

Active sensing coating for early detection of corrosion processes

Cite this: *RSC Adv.*, 2014, 4, 17780

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A corrosion sensing coating based on specially developed polymeric microcapsules with a pH-indicator is reported. The synthesis of the microcapsules is designed in a way to ensure their optimal compatibility with the polyurethane protective coatings and to allow release of the indicator at higher pH values. The obtained polyurea microcapsules have a regular and micro-sized morphology and a loading content of 12 wt%. The developed sensing coating applied on aluminium and magnesium alloys is able to indicate initiation of corrosion processes through a pink coating coloration, as a result of local pH increase in the cathodic areas.

Received 28th January 2014

Accepted 2nd April 2014

DOI: 10.1039/c4ra00826j

www.rsc.org/advances

1. Introduction

Corrosion processes lead to degradation of metal and corresponding alloys, which ultimately can cause structural failures if no action is promptly taken to tackle this issue at the initial stages. Early detection of corrosion can be a way to trigger necessary maintenance actions reducing the probability of potential structural failures and high costs associated with repair.

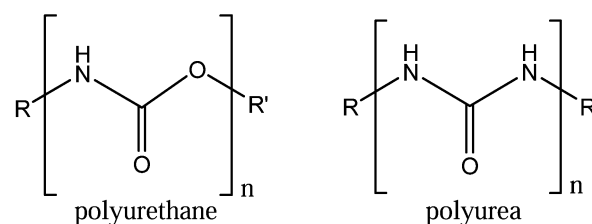
Very often the metallic structures are protected by coating systems to increase the service life. One of the most used types of coatings is based on polyurethane/polyurea due to its high performance, easy functionalization and ability to form different nanocomposites by incorporation and interaction with nano-pigments.¹ The range of PU coating applications is so wide due to versatility in selection of monomeric materials from a vast list of macrodiols, diisocyanates and chain extender.¹ According to the type of reaction promoted with diisocyanate compounds is possible to obtain different characteristic groups. The reaction of diisocyanate with a diol or with an amine, results in urethanes and ureas (Scheme 1), respectively.

The incorporation of corrosion sensors in a protective coating, simple and accessible to non-specialized personnel, is an important improvement with respect to traditional coatings and potentially complement some of the existing technologies for corrosion assessment of structures (electrochemical methods such as polarization resistance) and visual inspection of corrosion products.

Commonly, corrosion occurs according to two parallel processes: (i) metal oxidation in the anodic zone with possible hydrolytic acidification, and (ii) reduction of oxygen and/or water in the cathodic areas, leading to the formation of hydroxide anions.² The corrosion induced change of pH in the local defects of coatings or in confined areas can be used to detect the corrosion onset and locate the cathodic or anodic spots.

Different pH indicators can be employed for visualization of pH changes. For example phenolphthalein seems to be one of the best options because it is colourless at pH below 8.2 and turns pink at pH higher than 8.2. Therefore, it can be used to monitor the raise in pH associated with the cathodic reaction and overall with ongoing corrosion activity.

Since the pioneering work of Zhang and Frankel,³ where a paint system containing phenolphthalein and sensitive to corrosion processes was presented, several other researchers followed the idea. El-Nahhal and co-workers reported the immobilization of phenolphthalein in a sol-gel matrix for monitoring acid-base reactions.⁴ Showing the industrial relevance of this approach, Frankel and co-workers published a patent based on the introduction of a pH indicator in a gel based corrosion sensing coating able to modify its colour as a



Scheme 1 Generic chemistry of polyurethane and polyurea.

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response to a change in hydrogen ions concentration near the surface of the material.⁵

Although the direct incorporation of active compounds to some coating formulations can be simple but effective, normally it encloses some drawbacks such as deactivation or degradation of the active compound, and a decrease in adhesion and barrier properties provided by the coating itself.⁶ One of the best ways to overcome these problems can be the encapsulation or immobilization of active compounds in capsules that protect the compound from deactivation or interaction with the coating matrix and can additionally provide a triggered and localized response.

