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Development of self-healing anticorrosive coatings using phosphorylated polysaccharide-based microcapsules

Ayoub Ouarga

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Development of self-healing anticorrosive coatings using phosphorylated polysaccharide-based microcapsules

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Dedication

To my loving parents,

My Mother, Fatima Mayaz

My Father, Elkbir Ouarga

God Bless You

To my awesome Sisters,

Safae, Salma, Wiam and Chaimae

Présentation du manuscrit de thèse

Le manuscrit de thèse est structuré dans sa forme détaillée autour de quatre chapitres présentés en version anglaise. La partie introductive du manuscrit, les résumés des chapitres ainsi que la conclusion générale sont présentés en langue française. Les chapitres qui forment le squelette du manuscrit ont fait l'objet d'articles publiés ou en cours de finalisation.

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Main publications and communications of the thesis project

List of Publications:

Ayoub Ouarga, Hassan Noukrati, Itziar Iraola-Arregui, Allal Barroug, Abdelhamid Elaissari, Hicham Ben youcef. Phosphorylated microcapsules containing natural oil for potential self-healing use, *Materials Today: Proceedings*, Elsevier, (2021).

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Abstract

The aim of this research work is to develop self-healing anticorrosion coatings with enhanced flame-retardant properties to protect the surface of mild steel. The focus of our study was on extrinsic self-healing technology based on the encapsulation of healing agents, followed by embedding the prepared microcapsules in bulk material. To achieve our purpose, a natural healing agent (Almond oil) has been selected to be encapsulated in ethyl cellulose and phosphorylated ethyl cellulose shell materials using solvent-evaporation encapsulation technique. Thus, ethyl cellulose bearing phosphonate groups was prepared via phosphorylation reaction under specific conditions and used as shell material. The resulting modified ethyl cellulose and microcapsules were subjected to several characterization techniques. The effect of the phosphonate group in combination with the almond oil was investigated as anti-corrosion additives. Thus, metallic samples having a coating loaded with microcapsules were subjected to a mechanical scratch and their corrosion resistance was examined through several tests.

Keywords: Anti-corrosion coating; ethyl cellulose; encapsulation; phosphorylation; self-healing.

Résumé

L'objectif de ce travail de recherche est de développer des revêtements auto-cicatrisant et anticorrosion avec des propriétés retardatrices de flamme améliorées afin de protéger les surfaces d'acier doux. Notre étude s'est focalisée sur la technologie d'auto-cicatrisation extrinsèque basée sur l'encapsulation d'agents cicatrisant, suivie par l'incorporation des microcapsules préparées dans un matériau. Pour atteindre cet objectif, un agent cicatrisant naturel, l'huile d'amande, a été sélectionné pour être encapsulé dans l'éthylcellulose et l'éthylcellulose phosphorylée en utilisant la technique d'encapsulation par évaporation de solvant. Ainsi, l'éthylcellulose portant les groupes phosphonates a été préparée par réaction de phosphorylation dans des conditions spécifiques puis utilisée comme matériau de coque. L'éthylcellulose modifiée et les microcapsules préparées ont été examinées moyennant diverses techniques de caractérisation. L'effet du groupement phosphonate combiné avec l'huile d'amande a été étudié comme additifs anti-corrosion. Ainsi, des échantillons métalliques ayant un revêtement chargé de microcapsules ont été soumis à des rayures mécaniques et leur résistance à la corrosion a été examinée à travers plusieurs tests.

Mots-clés: Revêtement anti-corrosion; éthylcellulose; encapsulation; phosphorylation; auto-cicatrisation.

List of commonly used abbreviations

AO : Argan oil

BET : Brunauer-Emmett-Teller method

BSO : Black Seed Oil

DDPA : n-Dodecyl Phosphonic Acid

EA : Ethyl Acetate

EC : Ethyl Cellulose

EDX : Energy Dispersive X-ray spectroscopy

EIS : Electrochemical Impedance Spectroscopy

FTIR : Fourier Transform Infrared

ICP-OES : Inductively Coupled Plasma Optical Emission Spectrometry method

IPDI : Isophorone diisocyanate

LBL : Layer-by-Layer

LO : lavender oil

LO : Linseed oil

MC : Native microcapsules

MC-ddpa : Microcapsules based on DDPA

MC-sds : Microcapsules based on SDS

O/W : Oil-in-water

O/W/O : Oil-in-water-in-oil

OM : Optical Microscopy

P-EC : Phosphorylated Ethyl Cellulose

P-MC : Phosphorylated-microcapsules

PMMA : Polymethyl methacrylate

PPO : Prickly pear oil

SDS : Sodium Dodecyl Sulfate

SEM : Scanning electron microscopy

TEA : Triethanolamine

TGA : Thermogravimetric analysis

W/O : Water-in-oil

W/O/W : Water-in-oil-in-water

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Introduction générale

Les revêtements anti-corrosion sont considérés comme un moyen efficace souvent utilisé pour protéger les structures en acier contre la corrosion. Malgré les bonnes performances de ces revêtements en termes d'adhérence, de propriétés mécaniques et/ou de durabilité, les différentes contraintes mécaniques, chimiques ou thermiques subies par les produits durant leur cycle de vie conduisent à la formation de microfissures et à une dégradation prématurée du système de revêtement. L'entretien et la réparation des revêtements endommagés sur les grandes structures industrielles en acier, comme les plateformes pétrolières, les usines de traitement de l'eau (etc.) est connu pour être extrêmement onéreux. Les coûts des défaillances structurelles, de la pollution environnementale ainsi que des vies humaines sont parfois beaucoup plus élevés que cela.

Afin de trouver de solutions pour prolonger la durée de vie des revêtements anticorrosion, les recherches se sont référées à la capacité intrinsèque et la plus remarquable des matériaux biologiques à s'autoréparer et ont abouti à la mise au point d'une classe de matériaux polymères appelés auto-cicatrisants. Généralement, on entend par revêtements autocicatrisants les revêtements qui ont la capacité de restaurer leur intégrité structurelle après un micro-dommage. Les revêtements anticorrosion auto-cicatrisants sont des matériaux intelligents à plusieurs composantes. Ils ont été proposés comme moyen pour protéger durablement les structures en acier contre la corrosion. La cicatrisation se produit à l'emplacement de la microfissure et empêche la propagation de la fissure. Elle diminue la pénétration de l'eau, de l'oxygène et des ions jusqu'au substrat, protégeant ainsi le substrat métallique de la corrosion.

La voie technologique la plus prometteuse actuellement est basée sur des microcapsules, remplies d'agents de cicatrisation actifs ; celle-ci fait l'objet de notre travail de recherche. Les microcapsules sont constituées d'une enveloppe polymère solide et d'un noyau liquide.

Lorsqu'une microfissure, provenant d'une contrainte interne ou d'une contrainte physique, se propage à travers le revêtement, les microcapsules se rompent et libèrent des agents de cicatrisation, qui s'écoulent vers le plan de fracture grâce aux forces capillaires. Les agents de cicatrisation commencent alors à réagir, à former un réseau polymère et à remédier la fissure. Par ailleurs, une autre signification du terme "revêtement auto-cicatrisant" peut être trouvée dans la littérature. Ainsi, la libération de l'inhibiteur de corrosion / agent de cicatrisation rétablit

la fonction de protection contre la corrosion des revêtements, bien qu'il n'y ait pas de véritable cicatrisation de la fracture du revêtement.

Notre travail de recherche s'inscrit dans ce contexte et vise l'étude des enjeux pratiques associés au développement de nouveaux revêtements anticorrosion auto-cicatrisant destinés à la protection des structures métalliques, notamment de l'acier doux. Le travail de recherche présenté dans ce manuscrit s'articule autour de quatre parties. Le premier chapitre présente une synthèse bibliographique traitant des concepts de l'auto-cicatrisation, intrinsèque et extrinsèque, ainsi que des procédés d'encapsulation d'agents de cicatrisation anticorrosifs pour générer des micro/nano capsules destinées à la préparation des revêtements anticorrosion et auto-cicatrisant. Le choix de la méthode d'encapsulation à utiliser a été établi sur la base des données issues de la littérature. Ainsi, les matériaux à utiliser pour l'élaboration des microcapsules et la matrice polymère ont été définis.

La synthèse de l'étude bibliographique relative au travail de thèse est présentée sous forme de revue bibliographique intitulée « Towards smart self-healing coatings: Advances in micro/nano-encapsulation processes as carriers for anti-corrosion coatings development » en vue de soumission pour publication.

Le second chapitre porte sur la formulation de microcapsules remplies d'huiles préparées avec succès selon la méthode d'évaporation de solvant ainsi que leurs caractérisations. L'éthylcellulose (EC) native et l'éthylcellulose phosphorylée (P-EC) ont été utilisées comme matériaux d'enveloppe polymères pour encapsuler quatre huiles différentes : huiles à base de lavande, de graine noire, de figue de barbarie et celle d'argan. A notre connaissance, l'encapsulation des huiles susmentionnées en utilisant de l'éthylcellulose phosphorylée comme polymère formant de coque est rapportée pour la première fois. La composition des microcapsules a été évaluée par spectroscopie infrarouge à transformée de Fourier (FTIR), et les résultats obtenus ont prouvé que les microcapsules étaient uniquement composées du matériau de noyau d'huile étudié (lavande, graine noire, figue de barbarie ou huile d'argan) et le matériau de coque (éthylcellulose ou éthylcellulose phosphorylée). L'analyse thermogravimétrique (ATG) a été mise à profit pour examiner la stabilité thermique des microcapsules et a confirmé l'aspect ignifuge induit aux microcapsules phosphorylées (P-MC) par l'utilisation de P-EC comme matériau de coque. La teneur en huile a été déterminée pour les microcapsules obtenues. L'exploration de l'effet des propriétés de l'huile sur les capsules finales doit être approfondie afin d'élucider le processus. Les micrographies obtenues par

microscopie électronique à balayage (MEB) ont en outre confirmé l'efficacité de la méthode de préparation et ont montré la forme sphérique des microcapsules avec des tailles de particules couvrant la gamme de 10 à 170 μm . L'objectif principal de cette étude était de prouver le concept d'encapsulation d'huile en utilisant P-EC comme coque ; les microcapsules préparées seront destinées à la préparation de revêtements auto-cicatrisants anti-corrosion.

L'optimisation des données issues de cette partie ont permis de focaliser l'étude sur l'huile d'amande pour la préparation l'élaboration des microcapsules destinées à la préparation de revêtement anticorrosion auto-cicatrisant.

Le contenu de ce chapitre a fait l'objet d'un article scientifique intitulé «Phosphorylated microcapsules containing natural oil for potential self-healing use» publié en 2021 dans le Journal Materials Today: Proceedings sous le DOI : [10.1016/j.matpr.2021.05.093](https://doi.org/10.1016/j.matpr.2021.05.093).

Le chapitre 3 rapporte pour la première fois (à notre connaissance) sur la préparation de microcapsules contenant l'huile d'amande en utilisant de l'éthylcellulose phosphorylée comme matériau d'enveloppe. Des microcapsules d'éthylcellulose (MC) et d'éthylcellulose phosphorylée (P-MC) contenant de l'huile d'amande comme inhibiteur de corrosion, pour une utilisation dans des revêtements auto-cicatrisants, ont été préparées via la méthode d'encapsulation par évaporation de solvant. Les résultats obtenus ont montré que l'éthylcellulose modifiée englobe une teneur en phosphore d'environ 6,26% en poids, se caractérise par une surface spécifique élevée de valeur 21,4 $\text{m}^2.\text{g}^{-1}$ et présente un résidu carbonisé de 18% en masse à 400 °C après dégradation thermique. Les microcapsules préparées à base d'EC et de P-EC étaient toutes de forme sphérique. Les images du MEB ont montré que le processus de lyophilisation affecte la morphologie de surface des microcapsules. Le diamètre moyen des microcapsules MC et P-MC était d'environ 140 μm et 150 μm , respectivement.

Les propriétés anti-corrosion de revêtements à base d'époxy préparés chargés de microcapsules sur le substrat en acier doux ont été évaluées pendant 28 jours à l'aide d'un simple test de brouillard salin. L'échantillon contenant des microcapsules P-EC a montré la meilleure résistance anticorrosion. La fonctionnalisation de l'enveloppe des microcapsules d'éthylcellulose avec des groupements phosphonates peut améliorer encore la résistance anti-corrosion, la capacité ignifuge et les propriétés de chélation des métaux des revêtements finaux.

Les résultats issus du troisième chapitre ont été valorisés à travers un article intitulé «Development of Anti-Corrosion Coating Based on Phosphorylated Ethyl Cellulose

Microcapsules», lequel est paru en 2020 dans le Journal Progress in Organic Coatings sous le DOI : [10.1016/j.porgcoat.2020.105885](https://doi.org/10.1016/j.porgcoat.2020.105885)

Dans le chapitre 4, l'application de revêtements organiques pour la protection des métaux contre l'humidité et les ions corrosifs et l'utilisation de microcapsules à base d'éthylcellulose phosphorylée (P-EC) comme matériau d'enveloppe envers l'huile d'amande ont été entreprises. Pour cela, deux tensioactifs, le dodécylsulfate de sodium (SDS) et l'acide n-dodécylphosphonique (DDPA), ont été testés dans la préparation des microcapsules.

Les microcapsules préparées ont été dispersées dans des revêtements à matrice époxy dont les propriétés anti-corrosion et capacité d'auto-réparation ont été réalisés sur un substrat en acier doux, moyennant des tests au brouillard salin. Les résultats obtenus révèlent que les revêtements contenant des microcapsules ainsi élaborées présentent, comparés aux échantillons de référence, une meilleure résistance à la corrosion et d'auto-cicatrisation après 28 jours d'exposition aux conditions du test du brouillard salin. Ces observations attestent que les échantillons contenant les microcapsules à base de P-EC agissent par le biais de leurs performances comme des revêtements intelligents vis-à-vis de milieux corrosifs.

Le contenu de ce chapitre, intitulé «Preparation and application of phosphorylated microcapsules in self-healing Anti-Corrosion epoxy Coating», est en cours de préparation pour publication dans un journal scientifique.

Dans le dernier chapitre, une conclusion générale de ce travail est donnée et ses perspectives de développements futurs sont esquissées.

Chapter 1

Bibliographic Synthesis

Introduction to chapter 1

Les matériaux auto-cicatrisants ont été largement conçus au cours des dernières décennies, en s'inspirant de l'auto-cicatrisation des organismes, tels que la peau humaine, qui sont naturellement capables de se guérir eux-mêmes. En raison de la variété des groupes fonctionnels et de la présence de nombreuses interactions non covalentes fortes, les matériaux à base de polymères ont constitué la majorité des matériaux autocicatrisants.

Les matériaux auto-cicatrisants extrinsèques réalisent leur propriété d'auto-cicatrisation en libérant des agents cicatrisants qui sont encapsulés dans des capsules ou des capillaires. L'efficacité de ces matériaux a été démontrée à l'aide de diverses méthodes, dans différentes études, telles que l'incorporation de capsules contenant des agents de cicatrisation, à travers des réseaux vasculaires ou des capillaires creux discrets. De nos jours, l'approche basée sur les capsules est la plus utilisée pour préparer des matériaux auto-cicatrisants. Cette approche a été démontrée dans différents types de matériaux tels que les matrices thermodurcissables, les élastomères et les matériaux composites renforcés de fibres. Le concept des matériaux auto-cicatrisants extrinsèquement à base de capsules repose sur la rupture des nano/micro capsules incorporées dans le matériau en vrac en raison d'un ou de plusieurs stimuli, puis sur la libération de l'agent cicatrisant dans le site endommagé par action capillaire et, enfin, sur la polymérisation de l'agent cicatrisant grâce au contact avec le milieu environnant, le catalyseur incorporé ou le liquide de polymérisation secondaire.

L'objectif de ce chapitre est de fournir une vue d'ensemble des procédés d'encapsulation utilisés pour préparer des microcapsules remplies d'agents de cicatrisation ainsi que leur utilisation dans des applications de revêtements auto-cicatrisants extrinsèquement pour faire face à la corrosion des métaux. Dans ce chapitre, le concept de matériaux auto-cicatrisants et son utilisation potentielle pour protéger les métaux de la corrosion sont d'abord mis en évidence. Ensuite, les différents procédés d'encapsulation utilisés pour la préparation de micro/nano capsules sont classés en fonction de la nature des procédés (physique, chimique ou physico-chimique). Ces procédés sont présentés avec des exemples d'études et de recherches pour des applications d'autocicatrisation et anticorrosion. Enfin, les défis et tendances futurs sont discutés.

Ce premier chapitre est rédigé sous forme d'une revue bibliographique englobant les différents procédés d'encapsulation qu'il a fallu connaître afin d'effectuer le choix de la méthode

adéquate pour préparer des microcapsules contenant des agents de cicatrisation afin de développer des revêtements anti-corrosion. Cette revue bibliographique est en cours de soumission pour être publier dans un journal de renommé.

