyl THF and 13.80% for 2-butanone. In this study, DESMODUR Eco N 7300 (CAS 1976005-08-9) was used as the immobiliser.

2.2 Methods

2.2.1 Immobilisation reaction

The immobilisation reactions were conducted between a triisocyanate (Desmodur Eco N 7300) and the commercial pH indicator: phenolphthalein, diluted in one of three solvents (cyclohexanone; 2-methyl THF and 2-butanone) and introduced via a decantation funnel. In order to prevent leaching, as well as any potential environmental contamination, a condenser was attached to minimize the loss of volatile components. Once the indicator was fully added, reactions were maintained under inert atmosphere and continuous stirring (200-250 rpm) for a period of 48 hours.

For each reaction, a 1:1 molar ratio between the indicator and the chosen triisocyanate was maintained. Additionally, saturation tests were conducted for phenolphthalein and the chosen mass percentage (%m/m) is presented in Table 1.

In order to assess the effectiveness of the immobilisation process, Fourier transform infrared spectroscopy (FTIR) analysis was performed for each of the reaction's product on a PerkinElmer Spotlight 200i FT-IR Microscopy System. Four scans were performed at wavelengths from 4000 to 1000 cm^{-1}, at room temperature.

Table 1. Mass fraction (%m/m) used for phenolphthalein dilution.

Solvent	Mass fraction (% m/m)
Cyclohexanone	~35
2-methyl THF	~18
2-butanone	~15

2.2.2 Functionalized Coating Membrane Formulation

For this study, several coating membranes were selected (Table 2) and functionalised products were added in the proportion of 1% m/m to formulate the functionalized coating membranes.

In the pursuit of a comprehensive evaluation, a series of physical and chemical assessment was performed on the different formulations. In Table 3 a brief description of the ongoing experimental campaign is presented. For better characterization, tests were performed both before and after the addition of functionalized products.

In addition, lixiviation tests were conducted by keeping the coating formulations applied in acrylic supports (specimens of 10 cm × 5 cm) in contact with distilled water for a period of 45 days at room temperature. After this time, filtration was performed, followed by lyophilization to remove the water. Quantification of the indicator released from the membrane surface was performed by liquid chromatography-mass spectroscopy (HPLC-MS/MS).

Table 2. Designation and chemical nature of the tested coatings.

Coating designation	Chemical nature
M4.1	Aqueous "cross-linked" dispersion of an acrylic copolymer - version 1
M4.2a	Aqueous "cross-linked" dispersion of an acrylic copolymer - version 2
M4.2b	Aqueous "cross-linked" dispersion of an acrylic copolymer – derived from version 2
M5	Aqueous acrylic dispersion modified with polyurethane (hybrid system)

Table 3. Performance evaluation of the intelligent coating before and after the application of functionalised products.

Experimental Study	Standard	Ref.
Water vapor permeability	EN ISO 7783	[16]
Water permeability	EN 1062-3	[17]
Carbon dioxide permeability	EN 1062-6	[18]
Chloride permeability	LNEC E 468	[19]
Crack-Bridging	EN 1062-7	[20]
Pull-off tests	EN 1542	[21]

3 Results and discussion

The immobilisation reaction of phenolphthalein in cyclohexanone solution was unsuccessful, due to the solidification of the solution which rendered the desired application impossible. The other solvents were suitable, and the reaction was found to be satisfactory.

3.1 Immobilisation reaction

3.1.1 FTIR

The FTIR of the immobilised phenolphthalein in each reaction was aligned with its reagents, in order to facilitate the comparison of the peaks present in each one (Figures 1, 2 and 3). The identification of peaks was conducted on the basis of IR spectrum tables, with the analysis conducted in accordance with the frequency range specified in [22].

FTIR analysis revealed the presence of chemical bonds such as O-H, C-O, C=C, C=O and C-H, indicative of the phenolphthalein. Analysis of the triisocyanate (Desmodur Eco N 7300) spectrum also clearly showed the bonds present in the compound, such as C=O, C-H and N=C=O, the latter being essential for its characterization as an isocyanate.

The analyses related to the reaction products allowed identifying the formation of a polyurethane. This outcome was based on the verification of the peaks: N-H related to secondary amines and urethanes, N=C=O related to isocyanates, C=O and C-O, both related to urethanes.

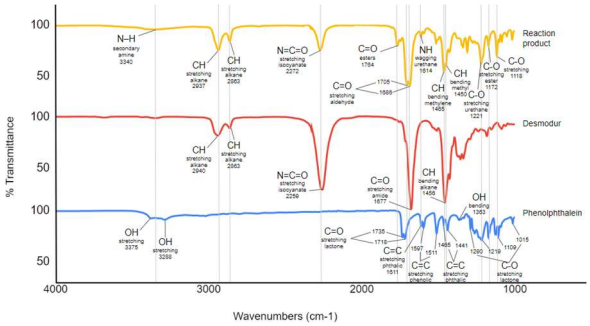

Fig. 1. Infrared spectrum of the reaction between triisocyanate (Desmodur Eco N 7300) and phenolphthalein in cyclohexanone solution.