Some examples available in literature show the application of nanostructured materials for phenolphthalein encapsulation. Engelmann and co-workers proposed dextran carbamates with hydrophobic properties as wall material for microparticles with core/shell structure for phenolphthalein encapsulation.⁷ In another work, Li and Calle described a new type of pH-sensitive microcapsules, based on film-forming monomers and pre-polymers including urea-formaldehyde and melamine-formaldehyde. The shell of those microcapsules is sensitive to alkaline pH, breaking down and releasing the pH indicator as a result of corrosion activity.^{8–10} A different approach for the application of encapsulated phenolphthalein was presented recently by Maia and co-workers, where silica nanocontainers filled with phenolphthalein were used as nanocontainers, with the colour change taking place inside the nanocontainers. Accordingly, no release of phenolphthalein was detected, only diffusion of hydroxide anions into the porous silica shell reacting with phenolphthalein inside the nanocontainer, and acting as a corrosion sensor when tested in solution or incorporated in coatings applied different metal substrates.¹¹

In this paper we report the encapsulation of phenolphthalein in polyurea microcapsules for the first time. The aim of this work is the incorporation of polyurea microcapsules containing phenolphthalein in a coating formulation based on polyurethane, resulted from the polymerization of hydroxy-functional polyacrylic with aliphatic polyisocyanates. The polymeric system for the microcapsule walls (polyurea) is suggested in order to improve the compatibility between the microcapsules and the coating matrix, due to their similar (polyurethane/polyurea) chemistry. This way is possible to obtain corrosion sensing feature in a uniform, homogeneous and compatible coating without compromising the barrier properties.

2. Experimental section

2.1. Materials

Phenolphthalein (PhPh), Span 85, diethylenetriamine (DETA) (99%), isophorone diisocyanate (IPDI) (98%) and acetone were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH), sodium chloride (NaCl) and buffer solutions were obtained from Riedel-de-Haën. Ethanol was supplied by Panreac. All chemicals were analytic grade and were used without further purification.

2.2. Phenolphthalein encapsulation

The synthesis of polyurea microcapsules (PU MC) and the encapsulation of PhPh in PU MC were performed for the first time in a single step, as described in Scheme 2.

PU MC were prepared using Span 85 as non-ionic surfactant and PhPh as encapsulated product. Firstly, a solution of 1 g Span 85 in 100 mL of water was prepared. Then, 3 g of IPDI and 150 mg of PhPh were dissolved in 20 mL of acetone and added to the aqueous solution, leading to an oil-in-water microemulsion (Scheme 2). With a vigorous agitation, 2 g of DETA were diluted in 20 mL of water and added drop-by-drop to microemulsion. Then the mixture was heated at 60 °C and stirred for 3 h. The obtained precipitate was filtered, washed with pure water and dried at room temperature.

2.3. PU MC-PhPh morphology characterization

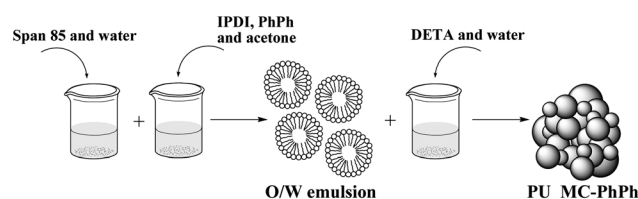
PU MC-PhPh morphology was characterized by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), using an Hitachi S-4100 system with electron beam energy of 25 keV, and by transmission electron microscopy (TEM) using an Hitachi H9000 system with electron beam energy of 300 keV.

In order to characterize the chemical and thermal properties of PU MC, ATR-FTIR spectra were recorded with a Bruker IFS55 spectrometer equipped with a single horizontal Golden Gate ATR cell. Thermogravimetric analysis (TG/DTA) was carried out in a TGA-50 Shimadzu system under nitrogen atmosphere, with a heating rate of 10 °C min⁻¹ from room temperature up to 800 °C.

2.4. Release studies of PhPh

The release profiles of PhPh were monitored by *ScanSpec* miniature UV-Vis spectrophotometer (ScanSci) at wavelength \approx 280 nm. The correlation coefficient of the calibration curves obtained with 5 PhPh standard solutions was higher than 0.999.