Towards smart self-healing coatings: Advances in micro/nano-encapsulation processes as carriers for anti-corrosion coatings development

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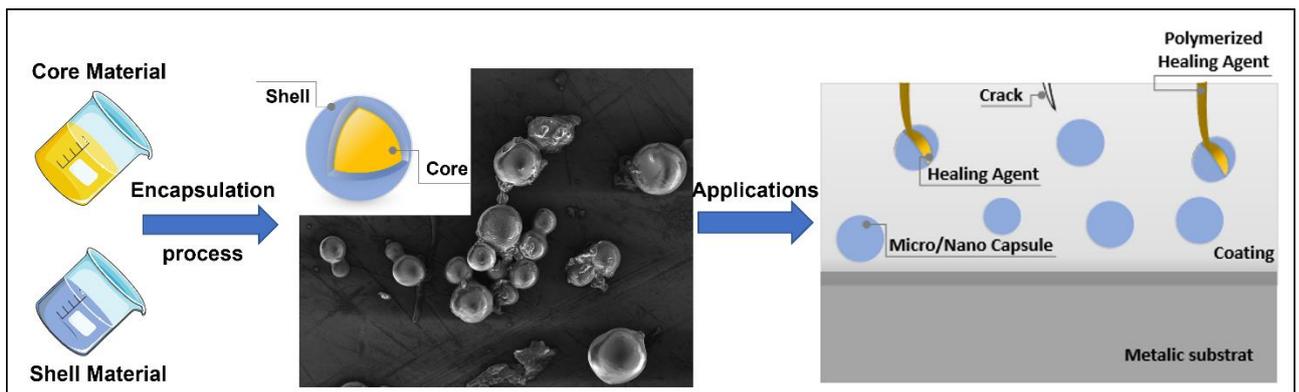
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Abstract

Smart materials based on the self-healing concept are used in different advanced applications such as buildings, batteries and coatings. The development of these materials follows two scenarios: the development of materials with intrinsic self-healing properties, or the preparation of extrinsic self-healing materials containing adds such as microcapsules filled with healing agents. Currently, the extrinsic self-healing technique is the most investigated and applied. Microcapsules preparation is a key step for extrinsic self-healing materials development. For this purpose, a variety of micro/nanoencapsulation processes have been reported. This review aims specifically to present recent advances and a critical overview of the encapsulation processes used to develop microcapsules for anticorrosion self-healing coatings. For each encapsulation method, the advantages and limitations are evaluated. The challenges facing the micro/nano encapsulation processes, recent proof-of concepts and future trends are also discussed.



Keywords: Self-Healing; Coatings; Encapsulation; Corrosion protection; Smart materials

Highlights

- Micro/nano-encapsulation processes for self-healing application are summarized.
- Extrinsic Self-healing approaches and strategies are highlighted.
- Micro/nano encapsulation processes Challenges and future trends are discussed.

1. General introduction

Since decades, polymers, metals and composite materials have been used in daily life and engineering applications (e.g., aeronautics, aerospace, equipment, and packaging). These materials are subjected to different stresses over their service life, such as fatigue, corrosion, abrasion or even UV radiation, which affect their performances and decrease their lifetime causing economical losses and ecological disturbances. For these reasons, several preventive and maintenance methods have been developed to increase their operational life. However, the classical methods of repair are not only expensive and time-consuming to implement, but also efficient for only visible and accessible damages. Thus, they are not appropriate for repairing inaccessible damages inside material matrices such as microcracks.

Having a material with the ability to recognize damages and to repair itself autonomously to reestablish its original properties seems to be an ideal solution to these damage issues. This self-healing ability is generally observed in some living systems, such as skin, blood vessels or bones [1–9].

Therefore, these natural systems served as inspiration for the concept of self-healing materials that was developed in the 1980s. Self-healing composites, for instance, are created by dispersing a hollow fiber network with an additive (i.e., healing agent), which is released in the matrix during a break or damage [10,11].

Theoretically, polymeric self-healing materials have the built-in potential to significantly recuperate their ability to transfer load after damage. These recoveries may happen spontaneously and autonomously or can be triggered by a direct stimulus. Processes for self-healing may usually be divided into extrinsic and intrinsic self-healing. These two self-healing categories are characterized by the chemistries experienced by the material in response to the damage. The intrinsic self-healing process is guided by the chemical bonding of the matrix itself, which is capable of reconstruction following dramatic damage in the face of external stimuli (e.g., sun light). On the other side, the extrinsic self-healing process is fulfilled by reparation of the damage through the release of the healing agent from the incorporated containers in the matrix [10,12,13]. In the present review, the focus will be mainly put on the capsules based extrinsic self-healing method.

Various types of extrinsic self-healing systems were made based on the process originally introduced by White et al. (2001) using a chemical reaction of substances incorporated in the

polymer matrix for microcrack healing [14]. Most of them are based on the encapsulation of a fluidic healing additive in a polymeric shell to prevent accidental contamination during processing and storage. Microcapsules loaded with curing agents and catalysts are incorporated in the polymer matrix. The healing additive release from the capsules occurs through the capillary action after a damage-induced crack propagation. The curing agent dissolves the catalyst which activates the polymerization reaction in fracture, and the developing polymeric product holds the plane's faces with each other in order to restore the structural integrity of the matrix. The healing approaches depend on the chemical reactions and the healing process. Any suggested self-healing system based on microcapsules must meet the following criteria: Both reagents and the resulting polymer product should be compatible with the polymer matrix and therefore should have a better adhesion after reaction. Both the healing agent and the shell material of the capsule should resist to degradation and different chemical reactions for a long time period.

The aim of the following review is to provide an overview of the encapsulation processes used to prepare microcapsules filled with healing agents and their application for anticorrosion extrinsic-self-healing-based materials. In this review, the concept of self-healing materials and its potential use to protect metals from corrosion is firstly highlighted. Then, different encapsulation processes used for the preparation of micro/nano capsules are classified and exposed with examples of research studies in anticorrosion self-healing applications. Finally, the challenges and future trends are discussed.

2. Self-healing materials for anticorrosion applications

Recently, self-healing materials have been widely designed, inspired from the self-healing of organisms (e.g., the human skin). Owing to the variety of functional groups and the presence of many strong noncovalent interactions, polymer-based materials have constituted the majority of self-healing materials.

Extrinsic self-healing materials realize their self-healing property by releasing healing agents that are encapsulated in capsules or pipes. The efficiency of those materials has been demonstrated using a variety of methods, in different studies, such as the incorporation of capsules containing healing-agents, through vascular networks or discrete hollow capillaries. Nowadays, the capsule-based method is the most used to develop self-healing materials. This approach has been demonstrated in different type of materials such as thermoset matrices,

elastomers and fiber reinforced composite materials [14,15]. The concept relies on the rupture of the embedded nano/micro capsules in the bulk material due to one or different stimuli, followed by a capillary induced release of the healing agent into the damaged site, then, the polymerization of the healing additive is triggered by the contact with the surrounding environment, the incorporated catalyst or the secondary polymerizing liquid (Fig. 1 A).

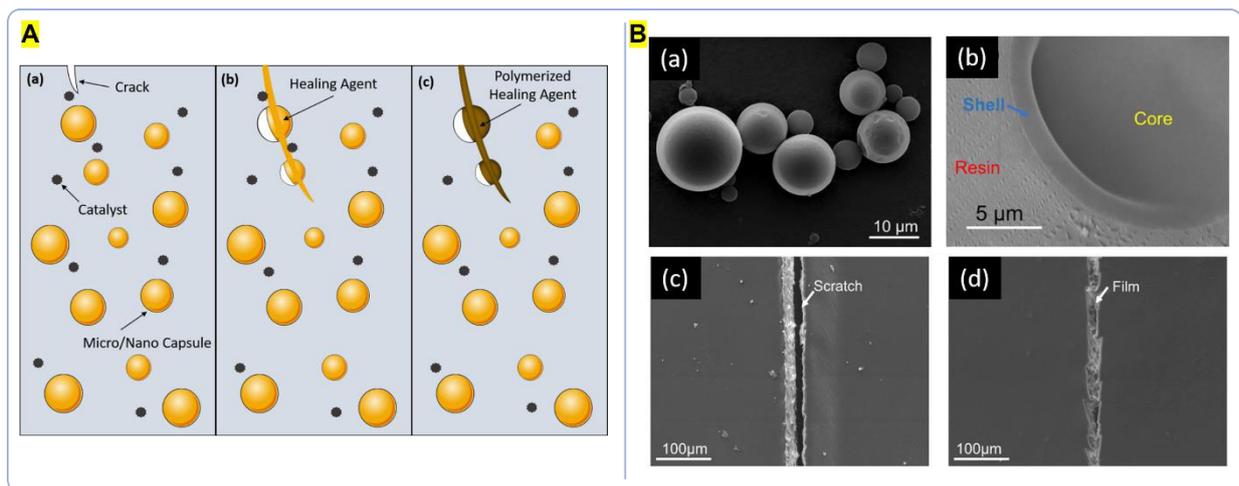


Fig. 1. A) Schematic diagram of capsule-based self-healing concept. (a) Crack forms in the material containing micro/nano capsules and catalysts, (b) Rupture of micro/nano capsules and release of healing agent, (c) Polymerization of healing agent stops the crack propagation. **B)** (a) SEM image of tung-oil-loaded microcapsules, (b) SEM image of the shell thickness of microcapsules, (c) SEM image of the scratched control coating, (d) SEM image of the healed scratched self-healing coating [16].

Anticorrosion self-healing coatings have garnered great interests to solve issues related to the degradation of metals. Such smart coatings are principally used to prolong the materials service-life, minimize the maintenance costs, and improve the reliability and safety of metals. Additionally, different healing agents have been microencapsulated to promote the self-healing process in anticorrosion coatings and stop the propagation of damages, including epoxy resin [17–22], linseed oil [23–32][33–39], tung oil [40,41], almond oil [42], lavender oil [43], cerium nitrate [44,45] and others (Table 1).

In a recent study, tung-oil-loaded microcapsules (average diameter $\sim 8.5 \mu\text{m}$) were prepared using urea-formaldehyde polymer as shell based material [16]. The morphology investigation by Scanning Electron Microscopy (SEM) shows the spherical shape and smooth outer surface of the microcapsules as depicted in (Fig. 1B a). The thickness of the microcapsules shell was about

1 μ m (Fig. 1B b). The microcapsules were embedded into an epoxy resin to prepare anticorrosion self-healing coating formulation with 5 wt.% capsules loading. The efficiency of coating containing microcapsules and the blank coating made of pure epoxy-hardener mixture, prepared by air spray with similar thickness value, were then compared using the AA2024-T3 substrates.

Both substrates were cured for 5 days at room temperature, then, were manually scratched and were allowed to cure for 48 h at room temperature. The induced damage and the self-healing effect were evaluated through SEM and Electrochemical Impedance Spectroscopy (EIS) tests. The SEM micrograph of the scratched area within the coating loaded with tung oil-filled microcapsules (Fig. 1B d) confirmed the filling with the healing agent and its effectiveness, while the scratch remained unfilled on the control coating (Fig. 1B c). Furthermore, the formed film on scratched self-healing coating exhibits a resistance value of more than $10^6 \Omega \cdot \text{cm}^2$, instead of $10^3 \Omega \cdot \text{cm}^2$ measured in the case of the scratched control coating. Additionally, the anticorrosion efficiency of the self-healing coating was confirmed by salt spray tests.

3. Classification of encapsulation processes

Microencapsulation can be defined as a technology allowing the preparation of individualized microparticles, made up of a coating shell material containing an active core substance. It could be used to provide a good protection to the encapsulated material, to control its release or even to facilitate the use of liquid products. Microencapsulation methods are numerous. Each technique corresponds to an encapsulation rate, capsules morphology and a particle size range. Different approaches could be adopted to classify the encapsulation methods based on different criteria. Some of these criteria are the nature of the dispersing medium (liquid, gas or a supercritical fluid), the materials used for encapsulation (preformed polymers, lipids or monomers), the use or not of organic solvent, and the process used for the microencapsulation. According to the last classification, there are typically three classes of encapsulation processes: (i) physical processes, which use mechanical techniques (for instance spraying and extrusion), (ii) physico-chemical processes, based on the regulation and control of different factors and parameters such as pH, temperature, solubility and precipitation of polymers, as well as the control of the polymers state changes, and (iii) chemical processes, based on *in situ* formation of the coating material by polycondensation, radical polymerization, or anionic polymerization of monomer units. That makes this process different from the others, because the use of

performed coating materials such as polymers or lipids is avoided. Studies on anticorrosive self-healing coatings using various encapsulation processes for anticorrosion healing agents are presented in (Table 1) and discussed throughout the review.

3.1 Chemical processes

3.1.1 Emulsification

Emulsions became a widely used technique for the preparation of different kinds of products (e.g., Food, cosmetics, healthcare, coatings, etc.). An emulsion is defined as a dispersion made up of two immiscible liquids. Different systems are obtained due to emulsification. An oil-in-water (O/W) emulsion is obtained after dispersion of oil droplets in an aqueous phase, while a water-in-oil (W/O) emulsion is prepared after dispersion of water droplets in oil phase. Double emulsion systems exist; for instance, water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) double emulsions (Fig. 2). The emulsification process constitutes a primordial step in chemical micro-encapsulation in general, and especially microencapsulation of oils [46,47].

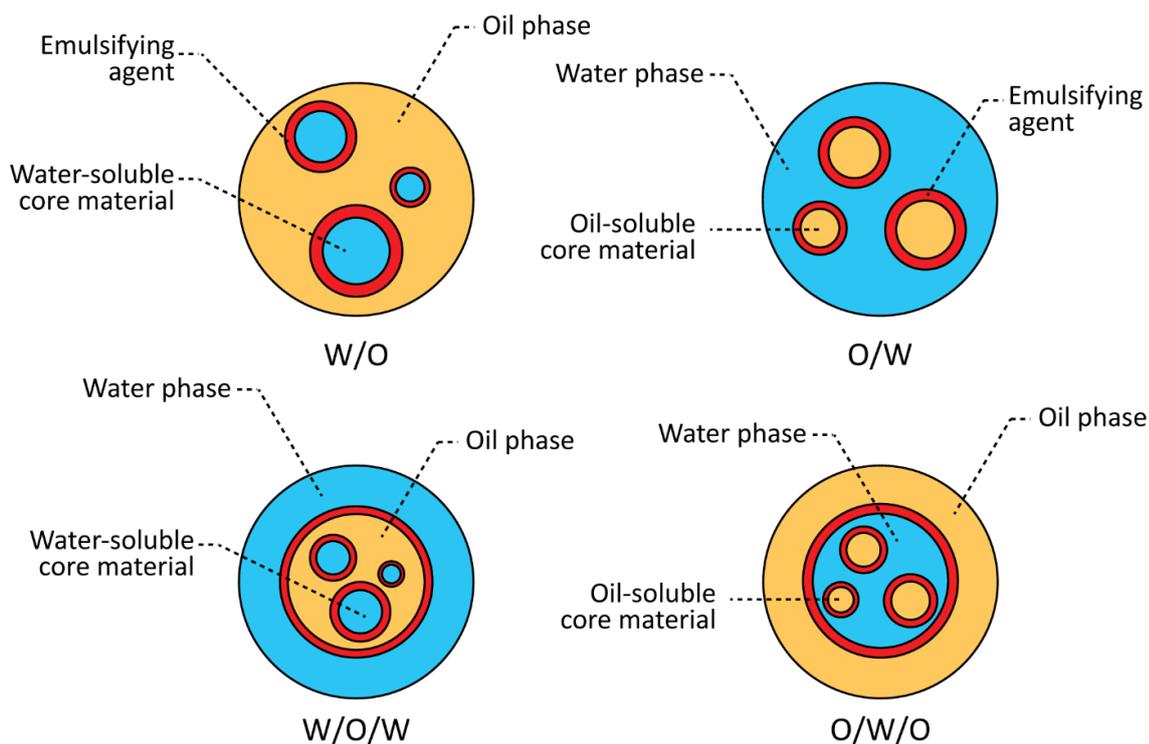


Fig. 2. Illustration of emulsion systems W/O, O/W, W/O/W and O/W/O.

The emulsification concept can be combined with other methods such as coacervation and extrusion processes. For instance, in the physical processes of freeze-drying and spray drying, the core and shell materials could be prepared as emulsions, then, a drying process is performed to prepare the microcapsules. Thus, emulsification is an important step of the

microencapsulation process. The stability of the emulsions is still one of the issues to control in this process. For this reason, emulsifiers are usually added to the emulsion system and homogenized via mechanical homogenizer devices [46].

The use of emulsions for microencapsulation reveals clear benefits over the techniques (e.g., freeze-drying, spray drying) stated above. Moreover, the emulsion process is one of the simplest and easiest processes. It offers a reduction of the containers preparation steps due to the use of liquid droplets as core and container materials at the same time [48].

Additionally, this technique presents many other advantages such as cost effectiveness and the ease of preparation. But it shows also some disadvantages regarding the controlled release and physical stability, especially when the emulsion is exposed to high or very low temperature values, drying and extreme conditions of pH and minerals concentration [49].

Nowadays, emulsions encapsulation remains extremely important due to the possibility to form directly spherical core-shell capsules containing a liquid core. This possibility is highly required and suitable in order to prepare micro and nano capsules for biomimetic self-healing materials or anticorrosion self-healing coatings [48].

Matsuda et al. (2016), (2019) used water in oil (W/O) emulsification technology successfully in the microencapsulation of Cerium nitrate using butylated urea-formaldehyde resin and urea-formaldehyde as shell materials to prepare pH-sensitive microcapsules containing corrosion inhibitor for end use in self-healing anticorrosive coating application [44,45]. Emulsion techniques were used by Schreiner et al. (2017) to prepare microcapsules using thermoset resins of melamine-formaldehyde and urea-formaldehyde which contain resins or inhibitors for self-healing protective coatings [50].

3.1.2 In situ polymerization

In situ polymerization has become the most frequently used process for microcapsules preparation (Fig. 3). This technique helps in the creation of a shell-wall by introducing a reactant inside or outside of the core material [51]. The absence and non-inclusion of reactants in the core material could be considered as the distinctive characteristic of *in situ* polymerization process for encapsulation in comparison with the other polymerization method. The polymerization takes place in the continuous phase and not on both sides of the interface phase-core material [46].

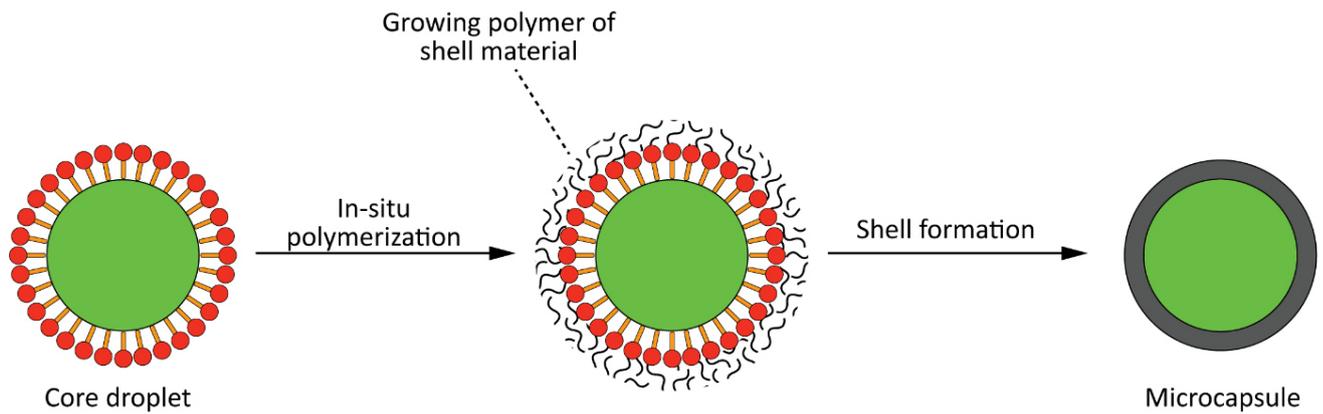


Fig. 3. Schematic diagram of microencapsulation by in situ polymerization.