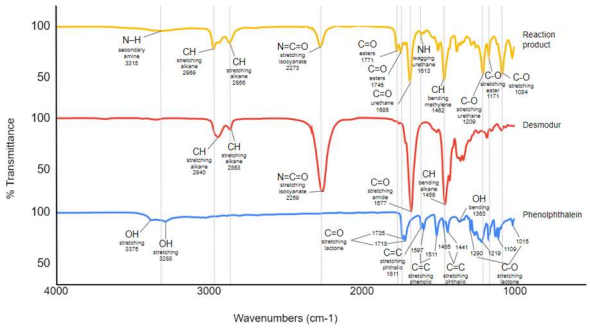

Fig. 2. Infrared spectrum of the reaction between triisocyanate (Desmodur Eco N 7300) and phenolphthalein in 2-methyltetrahydrofuran solution.

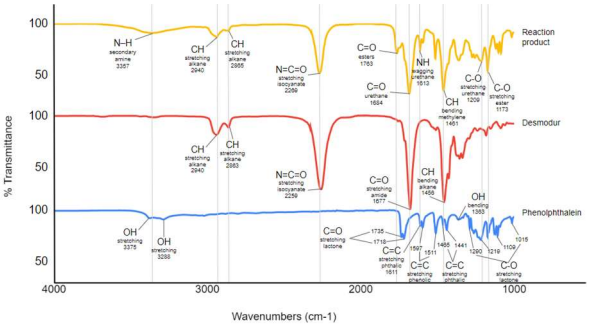

Fig. 3. Infrared spectrum of the reaction between triisocyanate (Desmodur Eco N 7300) and phenolphthalein in 2-butanone solution.

3.2 Functionalized Coating Membrane Formulation

Table 4 presents the results of the performance evaluation for three of the selected non-functionalized coating membranes. Based on water vapor permeability test results for membrane thickness of 200 and 250 µm, the coatings studied can be categorised as Class I {s_D (diffusion-equivalent air layer thickness) < 5m according to EN 1504-2 [23]}, meaning they are all permeable to water vapor. Among them, the coating M5 exhibited the lowest level of permeability, while the coating M4.1 demonstrated the highest level of permeability.

Table 4. Performance evaluation for three of the selected non-functionalized coating membranes.

Test		Coating Reference		
		M4.1	**M4.2a**	**M5**
Water permeability (EN ISO 7783)	w (kg.m^{-2}.h$^{-1/2}$)	0.01	0.01	0.01
Water vapor permeability (EN 1062-3)	Thickness range (µm)	222-330	222-286	205-272
	Diffusion resistance factor, μ	1416	1489	2740
	s_D (m)	0.30	0.34	0.55
	[Thickness] (µm)	[200] 0.37 [250]	[200] 0.42 [250]	[200] 0.68 [250]
Pull-off test (EN 1542)	Tensile bond strength (MPa)	2.4	2.0	2.5
Crack-Bridging, before ageing (EN 1062-7)	Thickness range (µm)	207-210	216-230	210-216
	Width (mm)	0.61	0.58	1.18
	Classification	**A$_3$**	**A$_3$**	**A$_3$**
Crack-Bridging, after ageing (EN 1062-7)	Thickness range (µm)	207-239	199-246	208-231
	Width (mm)	0.46	0.53	1.20
	Classification	**A$_2$**	**A$_3$**	**A$_3$**
Chloride Permeability (LNEC E 468)	P_R (m^2.s^{-1})	7.8×10^{-12}	8.0×10^{-12}	7.7×10^{-12}
Carbon dioxide permeability, before ageing (EN 1062-6)	Thickness range (µm)	202-212	217-221	213-233
	Diffusion resistance factor, μ	2.95×10^5	2.69×10^5	2.48×10^5
	s_D (m)	59	54	497
	[Thickness] (µm)	[200] 74 [250]	[200] 67 [250]	[200] 621 [250]
Carbon dioxide permeability, after ageing (EN 1062-6)	Thickness range (µm)	210-220	204-222	213-218
	Diffusion resistance factor, μ	2.11×10^5	2.28×10^5	2.11×10^5
	s_D (m)	42	46	422
	[Thickness] (µm)	[200] 53 [250]	[200] 57 [250]	[200] 528 [250]

Additionally, water permeability tests confirm that all coatings meet the required standard ($w < 0{,}1$ kg.m^{-2}.h$^{-1/2}$ according to EN 1504-2:2006 [23]). However, an analysis of the experimental curves (Figure 3) reveals that, although the water absorption coefficients are very similar at 24 hours, after 500 hours of testing, the coating formulated with M5 exhibits superior resistance to water penetration compared to the others. Its better resistance was also observed for the carbon dioxide permeability tests and for the crack-bridging tests.

Concerning chloride permeability, none of the tested coating membranes was able to pass the established parameters ($[P_R] < 1.0 \times 10^{-14}$ m^2.s^{-1}) according to the Portuguese Specification LNEC E 468:2005 [19].