For that purpose 100 mg of PU MC-PhPh were dispersed in 20 mL of aqueous solutions where temperature and pH were systematically varied: $T = 40, 60$ and 80 °C; pH = 4, 7 and 9 (pH buffer solutions were used to maintain the pH constant during the release studies). Then 1 mL sample of each mixture was extracted with a syringe, and filtered with a specific syringe filter (PTFE membrane with 0.20 μ m pore size). In order to determine the total amount of PhPh encapsulated, 100 mg of PU MC-PhPh were dispersed in 20 mL of ethanol during 24 hours to guarantee the maximum release of PhPh. Ethanol was the solvent selected because it is one of the solvents where



Scheme 2 Preparation of PU MC and encapsulation of PhPh.

phenolphthalein dissolves better.¹² 1 mL of the resulting solution was extracted with a syringe, filtered, and then analyzed. The encapsulation efficiency was determined by the expression:

$$\%E = n_{\text{PhPh}_{\text{ext}}}/n_{\text{PhPh}_i} \times 100,$$

where $n_{\text{PhPh}_{\text{ext}}}$ is the amount of PhPh extracted from capsules and n_{PhPh_i} is the initial amount of PhPh used in the encapsulation.

2.5. Preparation of substrates and coating

Magnesium alloy AZ31 specimens were abraded with sandpaper of different grain sizes finishing with 600/1200 grades to remove all oxides and impurities followed by cleaning with ethanol and immediately dried.

Aluminium alloy 2024 substrates were cleaned and etched according to a standard commercial procedure: alkaline cleaning in Metaclean T2001 (Chemie Vertrieb Hannover GmbH & Co KG) at 68 °C for 25 min, alkaline etching in Turco Liquid Aluminetch N2 (Turco Chemie GmbH) at 60 °C for 45 s and acid etching in Turco Liquid Smutgo NC (Turco Chemie GmbH) at 30 °C for 7 min, each step followed by washing in distilled water.

Dried and cleaned substrates (Mg and Al alloys) were coated with Bayhydrol® A 145, a water-reducible, hydroxyfunctional polyacrylic dispersion, used in combination with aliphatic polyisocyanates (Bayhydur® 304) with fast drying at room temperature, from Bayer. PU MC-PhPh were incorporated into the formulation (5 wt% with respect to the total wet formulation) and stirred during 30 minutes until obtaining uniform dispersion. Subsequently, the coating formulation was applied on metal plates (AA2024 and Mg AZ31) using a bar coater with a wet thickness of 30 µm. Samples were left to dry at room temperature (~25 °C) for 48 h. Finally, the edges and the backside of the metal plates were covered by a protective varnish (Lacomit® from Agar Scientific).

The remnants of the formulation were applied in a Teflon mould, dried and detached, in order to obtain a free standing coating composed by the PU matrix with the developed microcapsules (Film 1 and Film 2).

2.6. Sensing activity in solution, inside the coating matrix and on coated substrates

A suspension of PU MC-PhPh in water was prepared and one drop of 0.5 M sodium hydroxide solution was added to assess the ability of the prepared capsules in sensing pH changes in solution. The colour evolution was recorded with a digital camera during one week. A similar test was carried out with coatings modified with PU MC-PhPh. Film 1 was immersed in distilled water and one drop of 0.5 M sodium hydroxide solution was added. Film 2 was immersed for 48 hours and then removed before the addition of hydroxide solution to verify whether PhPh was released under neutral conditions. For evaluation of the corrosion sensing activity, aluminium and magnesium alloy specimens coated with coatings modified with PU MC-PhPh were immersed in a corrosive electrolyte (0.5 M NaCl) and monitored over time to follow any colour

development. The colour evolution was followed by visual inspection and recorded with a digital camera.