Different studies employed the *in situ* polymerization process to encapsulate epoxy resin in urea formaldehyde shell. The prepared microcapsules were embedded in water borne wood and epoxy coatings. These investigations examined the effect of stirring speed and materials concentration to prepare the desired microcapsules. The coating cracking prevention and toughness improvement were discussed. Also, the evaluation of the performance of different coating processes using microcapsules was performed [17–19].

Jialan et al (2019) prepared microcapsules containing epoxy resin as core material and urea formaldehyde as shell material [17]. The generated microcapsules showed a thermal stability temperature of about 250 °C and an average particle size of 55.7 μm after optimization. Different mass fractions of microcapsules (1%, 2% and 3%) were embedded into epoxy resin coatings to evaluate the corrosion resistance. It was highlighted that the coating with 2% microcapsules has the best corrosion resistance, while its service life was prolonged by about four times.

The epoxy-filled microcapsules prepared by Yan et al (2019) were added into the waterborne wood coating to study their influence on the properties of gloss, color change and toughness [19]. The results revealed a dependence between the properties and the capsules content. Remarkably, the 10% microcapsules content in the primer layer of the coating prepared via the process of three-layer primer and two-layer topcoat generate the highest gloss, the lowest color difference and the better toughness and compressive performance.

Linseed oil (LO) is considered as one of the important oils to use in self-healing coatings thanks to its drying oxidation mechanism. The encapsulation of LO and the study of its behavior in an epoxy based self-healing coating was published for the first time in 2008 by Suryanarayana et al [52–56]. Nowadays, linseed oil is one of the most encapsulated oils using *in situ*

polymerization technology. The prepared capsules are generally integrated in epoxy coating matrices for end use in self-healing corrosion protection coatings. Urea-formaldehyde is the common wall material to encapsulate LO. The resulting microcapsules are spherically shaped, with a size distribution between 10 and 350 μm . Some studies achieved nanometric capsules [23,24,33,34,25–32].

3.1.3 Radical & Interfacial polymerization

The radical polymerization includes four types of processes: suspension, emulsion, precipitation and dispersion polymerization. The difference between these processes is mainly the monomer solubility and the initiator in the polymerization medium. These processes generally take place in two stages: nucleation and growth (Fig. 4 a). The particle size ranges generally between few hundred nanometers and few micrometers, depending on the mixing speed for suspension and emulsion polymerization (formation of an emulsion), the concentration of the monomer/initiator/surfactant and the temperature [57].

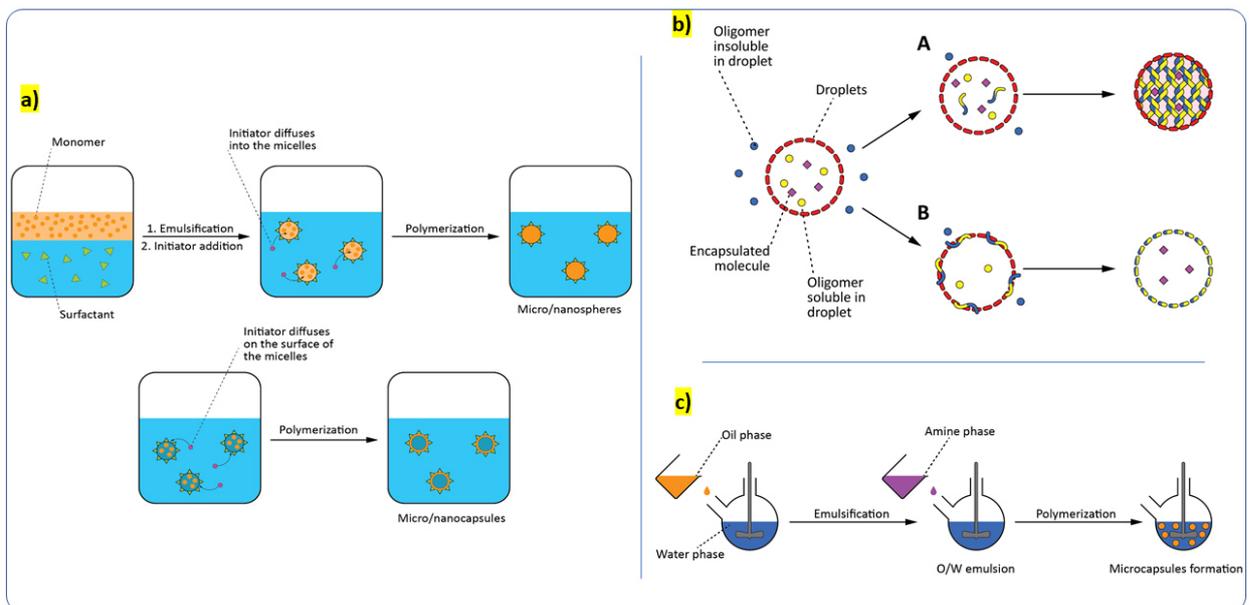


Fig. 4. a) Schematic diagram of microencapsulation by emulsion polymerization. **b)** Schematic diagram of microencapsulation by interfacial polymerization by two methods using: **(A)** Oligomer soluble in the droplet, **(B)** Oligomer insoluble in the droplet. **c)** Schematic diagram of polyurea microcapsules preparation using interfacial

To produce corrosion-inhibitor based nanocapsules, Changkyu et al. (2020) used Triethanolamine (TEA), an amine-based corrosion inhibitor, as a core material to prepare nanocapsules via free-radical polymerization [58]. The TEA was encapsulated in a seed latex

shell material, which was synthesized using four monomers: methyl methacrylate, methacrylic acid, butyl acrylate and ethylene glycol dimethyl acrylate. The prepared nanocapsules (average particle size of about 450 nm) were distributed in the epoxy resin to evaluate the long-term anticorrosion and self-healing performance of the coating after its application on an aluminium alloy substrate. A variety of analyses were carried out in this study to assess the coating performances, for instance optical microscopy, SEM Microscopy, X-ray spectroscopy, NMR, and corrosion tests.

The epoxy coating containing 10 wt% of nanocapsules has protected the scratched area for 60 days, owing to the formation of an inhibiting layer due to TEA adsorption on the metal surface. Optical microscope and SEM images revealed that the sample containing TEA nanocapsules was less discolored after 60 days of testing in 5 wt% NaCl solution compared with the control coating without capsules. An inhibition efficiency surpassing 85% was revealed by electrochemical impedance spectroscopy on day 60 showing the effective protection of TEA coating to prevent the corrosion of aluminium substrate.

Another technique, the interfacial polymerization, allows the *in situ* formation of the polymer at the surface of the emulsion droplets. There are two polymerization methods: i) anionic polymerization and ii) polycondensation/polyaddition.

i) To form capsules via anionic interfacial emulsion polymerization, there are two techniques: First, the monomers can be introduced into the organic phase of a reverse emulsion (W/O), by droplets containing the water-soluble active agent. Second, the organic phase (ethanolic solution of monomers + oil containing the active principle) is emulsified in an aqueous phase containing the surfactant. In both cases, the monomers diffuse towards the interfaces and polymerize by anionic polymerization in contact with the aqueous phase to form the poly-alkyl-cyanoacrylate membrane. The formed capsules find their application in the medical field to treat cancers for example [59–63].

ii) The microparticles synthesis by interfacial polycondensation is performed via direct emulsion (O/W), reverse (W/O) or even an oil in oil emulsion (O/O) allowing the encapsulation of hydrophilic or hydrophobic substances. The chemical reaction takes place at the interface between two immiscible liquids, each one containing a reactive monomer [64].

The morphology of the obtained particles depends on the oligomers solubility in the droplet (Fig. 4 b):

- if the oligomers are soluble in the droplet, they will grow and give a matrix system swollen by the solvent leading to the formation of microspheres.
- if the oligomers are not soluble in the droplet, the polymer precipitates at the interface and forms a membrane around the droplet, thus, promoting the formation of microcapsules. This process allows the *in situ* formation of the membrane of a particle with an organic or aqueous core [65,66].

Interfacial polymerization is used in different applications, such as microcapsules preparation. Alizadegan et al. (2018) applied this technique in an oil-in-water emulsion to encapsulate bulky isophorone diisocyanate (IPDI) using polyurethane as shell material [67]. The prepared microcapsules were embedded in polyurethane matrix for end use as a self-healing anticorrosion coating. Mechanical analysis, salt spray test and SEM analysis confirmed the improvement of healing efficiency by increasing the capsules content. The interfacial polymerization process was also used by Tatiya et al. (2016) to encapsulate tung oil in polyurea shell for self-healing anticorrosive coating applications (Fig. 4 c) [40]. The obtained results showed satisfactory encapsulation efficiency and good anticorrosive performances of the coating under accelerated corrosion test.

polymerization process. A stable emulsion was prepared by mixing the organic phase (the core material and the oil phase monomer for shell material) with the aqueous emulsifier solution. The shell formation starts by dropwise adding of the amine phase (water phase monomer in emulsifier solution). The final microcapsules are generated after a specified stirring period.

3.1.4 Pickering emulsion

Pickering emulsions are dispersions of immiscible liquids stabilized by solid particles instead of classical surfactant molecules (Fig. 5). The stability of this type of emulsion can be ensured by two phenomena: a solid shell formation around the droplets due to the particles adsorption at the liquid/liquid interface, which prevents the coalescence of the droplets, and a three-dimensional network formation in the continuous phase which traps the droplets, limiting their sedimentation or creaming. Therefore, the use of solid particles to formulate an emulsion allows the production of very stable interfaces. Thus, Pickering emulsions are of great importance for pharmaceutical and cosmetic applications, particularly for the encapsulation and controlled release of active substances [47,68–70].

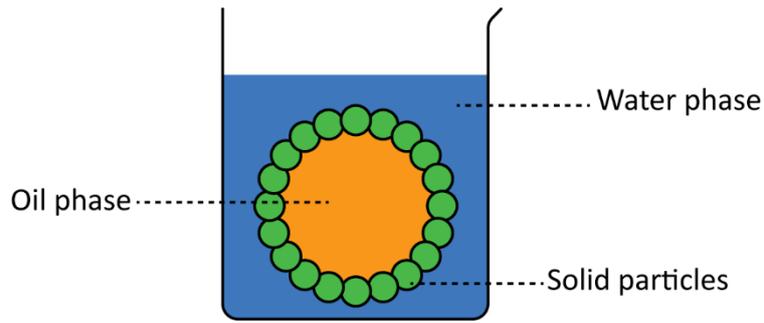


Fig. 5. Schematic diagram of a microcapsule prepared by Pickering emulsion process.

Owing to its advantages such as reduced toxicity, cost effectiveness and easy recovery properties compared to standard surfactants, Pickering emulsions have recently become the preference of many researchers. In this context, Li et al. (2017), proposed graphene oxide (GO) as shell material due to its ability to self-assemble at oil/water interfaces in Pickering emulsions [35,36]. This material has proven its quality to be used as microencapsulation shell material. Afterwards, they encapsulated linseed oil as healing agent in graphene oxide shells via Pickering emulsion process. The prepared microcapsules were embedded in a waterborne polyurethane composite coating in order to investigate the self-healing properties as a function of microcapsules contents. Morphological and electrochemical analysis of the coatings showed that coatings containing 10 wt.% microcapsules exhibited better self-healing effects.

3.2 Physicochemical processes

3.2.1 Processes based on supercritical fluid technology

There are three processes using the supercritical fluid technology: Rapid Expansion of Supercritical Solutions (RESS), Aerosol Solvent Extraction System (ASES), and the phase separation process. These processes use supercritical CO₂ which is advantageous because of its low critical point, its non-toxicity and its non-flammability (Fig. 6). It therefore allows a clean and environmentally friendly process. However, the application remains limited due to the low solubility of most polymers and active ingredients in supercritical CO₂ [46,71,72]. The different processes are not detailed.

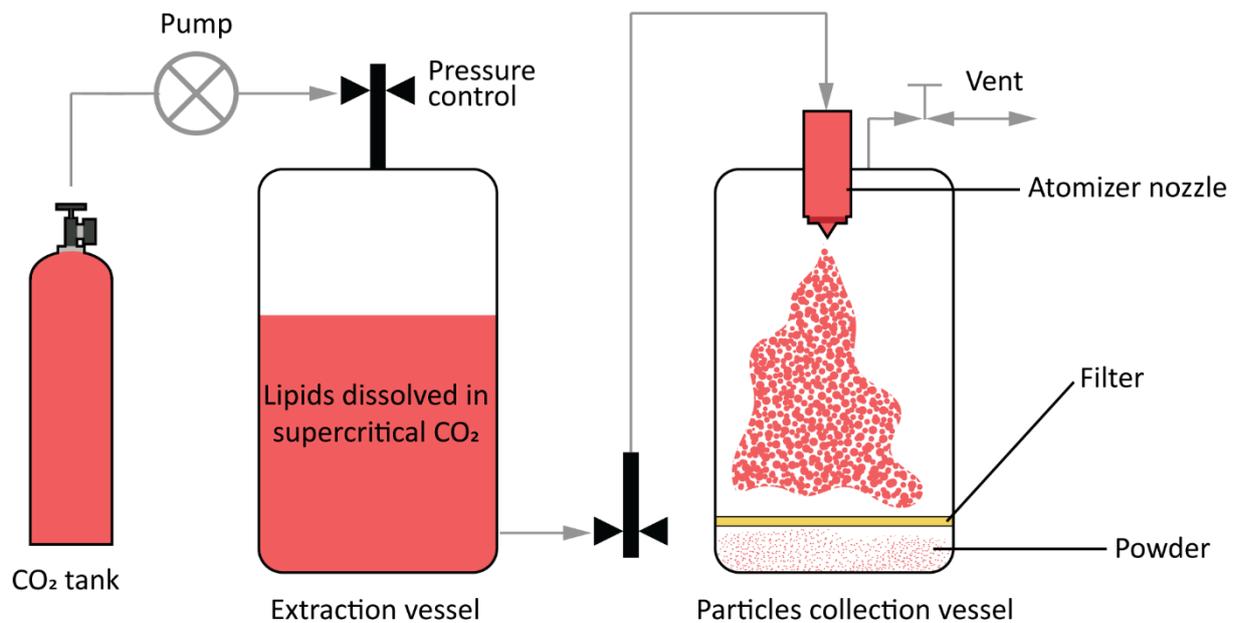


Fig. 6. Schematic diagram of supercritical fluid technology.

3.2.2 Phase separation: simple or complex coacervation

Coacervation refers to a process in which macromolecules are dissolved, resulting in phase separation within a solution. Thus, the coacervate (phase rich in polymer and poor in solvent) and the supernatant (phase rich in solvent and poor in polymer) are obtained.

Simple coacervation is based on a single polymer desolvation due to a change of temperature or the addition of a non-solvent, an electrolyte or even a second incompatible polymer. This leads to increased polymer-polymer interactions to the detriment of polymer-solvent interactions, thereby causing polymer desolvation. It can be carried out in an aqueous or organic medium. The active agent is introduced into the dispersed phase. It therefore makes it possible to encapsulate water-soluble and water-insoluble products [73,74].

Complex coacervation is based on the desolvation of two water-soluble polyelectrolytes carrying opposite charges. It is induced by a change in pH in order to balance the charges of the two polymers which then adsorb into the surface of the drops containing the active agent (Fig. 7). Generally, the used polyelectrolytes are gelatin (positively charged) and arabic gum, alginates or carrageenan (negatively charged) [75–77]. This technique allows high encapsulation rates and the use of little or no organic solvent. However, the materials choice is restricted and limited to pairs of polyelectrolytes with opposite charges and only liposoluble active materials can be encapsulated [78].

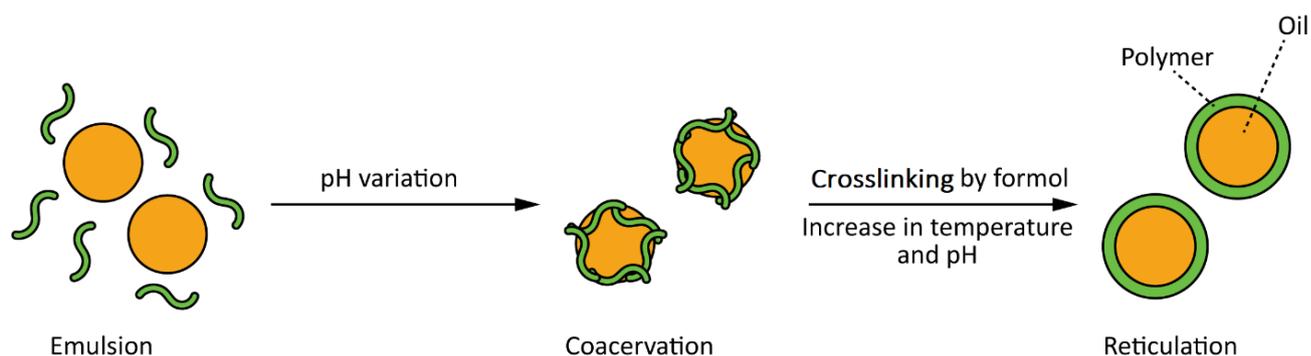


Fig. 7. Schematic diagram of encapsulation by complex coacervation process.