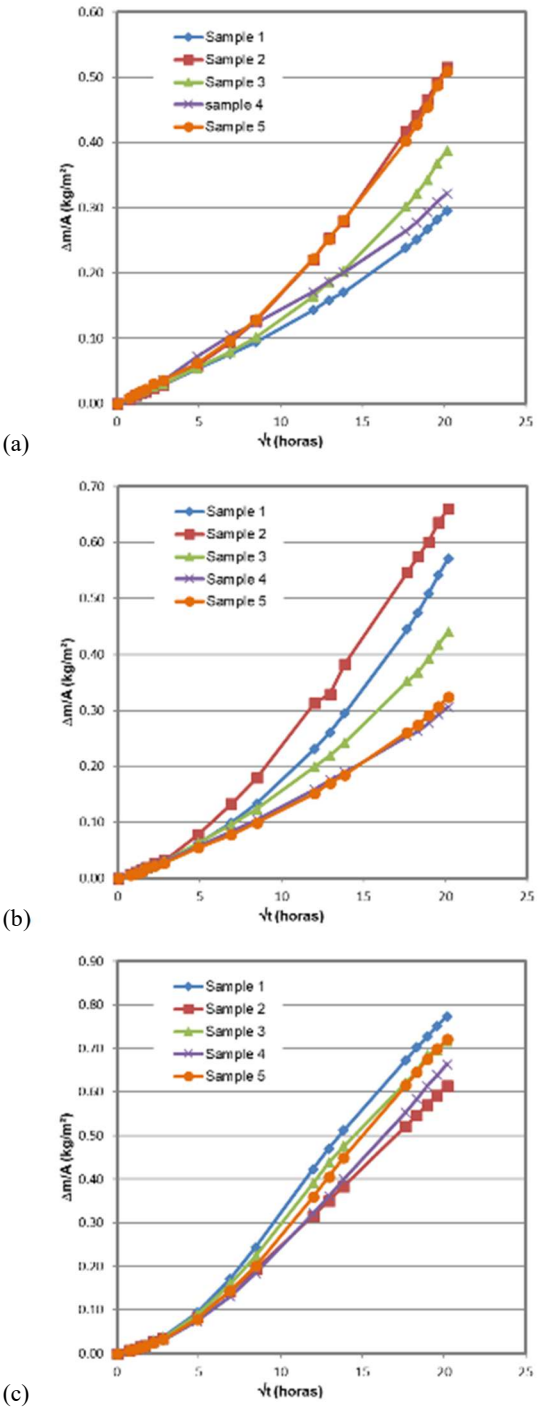

Fig. 3. Experimental curves of the water permeability test for the non-functionalized coatings (A) M4.1; (B) M4.2a and (C) M5.

All the coating membranes that were tested exhibited tensile bond strength superior to 0,5 MPa, as established by the EN 1504-2:2006 [23]. Additionally, no defects such as cracking, blistering, powdering, or detachment were observed, and no visible differences in colour were detected at the end of the aging period.

Some performance evaluation tests were conducted for functionalised coating membrane M4.2a and its variation: M4.2b. At this point comparisons are only possible for membrane M4.2a (Table 5). Water permeability tests confirm that this membrane meets the required standard.

Table 5. Performance evaluation for two of the functionalized coating membranes.

Test		Coating Reference	
		M4.2a	**M4.2b**
Water permeability (EN ISO 7783)	w ($kg.m^{-2}.h^{-1/2}$)	0.01	0.01
Water vapor permeability (EN 1062-3)	Thickness range (µm)	232-296	297-318
	Diffusion resistance factor, μ	1400	2100
	s_D (m) [Thickness] (µm)	0.28 [200] 0.38 [250]	0.42 [200] 0.53 [250]
Pull-off test (EN 1542)	Tensile bond strength (MPa)	*	1.0
Crack-Bridging, before ageing (EN 1062-7)	Thickness range (µm)	*	256-296
	Width (mm)	*	0.91
	Classification	*	**A_3**
Carbon dioxide permeability, before ageing (EN 1062-6)	Thickness range (µm)	*	229-239
	Diffusion resistance factor, μ	*	2.70×10^5
	s_D (m) [Thickness] (µm)	*	54 [200] 67 [250]

* *work in progress.*

Regarding tensile bond strength, it was found that all individual values exceed 0.5 MPa, with an average above 0.8 MPa, ensuring compliance with EN 1504-2:2006 [23]. Further comparisons are being made to better evaluate these membrane´s performance.

In addition, lixiviation tests conducted in immobilized and non-immobilized membranes present a loss in mass in the range 1-5 %. Additional tests are being conducted to fully characterize this loss in mass.

4 Conclusions

A percentage lower than 5% was obtained for preliminary lixiviation tests. The successful derivation of the indicator in the solvent that incorporates the membranes, was confirmed by FTIR analysis, which revealed the formation of a polyurethane material in the reactions. However, the solidification of the solution resulted in the failure of the immobilisation process for phenolphthalein in cyclohexanone solvent.

So far, comparative analysis is being made to address if the presence of the functionalised indicator does not have a significant effect on important properties of the membrane.

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