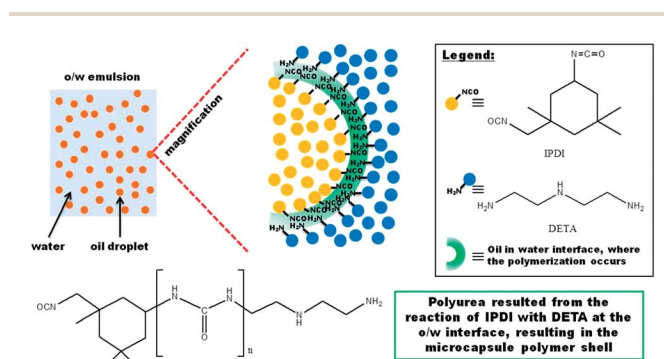
3. Results and discussion

3.1. Encapsulation of phenolphthalein and characterization of PU MC

Polyurea microcapsules of PhPh were synthesized by interfacial polymerization in an oil-in-water microemulsion. The suggested methodology allows the microcapsule synthesis and the encapsulation of hydrophobic compounds in a single step. The polymerization occurs at the interface between phases, where the surfactant plays an important role in the stabilization of the emulsion droplets. Initially, the hydrophobic phase containing PhPh and IPDI – a hydrophobic monomer – was dispersed in water, forming the emulsion. Then DETA, hydrophilic monomer, was added to the emulsion drop-by-drop to react with IPDI at the interface between phases (Scheme 3). This reaction, which consists of polymerization between IPDI and DETA, results in the formation of a shell and consequently encapsulation of PhPh within the hydrophobic core. For the best of our knowledge this is the first time that PhPh is encapsulated in polyurea capsules and also the combination of IPDI and DETA as monomers for the shell formation.

The obtained PU MC have spherical morphology and broad size distribution between 100 nm and 1 µm as shown in Fig. 1. The encapsulation of PhPh, when compared to empty capsules did not promote any significant morphological modification on PU MC and the obtained capsules do not appear to be porous. The TEM image of PU MC-PhPh (Fig. 2) shows that the wall thickness is approximately ~8 nm.

The resulting polyurea polymer used as a microcapsule shell presents the typical vibration bands of polyurea as depicted in Fig. 3. The most important bands for this specific polymer are the ones resulted from the vibration of N–H and C=O bonds, representing the urea linkage. In the spectra of Fig. 3 two bands are observed at 1738 cm⁻¹ and 1633 cm⁻¹ related to stretching of carbonyl group, corresponding to the hydrogen bonded to the carbonyl group.¹³ The broad band at 3334 cm⁻¹ is related to stretching of NH¹³ in particular to the secondary amines from DETA and the strong band at 1552 cm⁻¹ is related to the vibration of the stretching bond N–H



Scheme 3 Representation of the polyurea microcapsule shell formation at the oil in water interface.

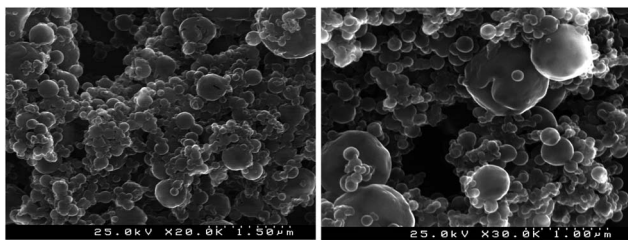


Fig. 1 SEM micrographs of: (left) empty PU MC and (right) PU MC PhPh.

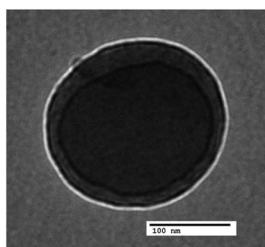


Fig. 2 TEM micrograph of a typical single PU MC PhPh microcapsule.

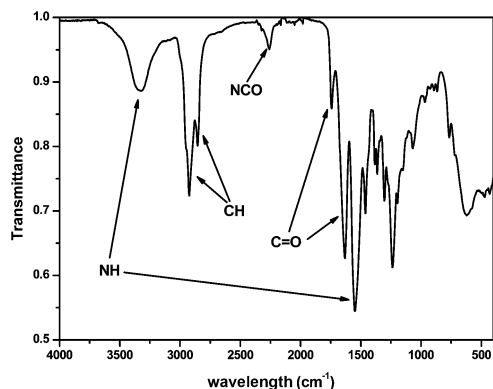


Fig. 3 FTIR spectra of polyurea microcapsules.

from the urea linkage, directly connected to the carbonyl group. The band presented at 2257 cm^{-1} corresponds to the stretching vibration of NCO bond, probably due to unpolymerized residues from the diisocyanate (IPDI) that was not fully consumed.

Thermogravimetry was used to investigate the thermal behaviour of polyurea as can be observed in Fig. 4. The resulted thermogravimetric profile shows that PU microcapsules are thermally stable until $300\text{ }^{\circ}\text{C}$ and after this temperature the degradation of soft and hard segments of the urea linkage¹⁴ is observed.

Using FTIR and TG techniques to characterize the prepared PU MC was possible to demonstrate the typical chemical and thermal properties of the polyurea polymer.