Song et al. (2016, 2018) prepared microcapsules containing $\text{Ce}(\text{NO}_3)_3$ or $\text{La}(\text{NO}_3)_3$ by the complex coacervation method [79,80]. These corrosion inhibitors were encapsulated in a gelatin-chitosan shell material. The average size of the capsules was between 30 and 50 μm . Both types of microcapsules were embedded in cerium-based conversion coating to evaluate the self-healing efficiency of the coating deposited on magnesium alloys. The cerium conversion coating containing microcapsules revealed a better corrosion resistance compared to the one without microcapsules and showed also a good self-healing performance.

3.2.3 Internal phase separation

The internal phase separation is an efficient process for the development of containers with liquid core and polymer shells. However, this technique is still very limited to hydrophobic core materials [81].

Internal phase separation is relevant to most polymers and can be used for large-scale particles preparation. This process is based on polymer dissolution in a solvent mixture consisting of a volatile and a non-volatile solvent (Fig. 8). An adequate amount of good solvent is necessary to guarantee the polymer dissolution. Then, this solution will be dispersed into a mixture of water and emulsifiers to prepare an oil-in-water emulsion. A change in the composition of the droplet will be caused by the volatile-solvent evaporation, then, a separation of the polymer-rich phase into small droplets will occur within the emulsion droplets. The droplets rich on polymer move to the interface between oil and water, then they coalesce to develop polymer particles. It has been shown that the microparticles morphology is determined by the thermodynamics, so as to ensure the minimum total interfacial free energy [82]. Thus, the internal phase separation caused by a reaction in the dispersed phase and/or the evaporation of a solvent from the dispersed phase can also contribute to the development of micro/nano capsules [83,84].

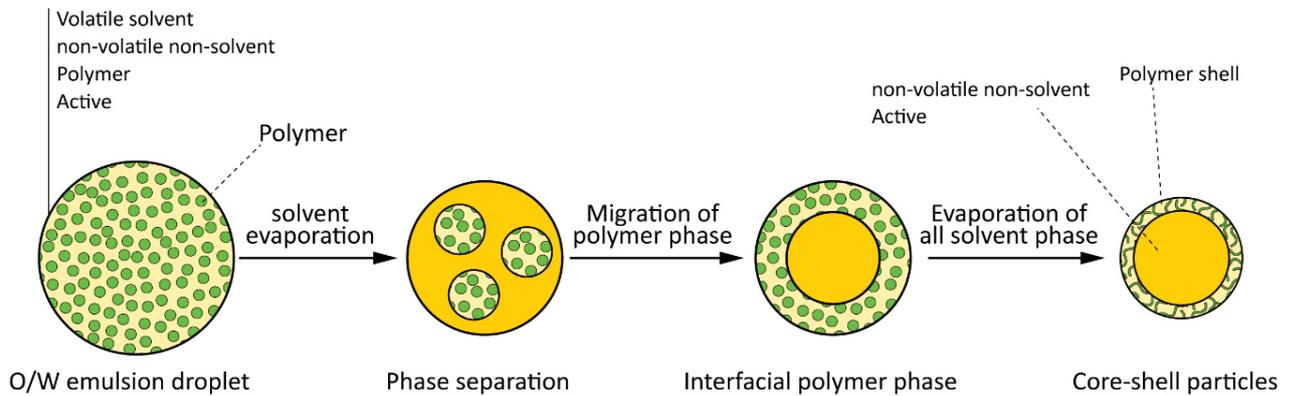


Fig. 8. Schematic diagram of microencapsulation by internal phase separation.

Ahangaran et al. (2017) used the internal phase separation method to incorporate epoxy prepolymer, 3-aminomethyl-3,5,5-trimethylcyclohexylamine, and pentaerythritol tetrakis (3-mercaptopropionate) as healing agents into polymethyl methacrylate (PMMA) based microcapsules [20]. The prepared microcapsules were used for self-healing purposes. The microcapsules preparation was evaluated through two different molecular weights of PMMA and two types of emulsifiers (polymeric and ionic). SEM results showed that the surface morphology of the capsules depends on the encapsulated core material, the molecular weight of the shell material and the concentration of the emulsifier.

3.2.4 Emulsion/solvent evaporation

This process involves evaporation of the organic solvent from the dissolved/dispersed phase of an emulsion by stirring. Both the polymer and the active material to be encapsulated are dissolved/dispersed in a volatile organic solvent within the same phase (dispersed phase). The dispersed phase is then emulsified in an external phase (non-solvent for the polymer, generally water) containing a surfactant to obtain an emulsion. When the emulsion is stabilized, the organic solvent diffuses to the continuous phase to evaporate. This causes the polymer precipitation and the formation of microparticles (Fig. 9). The drawback of this technique is that it requires the use of organic solvents leaving significant traces in the synthesized microspheres [85–87].

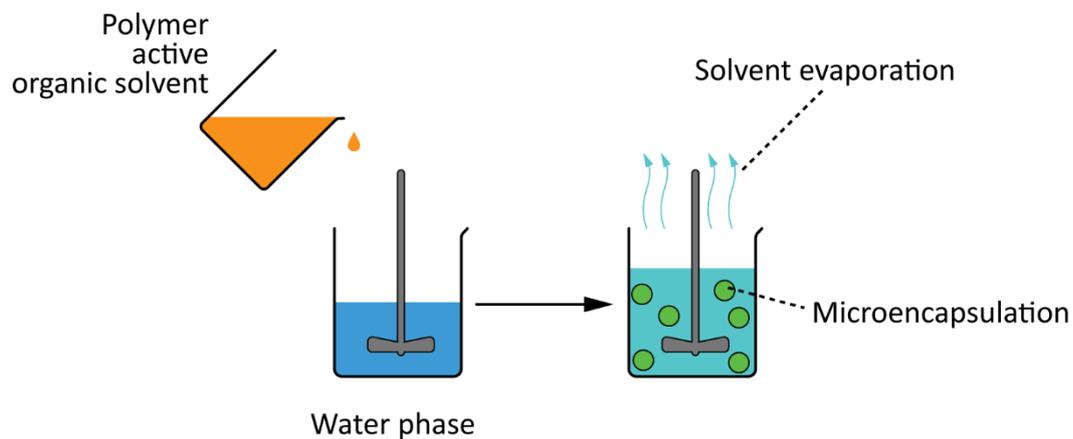


Fig. 9. Schematic diagram of microencapsulation by solvent evaporation. The organic phase containing the core and shell materials is emulsified in the water phase containing a surfactant. The solvent evaporates after emulsion stabilization induce the microcapsules formation.

In the studies of Abbaspoor et al. (2019), linseed oil (LO) constitutes the core material and ethyl cellulose is the shell material of the nano and microcapsules [37,38]. These capsules prepared by the emulsion solvent evaporation method were spherical with a size distribution ranging from 78 nm to 300 μm . The self-healing performance and corrosion resistance of the coatings containing capsules were studied. It was showed that the corrosion resistance of the coatings was improved, and the provoked coatings' scratches were successfully healed. It was also stated that a decrease of the nanocapsules size induces the increase of the self-healing performance. In a study reported by Cotting et al. (2016), the corrosion inhibitors (octylsilanol and Ce (III) ions) have been encapsulated in polystyrene shell material via solvent evaporation technique [88]. The prepared microcapsules were incorporated in an epoxy clear coating to evaluate the self-healing anticorrosion effect of the coating on carbon steel substrate. The obtained results revealed better performance of the coatings containing microcapsules compared to the blank coating.

3.2.5 Thermal gelation (hot melt)

This process consists of emulsion formation from the mixture of coating material in the molten state and active material, in a liquid of opposite polarity. The particles solidification is obtained by abrupt cooling of the emulsion (Fig. 10). The substances to be encapsulated, generally proteins or enzymes, are dispersed in a coating material in the molten state such as carnauba wax or cetyl alcohol.

This technique can be selected for the encapsulation of fragile materials such as living cells because the process takes place at room temperature. However, this advantage can become a disadvantage when this process is carried out with lipids. In fact, during cooling, crystalline forms are generated and modify the physical characteristics of the obtained microspheres (melting point, release kinetics, etc.) [86].

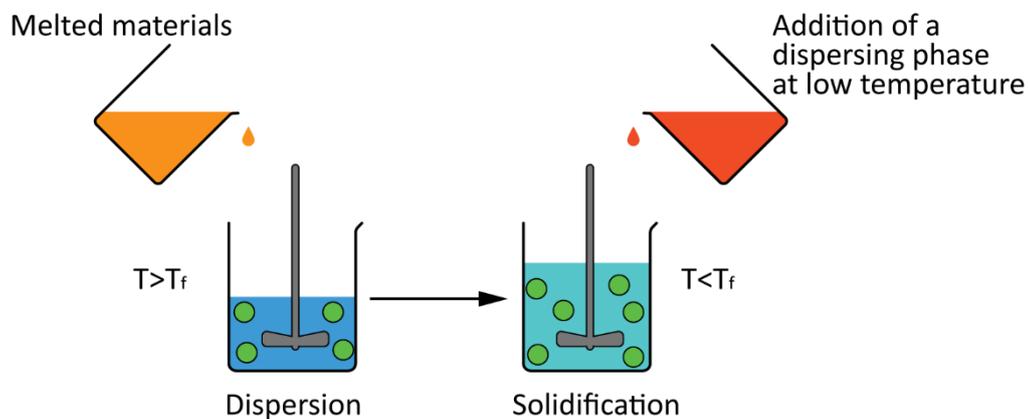


Fig. 10. Schematic diagram of microencapsulation by thermal gelation process. A mixture of melted shell and active material is dispersed in a liquid of opposite polarity. Then, a dispersing phase at low temperature is added to the emulsion to allow the capsules solidification and formation.

3.2.6 Layer by layer (LBL)

It is a self-assembly technique of polymers with opposite charges to form membranes. It consists in adsorbing alternately positively and negatively charged polyelectrolytes on organic or mineral particles which constitute the core of the particle. The core can be calcite, latex, silica, etc.

Depending on its nature, the size of the core can vary from few tens of nanometers to few tens of micrometers. After destruction of the core material in a suitable medium, hollow nano/micro capsules could be generated. To encapsulate a product, it could be mixed with the core material, or it could be adsorbed in the core before committing successive deposits of polyelectrolytes of opposite charge. The deposition of a polyelectrolyte layer may not be limited to a single layer of each charged polymer. Successive deposition of several layers is possible, which of course increases the final size of the microcapsule (Fig. 11).

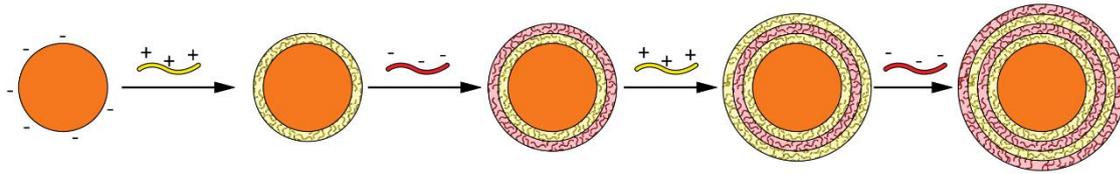


Fig. 11. Schematic illustration of microencapsulation via layer-by-layer process.

After the preparation of a stable and negatively charged emulsion droplets, positively charged polyelectrolyte is adsorbed on the droplets to form a positively charged capsules. The process is repeated using another polyelectrolyte with opposite charge until generation of desired shell thickness.

To produce complex microcapsules, different encapsulation techniques have been developed. Among them, the layer-by-layer (LBL) technique which is still a special and multipurpose encapsulation method. Thus, it has gained substantial interest for anticorrosion self-healing applications. The majority of studies on anticorrosion self-healing materials through a LBL process had a focus on the effect of pH changes attributed to the redox reactions between corrosive materials and metallic substrates [89,90].

In a study by Zheludkevich et al. (2007), multi-layered nanocapsules were prepared using silica nanoparticles; the benzotriazole corrosion inhibitor was entrapped in pH-sensitive polyelectrolyte multilayers of polyethylene imine (PEI) and polystyrene sulfonate (PSS) as shell materials that changes its permeability in function of the pH value of the surrounding medium [91]. This change allows the release control of the corrosion inhibitor, thus, stopping the corrosion process. The prepared nanocapsules had an average size of 100 nm. The nanocapsules were embedded in a sol-gel polymeric matrix coated on aluminum substrate. Corrosion tests were carried out to evaluate the nanocapsules-containing coating, and the results revealed enhanced long-term corrosion protection of the hybrid films containing nanocapsules in comparison with the undoped hybrid film.

3.2.7 Microfluidic encapsulation

A microfluidic process refers to fluid flow in channels with micrometric size. A generator of microfluidic droplets and a junction are the fundamental elements of the system (Fig. 12).

Microfluidic systems can be divided into two types: monophasic, working only with one fluid, or multiphasic, working with at least two fluids which are in contact through junctions. In these junctions, the contact of immiscible fluids can cause the flow segmentation of one of the fluids leading to microdroplets generation. This process allows a good control of the droplets size and shape as well as a high frequency generation. This technique is similar to emulsification, with the advantage of avoiding the use of surfactants [92–94].

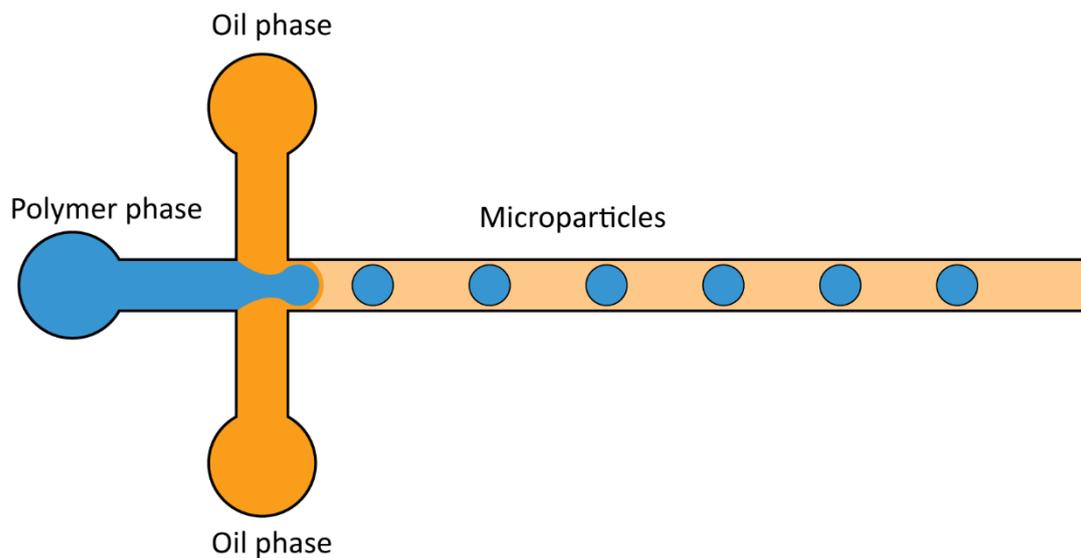


Fig. 12. Schematic diagram of microencapsulation by microfluidic encapsulation process.

The junction allows the sharing of the aqueous phase by the oil phase which generates droplets. As far as we know, microfluidic encapsulation processes are not used yet to prepare capsules containing corrosion inhibitors for end use in anticorrosion self-healing coatings. Besides, Philipp W. Chen et al. (2014) came with a new vision to encapsulate amines, avoiding other encapsulation process challenges due to amines miscibility and reactivity [95]. Their concept consists of amines encapsulation via double-emulsion templates made in a microfluidic device. The objective was to encapsulate two amines, triethylenetetramine (TETA) and diethylenetriamine (DETA), in acrylate shell material using the microfluidic approach. Amines encapsulation and reactivity have been investigated and confirmed through different analyses such as FTIR spectroscopy, TGA, SEM, NMR spectroscopy and mechanical tests. The prepared microcapsules were destined to develop epoxy-based self-healing materials.

In another study by Neuser et al. (2014), the previous described microfluidic encapsulation process has been used to prepare amine microcapsules, then combined with epoxy filled microcapsules prepared via *in situ* encapsulation process using urea-formaldehyde as shell material [96]. This work was a proof of concept to study the healing efficiency of two

components epoxy/amine self-healing system as well as to show the evidence and the feasibility of the microfluidic process to produce amine microcapsules.

3.3 Physical processes

3.3.1 Spray drying and coating

The spray drying technique ensures the preparation of dry particles from a liquid formulation which contains the active component and the coating agent (Fig. 13 a). Numerous steps are to be followed to obtain the desired microparticles. Firstly, a liquid solution composed of a solvent, a coating and an active agent should be atomized into droplets using a rotatory atomizer or a nozzle. Secondly, the solvent is evaporated using a heated gas in contact with the atomized feed via a gas sparger. While the liquid evaporates rapidly, microparticles are formed and fall into the bottom of the chamber. Finally, a cyclone or a bag filter will allow the powder collection from the exhaust gases (particles falls in the size range of 1 – 100 μm). This process is mastered, especially, in the food and pharmaceutical industries, but it can be used for other applications [46,66,97–100].