The encapsulation of PhPh in PU MC was successful and the loading content of PhPh, determined by extraction with ethanol (see Experimental section), was 611.5 ppm (loading content of

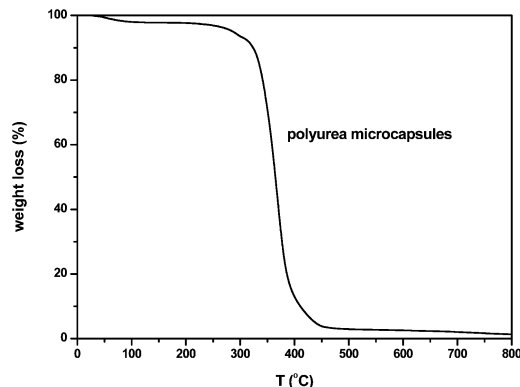


Fig. 4 TG profile of polyurea microcapsules.

$12.2\text{ wt}\%$ in the capsules), corresponding to an encapsulation efficiency of 82% .

Release studies were performed under different pH and temperature conditions. Since PU MC has a polymeric structure, temperature should play an important role on the viscoelastic behaviour and consequently on the release of PhPh. At the same time, sensing of corrosion *via* pH is a very important factor for assessing the application of PU MC-PhPh in protective coatings for corrosion, so pH was the second parameter under survey.

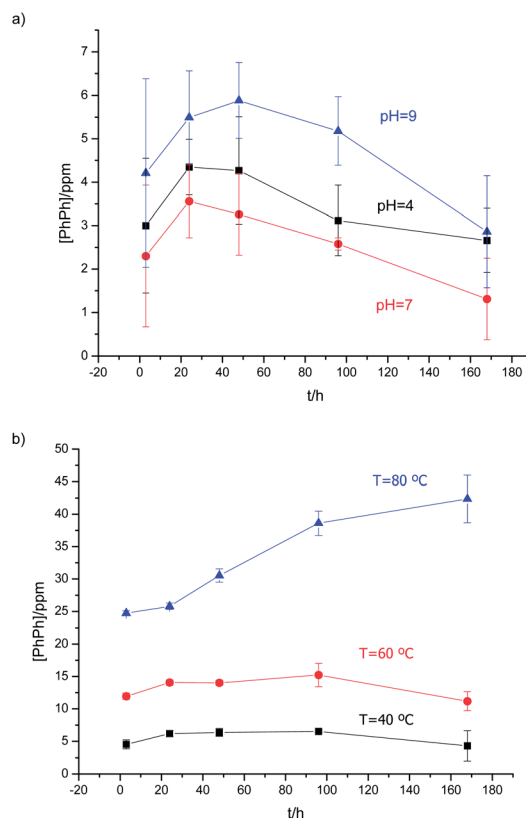


Fig. 5 Release of PhPh from PU MC at different: (a) pH and (b) temperature.

The release of PhPh under different conditions of pH (4, 7 and 9) and temperature (40, 60 and 80 °C) was performed four times for each condition and the mean is depicted in Fig. 5.

The concentration of PhPh released at different pH is less than 1% of the total loading content, due to the very low solubility of phenolphthalein in water, only with the increase of pH their solubility slightly increases,¹² and also due to the barrier effect of the microcapsule, limiting the PhPh release. More specifically, the concentration of PhPh released in neutral conditions (3.6 ppm) is lower than in alkaline (5.9 ppm) and acid conditions (4.4 ppm), as observed in Fig. 5a. The values have a high uncertainty associated because of very low concentrations near the detection limit of the analytical method.

PhPh release profiles at different temperatures are shown in Fig. 5b. The amount of released PhPh increases with temperature but is still lower than 10% of the total loading content: at 40 °C the concentration released is 6.5 ppm, at 60 °C is 15.2 ppm and at 80 °C the value reaches 42.4 ppm. The results obtained suggest that the increase of temperature promotes a higher mobility of the polymeric chains and consequently the PhPh permeation across the capsule wall to solution increases.

3.2. Sensing activity of PU MC-PhPh in suspension and incorporated into the coating matrix

In order to verify the pH sensitivity of PU MC-PhPh, one drop of 0.5 M sodium hydroxide solution was added to an aqueous suspension of PU MC-PhPh, and the results are depicted in Fig. 6. Immediately after the addition of sodium hydroxide the colour of solution turned pink, as a result of pH increase. After homogenization of the pink suspension, by manual stirring, part of the microcapsules begins to deposit in the bottom of the beaker and after 30 minutes the solution was found to remain pink while the microcapsules presented a very pale coloration. These findings imply that even the small amount of PhPh released under alkaline condition is sufficient to promote a visible coloration of the suspension.

Some materials lose their functionality when incorporated into a coating matrix, and before the characterization of the coated metallic alloys, the sensitivity of the free standing films composed by the coating matrix with PU MC-PhPh to pH changes was tested in contact with water.

Detached films (Film 1 and Film 2), with white coloration, were immersed in distilled water and one drop of 0.5 M sodium

hydroxide solution was added. The pH of the solution increased up to ~10 and the detached film started to be coloured, with a pink coloration, as can be observed in Fig. 7.

The coloration of Film 1 in the solution becomes more intense with time, due to the release of PhPh from PU MC. It seems that polyurea polymeric matrix allows the diffusion of hydroxide ions and phenolphthalein molecules, resulting into a pink coloration of the solution present in the *Petri dish*. One similar test was done with Film 2 to verify the influence of pH in the PhPh release from the coating matrix. Film 2 was immersed for 48 hours in the same conditions as Film 1, without the addition of sodium hydroxide solution. After that time, Film 2 was removed from the aqueous solution and one drop of 0.5 M sodium hydroxide solution was added and the coloration of the solution was not observed. It means that under neutral conditions the release of PhPh from the coating with capsules is very low being not sufficient to promote the colour change of the solution, which is in agreement with release studies performed before. To confirm that Film 2 was in good conditions, it was immersed again in the same solution, now with alkaline pH (due to the addition of sodium hydroxide) and the pink coloration was observed in a similar way like with Film 1. This experiment shows that PhPh is only released from polyurea microcapsules and from the coating matrix with alkaline pH, not only because of the higher solubility of PhPh at this pH, and probably, due to the higher mobility of the polymeric network, allowing the diffusion of the PhPh through the PU shell and the coating matrix. This is exactly the trigger that is intended to be used for self-sensing of corrosion protection.

3.3. Sensing activity of PU MC-PhPh in coated metallic substrates

In order to verify the ability of PU MC-PhPh to sense the corrosion onset, these microcapsules were incorporated into the coating formulation and applied on two metallic alloys (2024 Al alloy and AZ31 Mg alloy).

Since the polymeric shell of these microcapsules and the coating formulation have the same chemistry (based on polyurethane), the compatibility was visually good, leading to uniform and homogeneous coatings with no signs of aggregates or defects. The coated substrates were immersed in a 0.5 M sodium chloride solution to promote the corrosion activity and to verify the sensing ability of PU MC-PhPh.

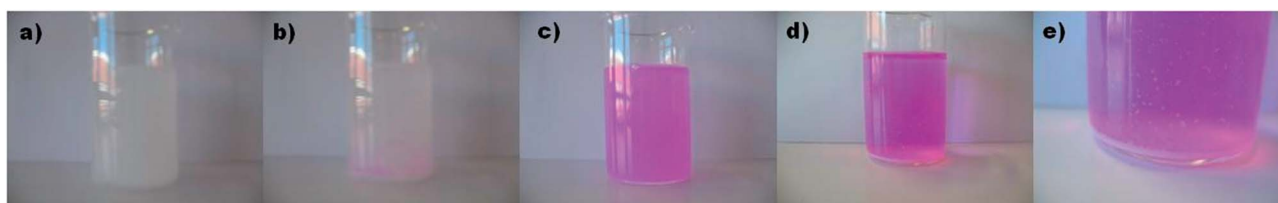


Fig. 6 Colour evolution of a PU MC PhPh suspension: (a) PU MC PhPh aqueous suspension, (b) after addition of one drop of sodium hydroxide solution (0.5 M), (c) after colour homogenization, (d) after 30 minutes (microcapsules deposition and solution with pink coloration) and (e) magnification of previous picture (microcapsules in the bottom with a very pale coloration).