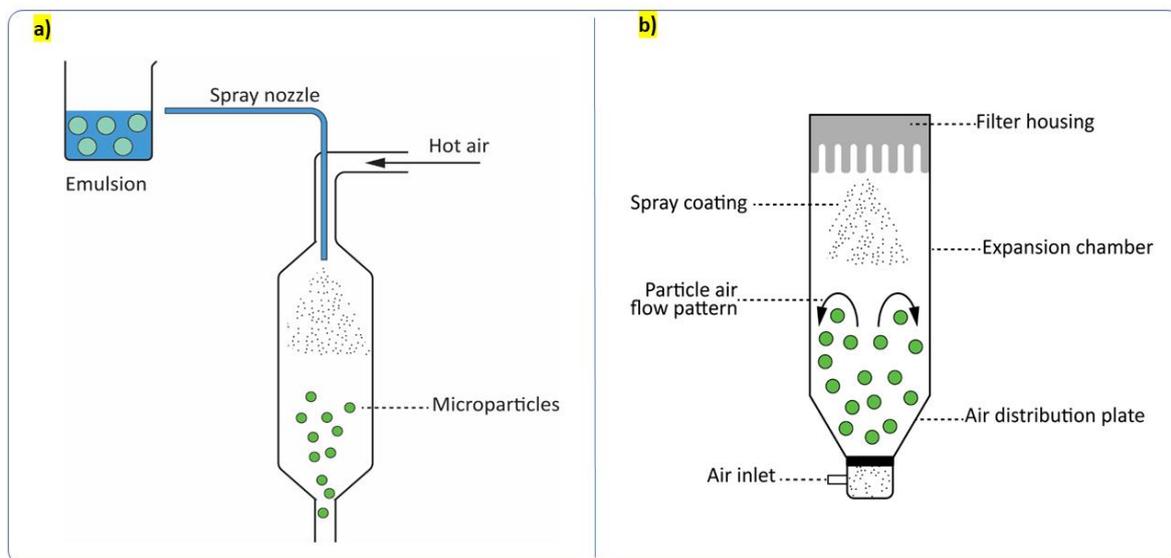


Fig. 13. a) Schematic illustration of microencapsulation by spray-drying process. The emulsion is sprayed through the nozzle to generate small droplets, which are transformed into dry particles by evaporation of the organic solvent caused by the heated dry air flow.

Thereafter, the particles are collected as dry powder. **b)** Schematic illustration of microencapsulation by spray-coating process. The particles are fluidized, spray coated, then the coating film is dried, and the final particles are collected.

As far as we know, spray drying process is not used yet to prepare microcapsules for end use in anticorrosion self-healing applications. However, this method was utilized for different applications, for instance in cosmetic and pharmaceutical applications. The spray drying technique has been optimized to achieve nano-scale particles. So, at the present time, Nano Spray Drying is considered as a relevant encapsulation technology [83].

Shirokawa et al. (2013) prepared temperature and water responsive microcapsules via spray drying method [101]. Ethyl cellulose, methyl cellulose and P-N-isopropylacrylamid were used as polymeric shell materials. The encapsulated core material was the hydroquinone. This material has been used by Sherine et al. (2010) to develop a corrosion inhibitor system composed from hydroquinone and zinc ions [102]. This system revealed very interesting results regarding the corrosion inhibition and the protection of carbon steel up to 97 % of inhibition efficiency when the proportions of 150 ppm of hydroquinone and 100 ppm of zinc ions were used. The exploitation of this system to prepare micro/nano capsules through the spray drying process could have a very promising application in anti-corrosion self-healing coatings.

The spray coating method is considered as the oldest encapsulation technique. It allows the coating of active ingredients consisting of solid particles (granules, crystals). The powder is initially fluidized, then the coating material is sprayed onto the particles and the obtained coating film is then dried (Fig. 13 b). However, this process requires solid particles with a narrow particle size distribution to obtain homogeneous coating with controlled thickness. In addition, it is not suitable to coat particles with a size less than 100 μm because of aggregation phenomena during the process. The coating film thickness is generally between few micrometers to 20 μm [103].

Usually, the capsules used for extrinsic self-healing materials contain liquid healing agents, which are not able to be encapsulated using the spray coating technique. The size of the particles generated via spray coating process is still not encouraging to use this technique to prepare particles for self-healing materials [86,104,105].

3.3.2 Prilling (Gelation or freezing)

Gelation of drops is carried out from a solution, dispersion or emulsion of active ingredients in an aqueous solution of polymers. These polymers must be capable of forming gels by changing a physical parameter (temperature) or chemical conditions (ionic concentration, pH, presence of compounds inducing precipitation, etc.). Freezing of drops consists of solubilization or

dispersion of the active agent in a coating material in the molten state. For these two techniques, the drops are formed through a vibrating nozzle and are collected in a medium allowing the gelling or solidification of the coating material (Fig. 14). The polymers used are generally alginate, chitosan or agarose for gelation and petroleum, animal or vegetable waxes for freezing.

The main drawbacks of these two methods are that they result in low density particles; the size distribution ranges between 200 μm and 800 μm and the encapsulation rate is low (between 10% and 30% by mass). However, they allow a very narrow particle size distribution [106].

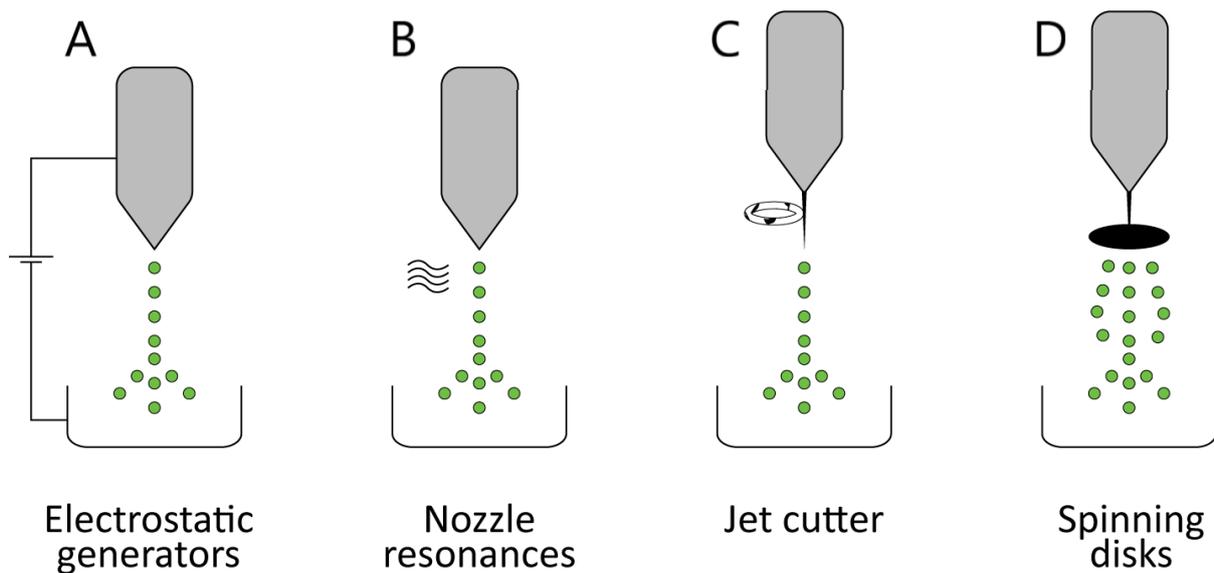


Fig. 14. Schematic illustration of different configurations of prilling microencapsulation process. (A) Electrostatic generator: Charges accumulate on the surface of the droplets by applying an electrostatic potential cause the opposition of the surface tension, allowing the formation of capsules. (B) Nozzle resonances: Formation of uniform droplets by applying a vibration to the liquid jet flowing from the nozzle and the formation of the capsules in a liquid. (C) Jet cutter: A hollow turntable cut the liquid jet at high speed, then capsules formation. (D) Spinning disks: Flow of liquid on spinning disk, then a jet of the droplets and capsules formation.

Such drawbacks could justify the reasons why the prilling encapsulation process is not used to prepare micro/nano capsules containing healing agents for end use in anticorrosion self-healing materials [107].

Table 1. Examples of encapsulation of anticorrosion healing agents via different encapsulation processes for anticorrosive self-healing coatings application.

Encapsulation method	Healing agent	Shell	Particle morphology	Micro/nano capsules diameter	Matrix	Description	Ref
In situ polymerization							
In situ polymerization & layer by layer	Linalyl acetate & Phenylthiourea (PTU)	Urea formaldehyde & polyethylenimine (PEI) and sulfonated polyether ether ketone (SPEEK)	Microcapsules	N/A	Epoxy resin	Polyelectrolyte encapsulation for corrosion protection coating	[108]
In situ polymerization	Linseed oil & cerium acetate (Ce) and 8-Hydrox Microcapsule (8-HQ)	Urea-formaldehyde	Microcapsules	20 -120 μm	Epoxy matrix	Corrosion protection coatings	[23]
In situ polymerization	Linseed oil	Polyurea-formaldehyde (PUF)	Microcapsules	20 - 150 μm	Epoxy coating	Surface capsules modification & corrosion protection coatings	[24]
In situ polymerization	Dimethyl sulfoxide (DMSO)	Melamine formaldehyde pentaerythritol tetrakis (3-mer-captopropionate) (MFPTT)	Microcapsules	800 - 9000 nm	Epoxy coating	pH-Responsive microcapsules & Corrosion protection coatings	[109]
In situ polymerization	Epoxy resin	Urea Formaldehyde	Microcapsules	N/A	Waterborne Wood Coatings		[18]
In situ polymerization	Epoxy resin	Urea formaldehyde	Microcapsules	Av. 55.7 μm	Epoxy coatings	Effect of concentration and stirring was discussed	[17]
In situ polymerization	Epoxy resin	Urea-formaldehyde	Microcapsules	3 - 5 μm	Waterborne wood coating	Improve the toughness of the coating and prevent the cracking of the coating. The effects of adding microcapsules in different coating processes on the performance of coatings were compared	[19]

In situ polymerization	Linseed oil	Poly (melamine-formaldehyde)	Microcapsules	8 - 71 μm	Nothing	Influence of the emulsifying system	[25]
In situ polymerization	linseed oil and linseed oil based alkyd resin	Urea formaldehyde	Microcapsules	N/A	Epoxy matrix		[26]
In situ polymerization	Diglycidyl ether bisphenol-A-based epoxy (EPON828) and pentaerythritol tetrakis (3-mercaptopropionate)	Urea (NH ₂ CONH ₂) and ammonium chloride (NH ₄ Cl)	Microcapsules	111 - 120 μm	Alkyd coating	Production of UV-curable alkyd coating with self-healing ability	[110]
In situ polymerization	epoxy resin and n-butyl glycidyl ether (BGE)	Urea formaldehyde	Microcapsules	Av. 200 μm	Epoxy coatings	Coating with underwater self-healing and anti-protein-fouling properties	[111]
In situ polymerization	Epoxy ester	Poly urea formaldehyde	Microcapsules	101 +/- 48 μm	Epoxy coatings	Self-healing and corrosion resistance	[21]
In situ polymerization	Linseed oil	Urea formaldehyde	Microcapsules	Av. 53 μm	Commercial under-coating formulation	Protection of Cementitious Materials	[27]
In situ polymerization	Linseed oil	Urea formaldehyde	Microcapsules Nanocapsules	3 to 238 μm	Epoxy coatings	Self-healing and corrosion resistance	[28]
In situ polymerization	Linseed oil and Linseed oil-based alkyd resin	Urea formaldehyde	Microcapsules	51 and 97 μm and 56 and 261 μm	Epoxy coating	Corrosion protection through self-healing.	[29]
In situ polymerization	Linseed oil	Urea formaldehyde	Nanocapsules	459-712 nm	Epoxy and polyurethane hybrid coatings	Self-healing and anticorrosion performance on the copper metal films.	[30]
In situ polymerization	Alkyd resin based on coconut oil	Poly (melamine-urea-formaldehyde) (PMUF)	Microcapsules	1 to 40 μm	Commercial epoxy coating	Self-healing and anticorrosion performance	[112]
In situ polymerization	Linseed oil	Poly urea formaldehyde (PUF)	Microcapsules	Av. 80 μm	Epoxy-polyamine coating matrix	Self-healing anticorrosive coating	[31]
In situ polymerization	Tung oil	Poly(urea-formaldehyde)	Microcapsules	Av. 105 μm	Epoxy resin	Self-healing and self-lubricating coatings	[41]
In situ polymerization	Sunlight-curable silicone-based resin	Melamine-urea-formaldehyde (MUF)	Microcapsules	32.1 to 327.1 μm		Suitable for self-healing materials	[113]
In situ polymerization	Epoxy	Poly(urea-formaldehyde)	Microcapsules	Av. 2.13 μm	Epoxy resin	Self-healing epoxy coating	[22]

In situ polymerization	Coconut oil-based alkyd	Poly (melamine-urea-formaldehyde)	Microcapsules	1 to 40 μm		Suitable for self-healing purpose	[114]
In situ polymerization	Linseed oil	Poly(urea-formaldehyde)	Microcapsules	N/A	Epoxy coating	Self-healing coating for anti-corrosion	[32]
In situ polymerization	Linseed oil	Urea-formaldehyde	Microcapsules	N/A	Epoxy coating	Impedance study of self-healing coating for anti-corrosion	[33]
In situ polymerization and sequential emulsion polymerization	Perfluorooctyl triethoxysilane (POT), ethanolamine (ETA), and diethanolamine (DEA)	Poly (urea-formaldehyde) and polystyrene (PS)	Microcapsules	N/A	Epoxy coating	Epoxy coating	[115]
In situ polymerization	Linseed oil	Melamine-urea-formaldehyde	Microcapsules	34 to 346 μm		Suitable For self-healing coating	[34]
In situ polymerization	Hexamethylene diisocyanate (HDI) biuret	urea-formaldehyde	Microcapsules	N/A	Alkyd varnish coatings (AVCs).	Self-healing coating	[116]
In situ polymerization	Carbon microspheres (CMSs)	poly (ethylene terephthalate) (PET)	Microcapsules	N/A	PET matrix	Study of flame retardancy	[117]
In situ polymerization	Nafion solution/ tributyl phosphate	Urea-formaldehyde	Microcapsules	1–5 μm	Self-healing membrane	Self-Healing Composite Membrane for Proton Electrolyte Membrane Fuel Cell Applications	[118]
Interfacial polymerization							
Interfacial polymerization in an oil-in-water emulsion	Isophorone diisocyanate (IPDI)	Sodium lignosulfonate (NaLS)	Microcapsules	43.4-118.3 μm	Polyurea	Anti-ultraviolet	[119]
Interfacial polymerization	Isophorone diisocyanate	Polyurethane	Microcapsules	10 to 500 μm depending on the mixing speed	Polyurethane coatings	Polyurethane coatings	[67]
Interfacial polymerization	Dimer-acid-based polyol	Polyurethane	Microcapsules	17–125 μm	Polyurethane	Self-healing anticorrosive coating	[120]
Interfacial Polymerization	Tung oil	Polyurea	Microcapsules	58-260 μm	PU composite coatings	Self-healing anticorrosive coating application	[40]

Interfacial polymerization	Isophorone diisocyanate (IDPI)	Polyurethane	Microcapsules	N/A	Acrylic-melamine clearcoat	Study the scratch resistance and self-healing features of synthesised acrylic melamine clearcoat.	[121]
Solvent evaporation							
Solvent evaporation	Linseed oil	Ethyl cellulose	Nanocapsules	472.8 and 78.8 nm	Polyurethane resin	Corrosion protection coatings	[37]
Solvent evaporation	Linseed oil	Modified poly(methyl methacrylate)	Microcapsules	2.6-11.6 μm	Epoxy coatings	The effect of mechanical mixing rate was studied	[39]
Solvent evaporation	Linseed oil	Ethyl cellulose	Microcapsules Nanocapsules	300 μm 150 nm	Polyurethane coatings	Corrosion protection coatings	[38]
Solvent evaporation	Almond oil	Ethyl cellulose and Phosphorylated Ethyl cellulose	Microcapsules	140 and 150 μm	Epoxy coating	Corrosion protection coatings	[42]
Solvent evaporation	810 Under water epoxy hardener (UEH)	PMMA	Microcapsules	Av. 70 μm	Epoxy coatings	Coating with underwater self-healing and anti-protein-fouling properties	[111]
Solvent evaporation	Silanol and Ce (III) ions	Polystyrene	Microcapsules	N/A	Epoxy	Corrosion protection	[88]
Complex coacervation							
Complex coacervation & In situ polymerization	Citronella oil	Gelatine with carboxymethylcellulose or with gum Arabic & melamine-formaldehyde prepolymers with a polyacrylic acid modifier	Microcapsules	10 to 200 μm	Papers for secondary packaging	Antimicrobial Paper Coatings Containing Microencapsulated Cymbopogon citratus Oil	[122]
Complex coacervation	Ce(NO ₃) ₍₃₎ or La(NO ₃) ₍₃₎	Gelatin-chitosan	Microcapsules	30–50 μm	Cerium-based conversion coatings	Self-healing conversion coating on magnesium alloys	[79]
Complex coacervation	La(NO ₃) ₍₃₎	Gelatin-chitosan	Microcapsules	Av. 30 μm	Conversion coating	Self-healing conversion coating on magnesium alloy	[80]
Water-in-oil emulsion polymerization							
Water-in-oil emulsion polymerization	Cerium nitrate or Aluminum nitrate	Butylated urea-formaldehyde resin	Microcapsules	N/A		pH sensitive microcapsules containing corrosion inhibitor	[45]
Water-in-oil emulsion polymerization	Resins or inhibitors	Urea-formaldehyde and melamine-formaldehyde	Microcapsules	N/A		Self-healing for coatings	[50]

Water-in-oil emulsion polymerization	Cerium nitrate	Urea-formaldehyde	Microcapsules	7-18 μm	Commercialized epoxy resin	pH sensitive microcapsules and self-healing anticorrosive coating	[44]
Pickering emulsions							
Pickering emulsions	Linseed oil	Graphene oxide	Microcapsules	Av. 8 μm	Waterborne polyurethane composite coatings	Study of Pickering emulsion for encapsulation and self-healing efficiency of the prepared microcapsules	[35,36]
Internal phase separation							
Internal phase separation	Epoxy prepolymer, 3-aminomethyl-3,5,5-trimethylcyclohexylamine, and pentaerythritol tetrakis (3-mercaptopropionate)	Polymethyl methacrylate (PMMA)	Microcapsules	N/A	Epoxy resin	For self-healing purposes	[20]
Radical polymerization							
Radical polymerization	Triethanolamine (TEA)	Seed latex	Nanocapsules	Av. 450 nm	Epoxy coating	Study of the anticorrosion performance of the coating, and its self-healing properties	[58]
Layer by layer							
Layer by Layer (LBL)	Benzotriazole	Polyethylene imine (PEI) and polystyrene sulfonate (PSS)	Nanocapsules	Av. 100 nm	Sol gel Polymeric matrix	Study of anticorrosive and self-healing effect of coatings through pH sensitive microcapsules	[91]

4. Challenges and future trends

The research in the self-healing materials field is now a promising crossroad. The structures involving the use of capsules containing healing agents have been extensively studied. They are becoming increasingly popular in literature and are still being improved towards the development of innovative alternative methods.

In fact, according to a recent research report by Grand View Research (2019), the global self-healing materials market size was estimated at USD 291.4 million in 2018. A 46.1% growth at a CAGR (Compound annual growth rate) from 2019 to 2025 is estimated. It is worth mentioning that 27.3% of the total market share in 2018 accounts for the coatings sector. Moreover, the automotive and aerospace industries' products development is projected to promote further this segment to reach 28.3% market share by 2025 [123]. In this context, micro/nano encapsulation technologies emerge as a necessary and reliable tool to follow the development of the self-healing materials market and to provide further benefits and innovative solutions to the capsule-based self-healing materials.

Thus, micro/nano encapsulation has a potentially significant future in the development of extrinsic self-healing materials for different applications. However, several significant challenges still face the microencapsulation processes of healing agents. For instance, determination of the adequate reagents and weighing of chemicals with high precision should be carefully controlled to avoid side reactions and prevent uncontrolled ones. Moreover, all the reagents including solvents and polymers used as shell materials should be well defined or even be standardized in terms of composition, purity grade, reaction conditions, source reproducibility, physical and chemical properties, in order to minimize the differences and variability in the results obtained by different studies.

The capsules containing healing agents are mostly susceptible to be degraded because of different factors such as storage conditions and surrounding environment. Indeed, to take advantage from the micro/nano capsules, it is mandatory to ensure their stability during the preparation process and storage, and their resistance to the processing during their incorporation in the bulk of the material to be self-healed. It is also necessary to overcome some limitations such as interactions of the capsules and their solubility. Thus, the selection of materials is one of the challenging issues that formulators are facing to prepare the appropriate micro/nano capsules for the targeted self-healing application.

One of the biggest challenges is the scaling-up of the encapsulation processes. The control of the parameters and reactions environment of the encapsulation processes as well as the quality of the prepared capsules are some of the key steps to investigate in order to scale-up the microencapsulation methods and make them at disposal of industrials to develop and commercialize self-healing materials. Finally, the cost of the capsules production is a relevant challenge. It is directly related to the used materials and formula, the selected encapsulation process and its complexity as well as the production scale.

5. Resume and Outlook

Microencapsulation is one of the best industrial technological solutions used in order to protect the active ingredient, improve its presentation or control its release. It has numerous applications in different fields such as pharmaceuticals, food, cosmetics and smart materials in general.

Microencapsulation is based on a wide range of processes, which are classified based on various criteria. In this work, we reviewed the encapsulation processes used for preparation of microcapsules needed to develop anti-corrosion self-healing coatings. These extrinsic self-healing materials offer a path for the preparation of smart polymeric coatings with less cost and higher reliability and lifetime. The literature review indicates that encapsulation of anticorrosion healing agents has highly improved the corrosion resistance properties of self-healing coatings. All described cases in this review showed evidently that coatings containing encapsulated anticorrosion healing agents exhibited better performances compared to those without capsules. Encapsulation processes are multiple; the most used in development of anticorrosion self-healing coatings is based on *in situ* polymerization. The choice of the encapsulation method depends on different factors such as the materials used for encapsulation and the targeted capsules size and morphology. Because of environment related reasons, the encapsulation processes applied to prepare self-healing coatings must get rid of using organic solvents. These processes need to evolve towards the use of generally recognized as safe constituents in order to develop on the market or move from lab scale to industrial scale. It is worth to mention that physical encapsulation processes are still not used to prepare micro/nano capsules for anticorrosion self-healing coating because of the aforementioned limitations. These physical processes could be a promising alternative to encapsulate solid anticorrosion healing agents if they are optimized to achieve this objective. The advance of developing new materials and applications based on microparticles will lead

to the emergence of new microencapsulation processes compatible with the targeted new formulations and applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this review.

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Chapter 2

Phosphorylated microcapsules containing natural oil for potential self-healing use

Introduction to chapter 2

Au cours de la dernière décennie, l'étude et le développement de structures et produits chimiques complexe ont été le sujet de plusieurs travaux de recherche. Parmi ces structures, on trouve les microcapsules fabriquées à l'aide de différentes techniques d'encapsulation. L'objectif principal de la préparation des capsules est d'envelopper un matériau dans le noyau par un matériau d'enveloppe afin d'être protégé du milieu environnant. Le stockage des composés et la possibilité de contrôler la libération du matériau de noyau ont rendu possible l'utilisation de microcapsules dans différentes applications commerciales, telles que les médicaments, les conservateurs alimentaires, les dispositifs électroniques, les produits cosmétiques et les matériaux auto-cicatrisants.

Parmi les différentes techniques de développement de matériaux auto-cicatrisants, la méthode extrinsèque basée sur la stratégie d'encapsulation est l'approche la plus étudiée. Elle repose sur l'encapsulation d'un agent cicatrisant dans un matériau polymère d'enveloppe. Les capsules doivent ensuite être intégrées dans une matrice permettant leur libération lors d'un événement de rupture et favorisant ainsi l'auto-cicatrisation.

Les microcapsules chargées d'inhibiteurs de corrosion pour l'application de revêtements auto-cicatrisants ont été l'objectif principal de diverses études. Cette application était basée sur le concept de système d'auto-cicatrisation extrinsèque initié par White et al. en 2001. Conceptuellement, un revêtement anticorrosion auto-cicatrisant est considéré comme une combinaison du composant passif, représenté par le revêtement de matrice conventionnel, et du composant actif représenté par les micro/nano-capsules contenant un inhibiteur de corrosion. Ce concept a été utilisé dans différentes études pour développer des revêtements anticorrosion. Par exemple, les huiles de lin et de tung ont été principalement encapsulées en utilisant l'urée-formaldéhyde comme matériau d'enveloppe, et les microcapsules préparées ont été incorporées dans des revêtements à base d'époxy afin d'étudier et de comprendre leur effet sur l'inhibition de la corrosion et les performances d'auto-cicatrisation.

Ce chapitre porte sur la préparation de diverses microcapsules remplies d'huile par la méthode d'évaporation du solvant. L'éthylcellulose et l'éthylcellulose phosphorylée ont été utilisées comme matériaux polymères pour encapsuler l'huile de lavande (LO), l'huile de graines noires (BSO), l'huile de figue de barbarie (PPO) et l'huile d'argan (AO). Les microcapsules préparées ont été caractérisées et l'effet de l'enveloppe phosphorylée sur les propriétés des microcapsules a été discuté. Les microcapsules obtenues sont destinées à être

utilisées dans nos prochains travaux pour développer des revêtements autocicatrisants anti-corrosion, mais peuvent être explorées dans d'autres applications.

Ce chapitre, intitulé « Phosphorylated microcapsules containing natural oil for potential self-healing use » est présenté sous la forme d'un article rédigé en anglais qui a été publiée en 2021 dans le journal Materials Today: Proceedings sous le DOI : [10.1016/j.matpr.2021.05.093](https://doi.org/10.1016/j.matpr.2021.05.093) .

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Phosphorylated microcapsules containing natural oil for potential self-healing use

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Phosphorylated microcapsules containing natural oil for potential self-healing use

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Abstract

This work reports on the preparation of oil-filled microcapsules for self-healing purposes. Biopolymeric microcapsules loaded with vegetable oils as green corrosion inhibitors were formulated using ethyl cellulose and phosphorylated ethyl cellulose as encapsulating materials. Chemical structure, thermal stability and surface morphology of microcapsules were characterized by Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). FTIR and TGA analysis confirmed the presence of oil core and polymer shell in the formulated microcapsules. The scanning electron microscopy was used to evaluate the shape and morphology of the prepared microcapsules. The obtained results revealed the spherical-like shape of the obtained capsules with diameters ranging from 10 up to 170 μm . Thus, the current study shows the potential application of phosphorylated ethyl cellulose for the development of new environmentally friendly microcontainers bearing corrosion inhibitors for end use in anti-corrosion self-healing coatings.

Keywords: Microencapsulation; Phosphorylation; Ethyl cellulose; Self-healing; Anti-corrosion coating; Core-Shell microcapsule.

1. Introduction

Over the last decade, the study and development of integrated chemical structures have attracted the attention of researchers. One of these structures are microcapsules made using different microencapsulation techniques. The main objective of preparing capsules is to envelope a core material by a shell material in order to be protected from the surrounding environment. Compounds storage and the possibility of controlling the release of the core material have made the use of microcapsules possible in different commercial applications, such as drug delivery systems, food preservatives, electronic devices, cosmetic products, and self-healing materials. [1]–[4]

Among the various techniques of self-healing materials development, the extrinsic method based on encapsulation strategy is the most considered approach. It is based on the encapsulation of a healing agent in a polymeric shell material. Then capsules have to be embedded into a matrix material allowing their release during a rupture event and therefore promoting self-healing. [5]

Corrosion inhibitors-loaded microcapsules for the application in self-healing coatings were the main objective of various studies. This application was based on the concept of extrinsic self-healing system firstly initiated by White et al. in 2001.[6] Conceptually, a self-healing anticorrosion coating is considered as a combination of the passive component, represented by the conventional matrix coating, and the active component represented by the corrosion inhibitor-containing micro/nano capsule. This concept has been used in different studies to develop anticorrosion coatings. For instance, linseed and tung oils were mainly encapsulated using urea-formaldehyde as the shell material, and the prepared microcapsules were incorporated into epoxy-based coatings in order to study and understand their effect on corrosion inhibition and healing performance. [7], [8]

In this study, various oil-filled microcapsules were prepared via solvent evaporation method. Ethyl cellulose and phosphorylated ethyl cellulose were used as polymeric shell materials to encapsulate lavender oil (LO), black seed oil (BSO), prickly pear oil (PPO) and argan oil (AO). The prepared microcapsules were characterized and the effect of the phosphorylated shell on the properties of the microcapsules has been discussed. The obtained microcapsules are destined to be used in our upcoming work to develop anti-corrosion self-healing coatings, but, can be explored in additional key applications (e.g., biomaterials). [9]

2. Experimental

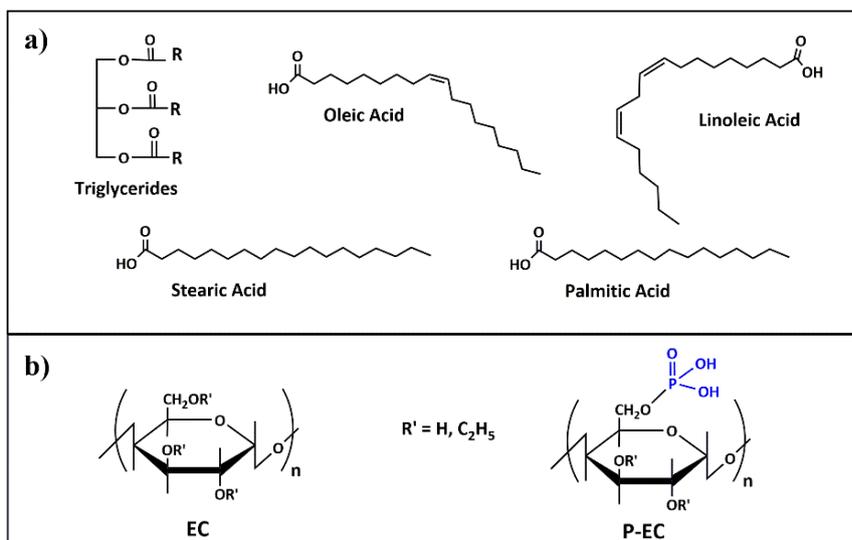
2.1 Materials

Ethyl cellulose (EC) powder, sodium dodecyl sulfate (SDS) and urea powder were purchased from Sigma Aldrich. Orthophosphoric acid (85 %) and methanol were obtained from Merck KGaA. The ethyl acetate (EA) was supplied by Somaprol, and Sodium hydroxide was provided by VWR. Lavender oil (LO), black seed oil (BSO), prickly pear oil (PPO) and argan oil (AO) were purchased from a drugstore in order to be used as core materials for the microcapsules. All chemicals were analytical reagents grade and were used without any further purification.

2.2 Preparation of microcapsules

Oil-filled microcapsules were prepared using a two stage solvent evaporation method as described elsewhere. [10], [11] Both, ethyl cellulose (EC) and phosphorylated ethyl cellulose (P-EC) were used as shell materials for the microcapsule's preparation (Scheme 1). The P-EC used as shell material was obtained through phosphorylation reaction of commercial ethyl cellulose (EC). The chemical modification of EC was performed using orthophosphoric acid in molten urea, following previously reported procedure. [10], [12] EC powder or P-EC powder were dissolved in ethyl acetate for 2 hours under room temperature and magnetic stirring at 650 rpm. The oil was then added to the solution stirring for 30 minutes more. In parallel, a 1wt.% sodium dodecyl sulfate aqueous solution was prepared. The polymeric solution (oil phase) was then added dropwise to the aqueous solution (water phase) under continuous mechanical mixing at a temperature of 60 °C for 90 minutes. The obtained mixture was freeze-dried, rinsed with distilled water, filtered, and then dried to generate the final native microcapsules (MC) and phosphorylated-microcapsules (P-MC).

To investigate the effect of shell materials and different oils on the microencapsulation process, the preparation was conducted using EC and P-EC as shell materials and lavender, black seed, prickly pear and argan based oils as core materials (Scheme 1).



Scheme. 1. a) Structure of major components in different vegetable oils (Lavender oil, Prickly pear oil, Black seed oil and Argan oil). b) Structure of Ethyl cellulose (EC) and phosphorylated ethyl cellulose (P-EC).

2.3 Characterization

Fourier Transform Infrared (FTIR) analysis was performed for initial raw materials, phosphorylated ethyl cellulose and prepared microcapsules to identify the core and shell materials. The FTIR spectra were recorded by a PerkinElmer FTIR spectrophotometer (Wellesley, MA, United States) using attenuated total reflection (ATR) technique and collecting 16 scans in the $4000\text{--}600\text{ cm}^{-1}$ range with a resolution of 4 cm^{-1} .

Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (Model –TGA 5500, Discovery series, TA Instruments, United States) to evaluate the thermal stability of the initial raw materials, phosphorylated ethyl cellulose and the prepared oil-filled microcapsules. The analysis was performed under a nitrogen atmosphere with a heating rate of 10 °C/min from room temperature up to 700 °C .

The surface morphology and the shape of the prepared microcapsules were observed using a scanning electron microscope ((Philips XL 40 ESEM). Before analysis, the microcapsules were coated with gold to improve imaging.

3. Results and discussion

3.1 Characterization of microcapsules

Fourier transform infrared (ATR-FTIR) spectroscopy was used to characterize the core materials (LO, BSO, PPO and AO), the shell materials (EC and P-EC) and the prepared oil-filled

microcapsules. The FTIR spectra of the core, shell and microcapsules are reported in Fig. 1. The obtained results revealed that the FTIR spectra of microcapsules have been found matching with all the encapsulated oils spectra. The structure of major components in the different vegetable oils used in this study are presented in scheme 1-a).

The FTIR spectra of lavender oil showed sharp peaks at 620 cm^{-1} , 730 cm^{-1} and 893 cm^{-1} attributed to C-H vibrations. The peak at 997 cm^{-1} was assigned to -CH₂ vibrations. The peaks at 1095 cm^{-1} , 1163 cm^{-1} and 1238 cm^{-1} were related to C-O stretching vibrations. The peaks at 1373 cm^{-1} , 1426 cm^{-1} and 1456 cm^{-1} belong to C-H bending vibrations. The peak at 1651 cm^{-1} was due to C=C stretching vibrations. The peak at 1748 cm^{-1} corresponds to C=O stretching vibrations and the peaks at 2861 cm^{-1} , 2921 cm^{-1} and 3004 cm^{-1} were associated with the -CH₂ stretching, while the band at 3300 cm^{-1} was ascribed to -O-H stretching vibrations. Those values were close to the ones reported in a previous work. [13]

The FTIR spectra of EC showed characteristic peaks at 1056 cm^{-1} assigned to -C-O-C- stretching vibrations. The peaks at 2878 cm^{-1} and 2971 cm^{-1} correspond to -CH stretching vibrations. The peak at 1373 cm^{-1} was attributed to -CH bending vibrations and the peak at 3475 cm^{-1} was associated to -O-H stretching vibrations. [14]

New small peaks appeared in the FTIR spectra of phosphorylated ethyl cellulose as well as phosphorylated microcapsules. The peaks observed at 810 cm^{-1} and 1630 cm^{-1} were attributed to P-O-C and O=P-OH groups, respectively. [10] These new peaks appeared thanks to the presence of phosphorus in the P-EC shell material.

The infrared spectra of the microcapsules revealed all the characteristic peaks of the core material and the shell material for all the encapsulated oils using EC or P-EC as shell material (in yellow in Fig. 1), which confirmed clearly that the encapsulation was correctly carried out using different oil core and polymer shell materials. Furthermore, for all prepared microcapsules, no peaks related to the free chemicals used in the encapsulation process have been identified, so the efficiency of the capsule cleaning process has been demonstrated.