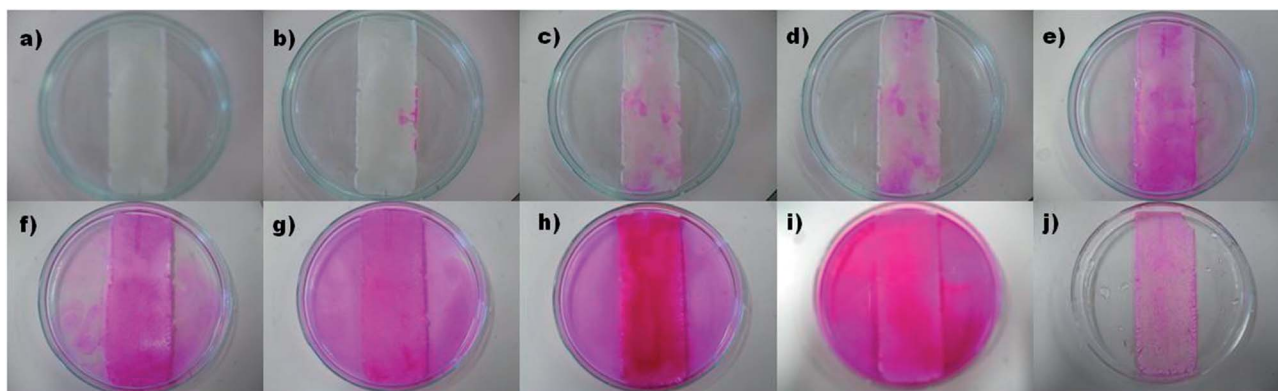


Fig. 7 Scheme of pH sensing response detached Film 1, after addition of one drop of sodium hydroxide solution (0.5 M). (a–i) Colour evolution with time; (j) after removing the solution from *Petri dish*.

After 24 h of immersion coatings applied on AA2024 substrates showed small pink spots, as a result of the corrosion activity (Fig. 8). However, these spots fade away rapidly due to the diffusion of hydroxide ions into the bulk solution.

Using a similar strategy, coated AZ31 magnesium alloy was immersed in a 0.5 M NaCl solution. After 20 hours of immersion the effects of the cathodic reaction are remarkably different compared to AA2024 (Fig. 9). There is formation of bubbles as a result of hydrogen evolution and the pink coloration comes from the formation of hydroxide ions.

For this coated substrate the sensing ability of the modified coating (with PU MC-PhPh) is more evident due to the higher reactivity of magnesium and consequently to the higher amount of hydroxide ions formed. Additionally, Mg^{2+} is stable in solution up to pH 10–11,^{15,16} thus allowing for the accumulation of OH^- and its detection by PhPh. As observed before, the coating matrix allows the diffusion of ions and molecules, particularly under these alkaline conditions and the reaction between phenolphthalein and hydroxide ions is clearly observed by the coloration of the coating.

The importance of this type of functional coatings is recognized, but for very reactive substrates, such as magnesium, it is even more important because their degradation rate is very high.¹⁷ Thus, it is very important to detect the degradation in early stages and act in a preventive way in order to guarantee the structural safety of the materials.

Fig. 10 depicts the specimen of Fig. 9 after 72 hours of immersion. The Mg alloy is damaged and the coating is heavily delaminated, as a result of the corrosion processes and associated coating degradation. An intense pink coloration is also observed, underlining the ability and usefulness of this system (PU MC-PhPh).

After one week of immersion, coated samples were removed from NaCl solution and dried at room temperature. In Fig. 11, it is possible to observe the corroded surfaces of both alloys. Those surfaces present signs of corrosion activity, namely pitting and delamination. This observation confirms that the coloration observed in the coating is due to the beginning of corrosion activity and not only due to the release of PhPh. And also because PhPh needs the hydroxide ions (to increase pH)

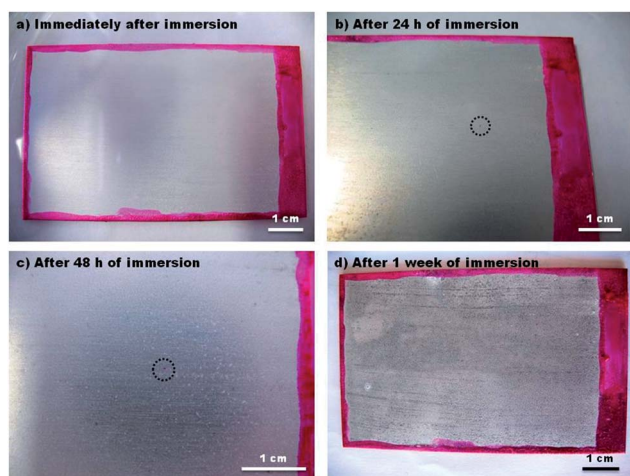


Fig. 8 Evolution of coated AA2024 immersed in a 0.5 M NaCl solution.