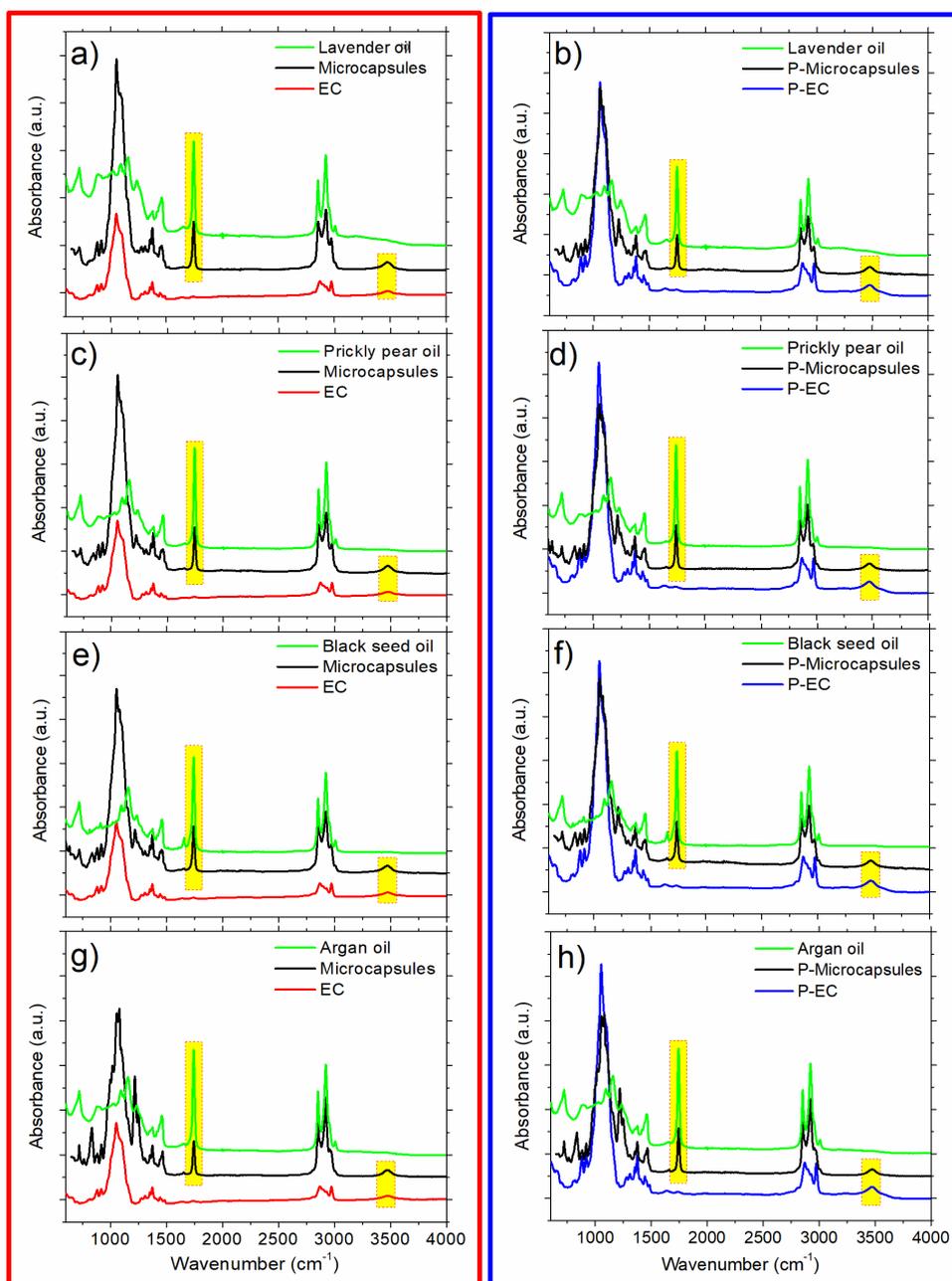


Fig. 1. (a) FTIR spectra of (a, b) lavender oil, (c, d) prickly pear oil, (e, f) black seed oil, (g, h) argan oil, ethyl cellulose (a, c, e, g), phosphorylated ethyl cellulose (P-EC) (b, d, f, h)) and the corresponding oil filled microcapsules.

3.2 Microcapsules thermal characteristics and content

Thermogravimetric analysis (TGA) has been used to investigate the thermal stability of the prepared microcapsules, the encapsulated oils (LO, PPO, BSO and AO) and the shell materials (EC and P-EC). The obtained results are shown in Fig. 2.

The phosphorylated and non-phosphorylated oil-filled microcapsules (MC and P-MC) exhibited two stages of weight loss. For instance, lavender oil microcapsules show two stages at 180–285 °C and 285–480 °C, corresponding to the decompositions of ethyl cellulose shell

and the lavender oil core, respectively. In the case of prickly pear oil microcapsules, the two stages related to the decomposition of EC and PPO were observed at 195-285 °C and 285-475 °C, respectively. The black seed oil microcapsules and argan oil microcapsules also exhibit two stages of weight loss related to EC and the encapsulated oils (Table 1). The thermogram of the phosphorylated microcapsules filled with lavender oil shows a first stage weight loss at 165–280 °C related to the decomposition of phosphorylated ethyl cellulose. The second stage of weight loss related to the lavender oil decomposition was observed between 280 °C and 505 °C. The decomposition of phosphorylated microcapsules containing prickly pear oil was observed through two stages of weight loss at 170-280 °C and 280-520 °C. The phosphorylated microcapsules containing black seed oil and argan oil show two stages of weight loss as well (Table 1).

Table 1. Thermogravimetric analysis (TGA) results of the prepared microcapsules.

Sample	1 st region		2 nd region		Final residue (%) at 600 °C
	Range °C	Peak* °C	Range °C	Peak* °C	
LO microcapsules	180–285	192	285–480	381	4.67
LO P-microcapsules	165–280	178	280-505	393	3.62
PPO microcapsules	195-285	201	285-475	391	4.93
PPO P-microcapsules	170-280	183	280-520	402	4.02
BSO microcapsules	215-290	220	290-490	391	7.43
BSO P-microcapsules	165-280	180	280-525	377	6.70
AO microcapsules	190-290	202	290-513	386	10.9
AO P-microcapsules	170-283	187	283-590	384	4.47

* From derivative thermogravimetry (DTG) curve of all samples

The thermal degradation shows an overlapping temperature range of the core and shell materials which limits the accurate determination of the percentage of each component. This limitation led us to determine the percentages of encapsulated oils and polymeric materials used as shell materials for encapsulation via the solvent extraction method. Thus, a determined weighed mass (m_1) of each prepared microcapsule was mixed with n-hexane and sonicated for 10 min. The suspension was filtrated, and the obtained solid filtrate was dried in an oven at 50 °C until the generation of a constant weight (m_2). The oil content of the microcapsules was then determined using the following equation (1):

$$\text{Oil content (\%)} = \frac{(m_1 - m_2)}{m_1} 100\% \quad (1)$$

The obtained results are summarized in Table 2.

Table 2. Oil content of the prepared microcapsules.

Sample	LO MC	LO P-MC	PPO MC	PPO P-MC	BSO MC	BSO P-MC	AO MC	AO P-MC
Oil content (%)	63.60	72.14	67.16	72.02	51.31	69.60	44.38	67.56

It is worth to mention that the thermal degradation of the microcapsules resulted in a final residue higher in the case of MC compared to the P-MC for each encapsulated oil; this fact could be related to the oil content of the microcapsules. The TGA analysis reported the absence of the other materials used for the encapsulation, especially the sodium dodecyl sulfate (SDS) material usually characterized by a degradation temperature range between 162 °C and 218 °C.

The thermal degradation of the prepared P-MC exhibits a flame retardancy behavior due to the phosphorylated ethyl cellulose on the microcapsules shell. the phosphorous groups on the P-EC shell cause an early degradation of the microcapsules outer surface, which promote the protection of the entire microcapsules through the formation of a protective layer on the polymeric shell.

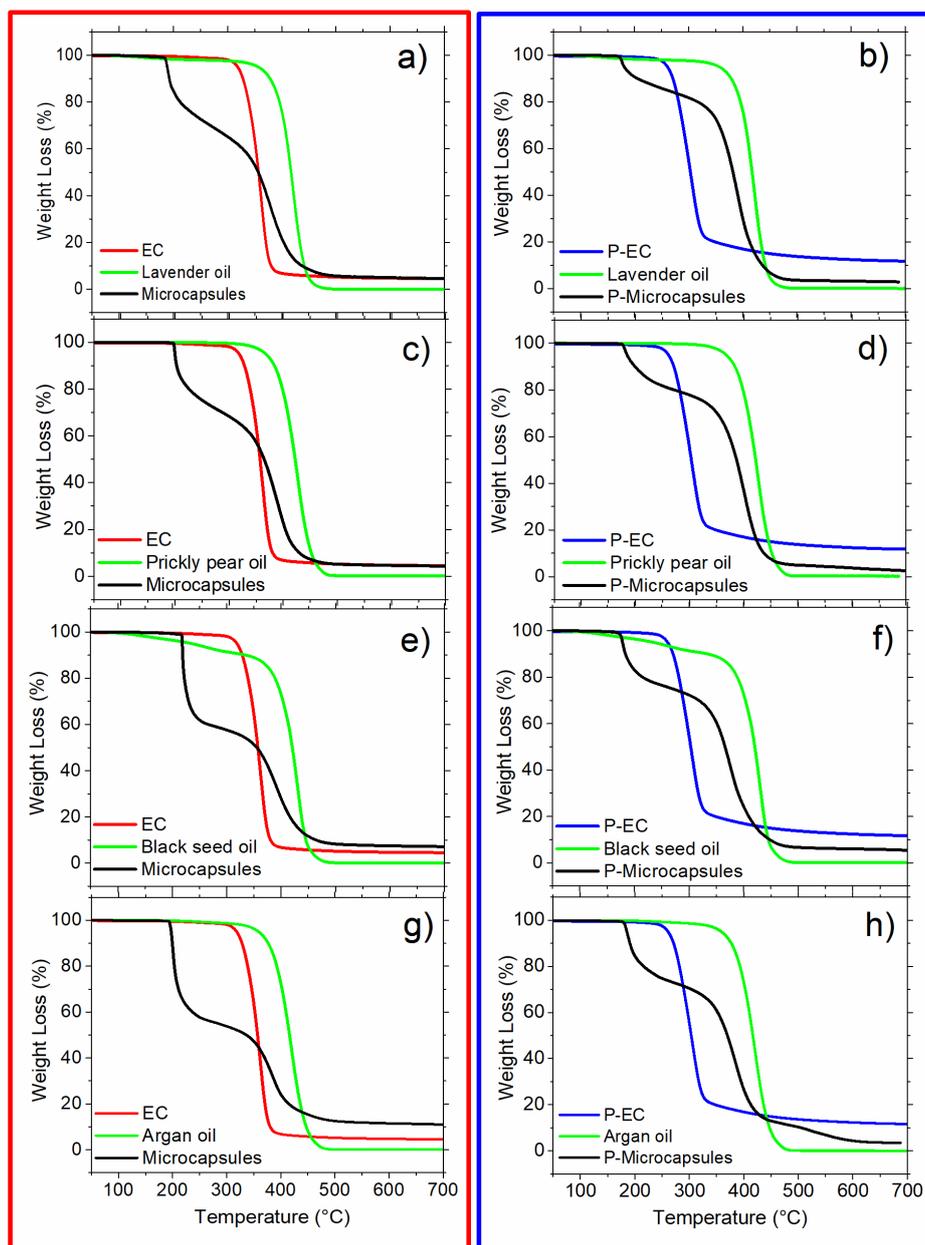


Fig. 2. TGA weight loss curves of (a, b) lavender oil, (c, d) prickly pear oil, (e, f) black seed oil, (g, h) argan oil, ethyl cellulose (a, c, e, g), phosphorylated ethyl cellulose (P-EC) (b, d, f, h)) and the corresponding oil filled microcapsules.

3.3 Microcapsules morphology

The morphology of the prepared oil-filled microcapsules was investigated by SEM. The obtained micrographs are illustrated in Fig. 3. It was clearly shown that the obtained microcapsules are spherical in shape with some roughness and cavities on the surface which may induce a better compatibility effect with the coating matrix. The freeze-drying performed as the last step in the microcapsule's preparation could be the source of the observed cavities and some broken capsules as well. [15]

As expected, micrometric size distribution of the generated capsules can be clearly observed from the micrographs in Fig. 3, indicating the efficiency of the preparation method using both native ethyl cellulose and phosphorylated ethyl cellulose with the four encapsulated oils (lavender, black seed, prickly pear and argan based oils). Furthermore, a wide size distribution of the microcapsules was extracted from the micrographs and estimated to be in the range up to 170 μm .

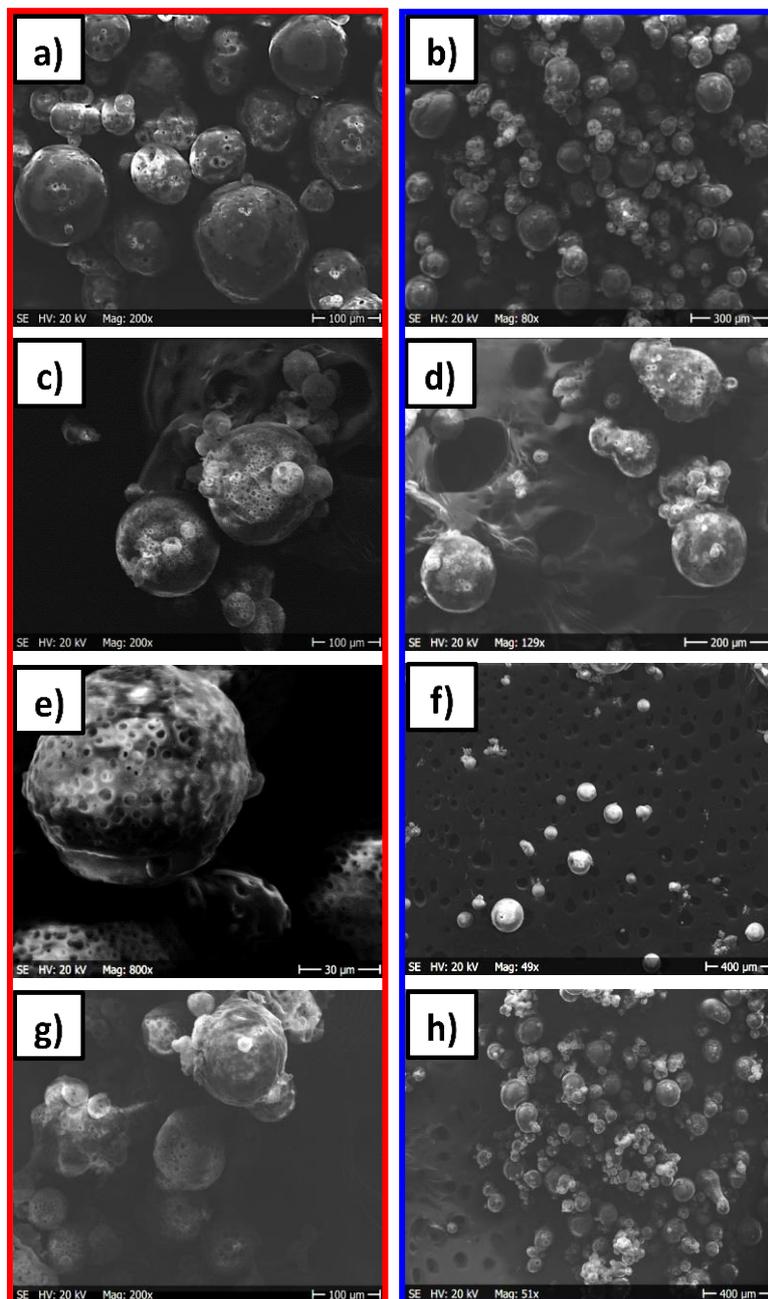


Fig. 3. SEM micrographs of oil-filled microcapsules using ethyl cellulose (a) , c) , e) , g)) and phosphorylated ethyl cellulose (b) , d) , f) , h)) as shell material. The microcapsules core material are based on (a) , b)) lavender oil , (c) , d)) prickly pear oil , (e) , f)) black seed oil , (g) , h)) argan oil.

4. Conclusions

In this study, oil-filled microcapsules were successfully prepared via solvent evaporation method. Native ethyl cellulose and phosphorylated ethyl cellulose were used as polymeric shell materials to encapsulate four different oils (lavender, black seed, prickly pear and argan based oils). As far as we know, this was the first time to encapsulate the above-mentioned oils using phosphorylated ethyl cellulose as a shell-forming polymer. The microcapsules composition was evaluated by FTIR, and the obtained results proved that the microcapsules were only composed of the studied oil core material (lavender, black seed, prickly pear or argan based oil) and the shell material (ethyl cellulose or phosphorylated ethyl cellulose). TGA analysis was used to investigate the thermal stability of the microcapsules and it confirmed the flame-retardant aspect induced to the P-MC through the use of P-EC as a shell material. The oil content was determined for the obtained microcapsules. More exploration of the oil's properties effect on the final capsules needs to be investigated. The SEM micrographs further confirmed the efficiency of the preparation method and showed the spherical shape of the microcapsules with a particles size range of 10-170 μm . The main objective of this study was to proof the concept of oil encapsulation using P-EC as a shell; the prepared microcapsules will be destined for the preparation of anti-corrosion self-healing coatings.

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Chapter 3

Development of Anti-Corrosion Coating Based on Phosphorylated Ethyl Cellulose Microcapsules

Introduction to chapter 3

La corrosion est considérée comme un phénomène naturel, régi par une thermodynamique, qui peut détériorer généralement tous les matériaux, et particulièrement les métaux. Il s'agit d'un processus chimique qui décompose progressivement les matériaux par échange d'électrons et formation de nouvelles molécules.

Pour prévenir et protéger les métaux contre la corrosion, de nombreuses méthodes existent et sont couramment utilisées. Par exemple, la protection cathodique et les méthodes de revêtement anticorrosion. Cependant, ces méthodes sont coûteuses et nécessitent le remplacement périodique de l'anode sacrificielle ou le renouvellement du revêtement, ce qui implique l'utilisation de produits chimiques très toxiques et nocifs pour l'environnement. Jusqu'à présent, de nouvelles approches ont été adoptées pour protéger les matériaux contre la corrosion, en particulier les techniques d'auto-réparation, qui permettent une protection rentable contre la corrosion et qui adopte des approches plus respectueuses de l'environnement.