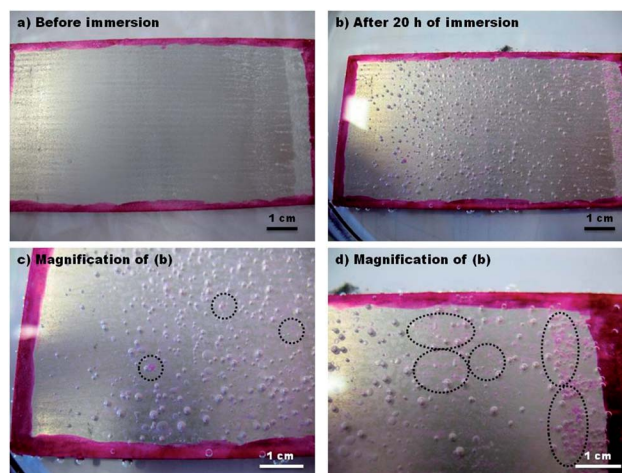


Fig. 9 Evolution of coated AZ31 Mg alloy immersed in a 0.5 M NaCl solution.

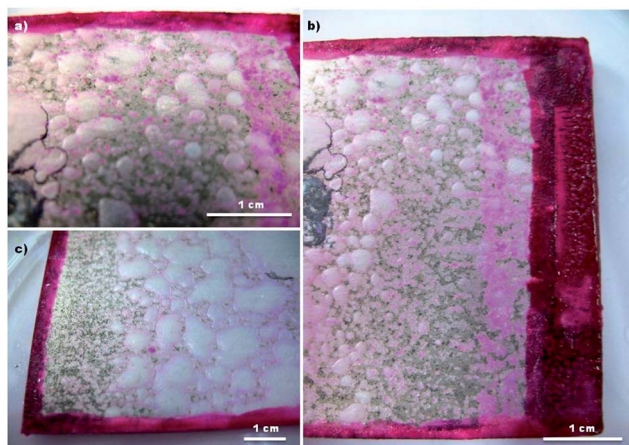


Fig. 10 Coated AZ31 Mg alloy after 72 h of immersion in 0.5 M NaCl.

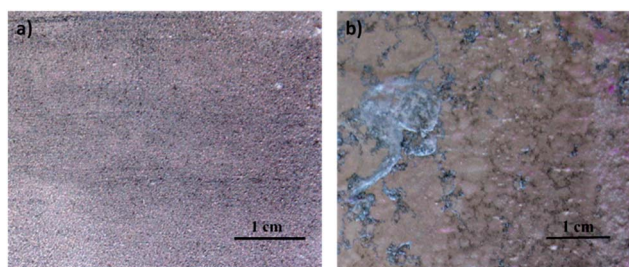


Fig. 11 Surface of coated (a) AA2024 and (b) AZ31 Mg alloy after immersion tests.

resulted from the cathodic process to turn pink, otherwise it continues colourless.

4. Conclusions

This paper reports the new synthesis for encapsulation of phenolphthalein to be used as corrosion sensor in multifunctional protective coatings.

This system is based on polyurea microcapsules with a regular and microsized morphology and with a loading content of 12 wt%. The same chemical nature of coating and capsules improves their compatibility resulting in very uniform and homogeneous coatings. Alkaline pH induces the release of phenolphthalein which ensures sensing the localised corrosion onset.

Aluminium and magnesium alloys coated with a formulation, containing polyurea microcapsules with encapsulated phenolphthalein, acted as a corrosion sensor, displaying the corrosion processes, through a pink coating coloration, as a result of local pH increase in the cathodic areas. The sensing

performance expectedly works better for magnesium alloy than for aluminium alloy. This seems to be a simple, compatible and promising solution to be used in general coating technologies for metallic structures, being useful to identify the corrosion degradation in early stages. These PU microcapsules confer a way to immobilize/encapsulate different functional compounds to attribute different functionalities to protective coatings, *i.e.* anticorrosive and antifouling properties.

Acknowledgements

The authors thank CICECO (ref. PEst-C/CTM/LA0011/2013) and FM thanks FCT for PhD grant SFRH/BD/72663/2010.

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