Dans ce chapitre, nous présentons notre travail de recherche visant à incorporer de l'huile d'amande dans le noyau de microcapsules à base d'éthylcellulose et d'éthylcellulose phosphorylée comme matériaux d'enveloppe, et leur utilisation ultérieure dans un revêtement anticorrosion auto-cicatrisant. À cette fin, l'éthylcellulose portant des groupes phosphonates a été préparée par une réaction de phosphorylation dans des conditions bien spécifiques. Nous rapportons dans ce travail et pour la première fois la préparation des microcapsules combinant de l'éthylcellulose phosphorylée avec de l'huile d'amande dans un revêtement auto-cicatrisant. L'huile d'amande a été choisie en raison de sa composition et de ses capacités d'inhibition de la corrosion. L'éthylcellulose modifiée et les microcapsules obtenues ont été soumises à plusieurs techniques de caractérisation. L'effet du groupe phosphonate en combinaison avec l'huile d'amande a été étudié en tant qu'additifs anti-corrosion. Ainsi, des échantillons métalliques ayant un revêtement chargé de microcapsules ont été soumis à des rayures artificiels et leur résistance à la corrosion a été analysée par des tests au brouillard salin.

Ce chapitre, intitulé «Development of Anti-Corrosion Coating Based on Phosphorylated Ethyl Cellulose Microcapsules» a été rédigé sous la forme d'un article scientifique en anglais qui a été publiée en 2020 dans le journal Progress in Organic Coatings sous le DOI : [10.1016/j.porgcoat.2020.105885](https://doi.org/10.1016/j.porgcoat.2020.105885)



Development of anti-corrosion coating based on phosphorylated ethyl cellulose microcapsules

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Development of Anti-Corrosion Coating Based on Phosphorylated Ethyl Cellulose Microcapsules

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Abstract

This study reports for the first time the preparation of almond oil-based microcapsules using phosphorylated ethyl cellulose as shell material. Microcapsules of ethyl cellulose (EC) and phosphorylated ethyl cellulose (P-EC) containing almond oil as anti-corrosion inhibitor, for end use in self-healing coatings, were prepared by a solvent evaporation method. The results showed that phosphorus content in the modified ethyl cellulose was 6.26 wt.%, the specific surface area reached a high value of 21.4 m²g⁻¹ and a char residue of 18 wt.% at 400 °C after thermal degradation. Both prepared EC and P-EC based microcapsules were spherical shape-like. The scanning electron microscope (SEM) images showed that the freeze-drying influences the microcapsules surface morphology. The mean diameter of EC and P-EC microcapsules was about 140 μm and 150 μm, respectively. Anti-corrosion properties of prepared epoxy-based coatings loaded with microcapsules on the mild steel substrate were evaluated for 28 days using a simple salt spray test. The sample containing P-EC microcapsules showed the best anticorrosion resistance. The functionalization of the ethyl cellulose microcapsules shell with phosphonate groups can improve further the anti-corrosion resistance, the flame-retardant ability and the metal chelating properties of the final coatings.

Keywords: Anti-corrosion coating; biopolymers; ethyl cellulose; microencapsulation; phosphorylation; self-healing

Highlights

- Novel phosphorylated ethyl cellulose based microcapsules containing almond oil were prepared.
- Phosphorylation induced an increase of the carbonaceous residue formation and an improvement of heat resistance
- Addition of phosphorylated ethyl cellulose based microcapsules to coatings enhances their anti-corrosion performance.

1. Introduction

Corrosion is a widespread thermodynamically governed natural phenomenon that can deteriorate materials generally, and metals specifically. It is a chemical process that breaks down materials gradually by electron exchange and new molecules formation [1]. At present, enormous investment is allocated all over the world to protect materials from corrosion, especially metals. In 2016, the global cost of damage caused by corrosion was estimated to be US \$2.5 trillion [2]. To prevent and protect metals against corrosion, many methods exist and are used commonly. For instance, the cathodic protection and the anti-corrosion coating methods. However, these methods are costly and need periodic replacement of the sacrificial anode or renewal of the coating, implying the use of chemicals with high toxicity and harmful effect on the environment [3-6]. So far, new approaches have been adopted to protect materials from corrosion, especially self-healing techniques, which allow cost-effective corrosion protection in more environmentally friendly approaches [7].

The self-healing phenomenon can be classified into two types: intrinsic and extrinsic, depending on the way of healing. The first type is based on special characteristics of the polymer that allow repairing under certain stimuli. In the second type, extrinsic self-healing, the polymeric matrix is not healable. Thus, the healing agent must be encapsulated and pre-embedded in the bulk material [8, 9]. The microencapsulation of natural self-healing agents is an active research area. A significant part of these investigations is dedicated to specific materials that protect and cover the defects of metal coatings caused by several surrounding conditions and stimuli [10-16]. Microencapsulation technology has been considered a relevant method to develop new and versatile smart materials for different applications, especially in the field of self-healing composite materials. Within the coating application, microencapsulation allows the protection of solid, liquid or gas materials using polymeric

shells. This technology is considered as the first and primordial step in the preparation process of extrinsic self-healing materials [16-19].

Microcapsules for anti-corrosion coating applications are based on core materials containing an anti-corrosion healing agent. Then, microcapsules must be embedded in paints as part of the anti-corrosion coating [12, 20]. Among shell materials for microencapsulation, cellulose and derivatives were widely used for diverse applications. In fact, cellulose and derivative materials are sustainable, biocompatible, non-toxic and possess good chemical and mechanical properties, that promote their use in the microcapsules preparation [21-23]. The main approaches for the preparation of these materials for microencapsulation include emulsion-based methods such as temperature-induced phase separation, emulsion solvent evaporation and solvent evaporation from oil-in-water emulsion [24, 25].

Vegetable oils have received recurrent attention in the last decades due to their eco-friendliness, low cost and availability which make them suitable materials for several purposes, including: food industry, paints and anticorrosion applications [26, 27]. Linseed, soybean and tung, are the most studied vegetable oils due to their abundance and ease of extraction from renewable and sustainable resources [28]. They are used in edible applications such as food industry, as well as non-edible applications such as self-healing materials [10, 14, 28, 29]. In this context, we report hereby almond oil as a promising green corrosion inhibitor. The chemical structure of vegetable oils is generally composed of 90 to 98 % of triglycerides, which are esters containing multiple fatty acids, that comprise oleic, linoleic, alpha linoleic, palmitic, palmitoleic and stearic acids [30]. Almond oil is generally a combination of 68 % oleic acid, 25 % linolenic acid and 4 % palmitic acid. High content of double bonds-rich fatty acid as oleic acid offers this material the ability to protect metals against corrosion by free radical auto-oxidation reaction mechanism of the double bonds with oxygen [31-34].

Our research work aimed to incorporate almond oil in the core of microcapsules based on ethyl cellulose and phosphorylated ethyl cellulose as shell materials, and their subsequent use in a self-healing anti-corrosion coating. For this purpose, ethyl cellulose bearing phosphonate groups was prepared by phosphorylation reaction under specific conditions. We report for the first time, microcapsules combining phosphorylated ethyl cellulose with almond oil in self-healing coating. Almond oil was selected due to its composition and corrosion inhibition abilities. The resulting modified ethyl cellulose and microcapsules were subjected to several characterization techniques. The effect of the phosphonate group in combination with the

almond oil was investigated as anti-corrosion additives. Thus, metallic samples having a coating loaded with microcapsules were subjected to a mechanical scratch and their corrosion resistance was monitored via salt spray tests.

2. Experimental

2.1 Materials

The reagents used for the materials preparation were ethyl cellulose powder (viscosity 10 cP, measured as a 5 % vol in toluene/ethanol 80:20 (vol), extent of labeling: 48 % ethoxyl), urea powder and sodium dodecyl sulfate (SDS) (Sigma Aldrich), ethyl acetate (EA) (Somaprol), orthophosphoric acid (85 %), methanol (Merck KGaA) and Sodium hydroxide (VWR). Sweet almond oil was purchased from a drugstore and used as a core material for microcapsules. All chemicals were analytical reagents grade and were used as received.

2.2 Ethyl Cellulose phosphorylation

The ethyl cellulose phosphorylation was performed under homogeneous conditions using phosphoric acid in molten urea [35, 36]. 5 g of ethyl cellulose were dispersed under stirring in 25.7 g of phosphoric acid H_3PO_4 and 7 g of distilled water. 16 g of urea were melted in a two-necked flask attached to a condenser at 140 °C. The dispersion was added to the molten urea while the temperature was adjusted to 150 °C, and the reaction was carried out for 30 minutes. The obtained combination was then dissolved in a solution of NaOH, precipitated in methanol, filtered, washed and purified via membrane-based dialysis process in distilled water. Finally, the phosphorylated ethyl cellulose was freeze dried for 72 hours.

2.3 Preparation of microcapsules

In order to prepare almond oil-filled microcapsules using ethyl cellulose (EC) or phosphorylated ethyl cellulose (P-EC) as shell material, we followed the procedure described elsewhere [25]. The selected microencapsulation method is considered as a two-stage solvent evaporation method. The first preparation, oil phase, consists on dissolving the ethyl cellulose powder or the phosphorylated ethyl cellulose in ethyl acetate (90 wt.%) under magnetic stirring of 650 rpm at ambient temperature. The dissolution was done in 2 hours. Almond oil was then added gradually to the above-mentioned solution. The system was kept under magnetic stirring at room temperature for further 30 minutes. For the second preparation, water phase, an aqueous solution of 1 wt.% sodium dodecyl sulfate (SDS) was prepared. The

oil phase was then added drop wise to the water phase under mechanical mixing at 60 °C for 90 minutes. The mixture was freeze-dried then washed with distilled water and filtered to remove the remaining surfactant and generate the final microcapsules. Obtained microcapsules based on EC and P-EC are designated by MC and P-MC, respectively.

2.4 Characterization

The surface morphology of ethyl cellulose (EC) and phosphorylated cellulose (P-EC) were observed by scanning electron microscopy (SEM) using a Quanta FEG 250. The presence of phosphorus (P) in the P-EC was examined by Energy Dispersive X-ray spectroscopy (EDX) using IDFix software by SAMx attached to the Quanta FEG 250 electron microscope.

Fourier Transform Infrared (FTIR) Spectra of initial raw materials, phosphorylated ethyl cellulose and prepared microcapsules were recorded by a PerkinElmer FTIR spectrophotometer (Wellesley, MA, United States), collecting 16 scans in the 4000-600 cm^{-1} range with 4 cm^{-1} resolution.

The phosphorus (P) content of the modified ethyl cellulose was measured using the inductively coupled plasma optical emission spectrometry method (ICP-OES), on Agilent 5110 ICP-OES Instrument. The specific surface area of the EC and P-EC powders was determined by the BET method, using nitrogen adsorption measurements (Micromeritics Gemini VII 1014 Instrument).

The prepared microcapsules were observed by an optical microscope (Nikon metallographic microscope LV100ND) under 20-100 X magnification. The microcapsules morphology and shell thickness were examined using a scanning electron microscope (Philips XL 40 ESEM). The microcapsules size was determined by a laser particle size analyzer (Malvern, Mastersizer 2000).

Microcapsules thermal stability was evaluated by means of thermogravimetric analysis (TGA) technique using a thermogravimetric analyzer (Model –TGA 5500, Discovery series, TA Instruments, United States). The tests were performed under a nitrogen atmosphere and heating from room temperature up to 700 °C using a heating rate of 10 °C/min.

The oil content in the microcapsules was determined by solvent extraction. Weighed mass of microcapsules (m_1) was mixed with 200 mL of n-hexane and the mixture was sonicated for 10 min. The suspension was then filtrated, and the solid filtrate was then collected and dried in an oven at 50 °C until a constant weight is measured (m_2). The oil content encapsulated in the microcapsules can be determined using the following equation:

$$\text{oil content (\%)} = \frac{(m1 - m2)}{m1} 100 \%$$

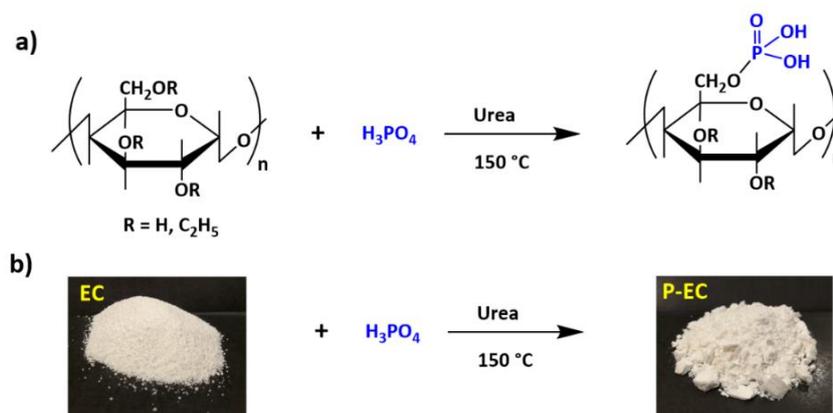
2.5 Preparation of coating samples containing microcapsules

Mild steel substrates with a dimension of 100 × 45 × 1 mm were ground to 1000-grits with abrasive paper, degreased in acetone and dried in air. 15 wt.% of microcapsules were gently dispersed into the epoxy resin under manual mixing using spatula. A stoichiometric amount of the hardener was then added to the mixture. The coatings were applied on degreased and polished steel substrates using a manual film applicator. The coated steel panels were dried overnight in a fume hood at room temperature. The average thickness of dry film samples was measured as 500 ± 15 μm.

3. Results and Discussion

3.1 Phosphorylated Ethyl-Cellulose characteristics

Phosphorylated polysaccharides are a very interesting class of materials that can exhibit practical properties (e.g., biocompatibility, bactericidal activity, bio absorbability, and metal-chelating). In this study, P-EC was prepared by the phosphorylation of the EC using the procedure depicted in the scheme 1. The phosphorylation protocol was performed at 150 °C to activate the attachment of phosphonate groups in order to obtain a high degree of substitution [37]. Urea was used in excess to fulfil a dual role in the functionalization procedure. On one hand it promotes the phosphorylation reaction, and on the other hand it protects the polymeric matrix at high temperature from degradation in the aggressive acidic conditions (10.7 M) [38].



Scheme 1. **a)** Schematic of the phosphorylation reaction of the ethyl cellulose (EC). **b)** Visual aspect of ethyl cellulose (EC) and phosphorylated ethyl cellulose (P-EC).

These conditions and the drying technique did not affect the visual powder like aspect of the obtained P-EC final product (scheme 1). Interestingly, the specific surface area of P-EC adsorbent, determined by the N₂-BET method, was highly increased compared with that of the native ethyl cellulose. In fact, the obtained results were 1.1 m²g⁻¹ for EC and 21.4 m²g⁻¹ for P-EC.

It was expected that the phosphorylation reaction will induce a change in the intermolecular interactions between the P-EC chains, thus, modifying the compactness properties due to steric effect and surface charge modification. The polysaccharide samples were sputter coated with copper (Cu) before SEM-EDX analysis. The SEM images of the lyophilized P-EC powder showed a spongy aspect after freeze drying, as can be depicted in (Fig. 1 (a-b)). This new roughness may be the reason for the measured specific surface area increase. The phosphorus element (P) mapping image showed almost uniform distribution in the characterized sample (Fig.1(d)). Even if the mapped sample is rough, the obtained result supports the effective chemical modification and the phosphorylation of the ethyl cellulose.

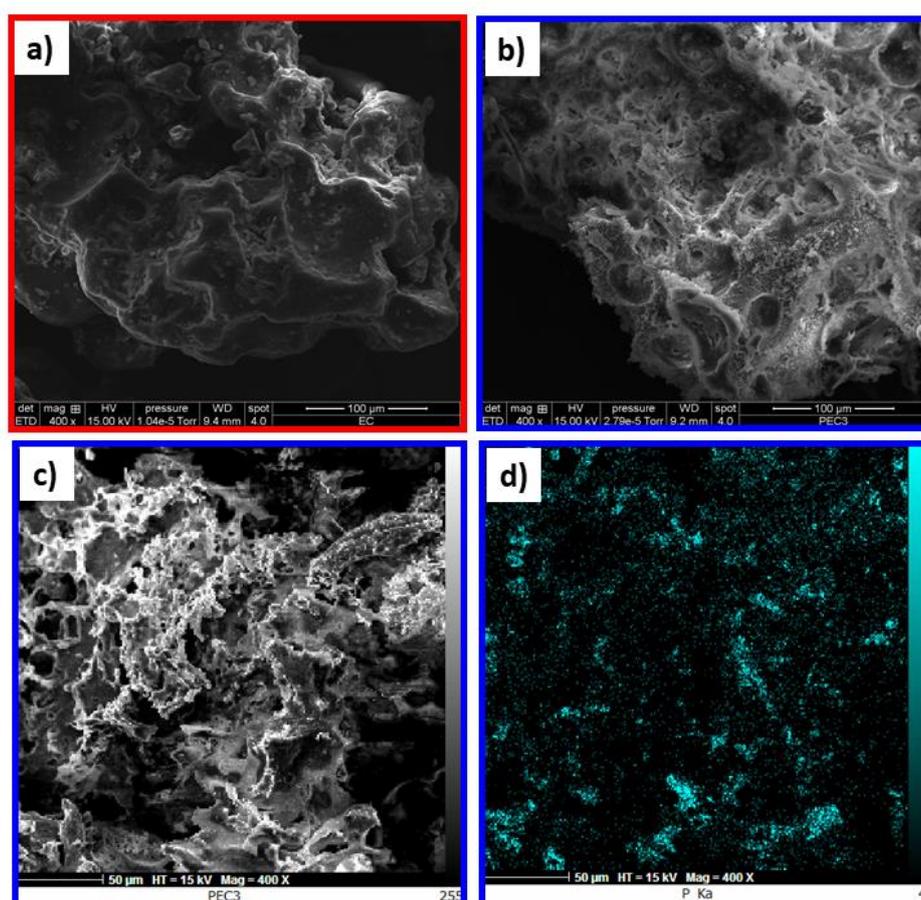


Fig. 1. SEM micrographs of (a) ethyl cellulose (EC) and (b-c) phosphorylated cellulose (P-EC). (d) Mapping of phosphorus element for phosphorylated ethyl cellulose (c).

The ethyl cellulose phosphorylation was confirmed by FTIR measurements (Fig. 2). The FTIR spectrum of the modified ethyl cellulose showed the characteristic peaks of both native ethyl cellulose and new peaks related to phosphorus groups. The peak at 800 cm^{-1} is assigned to P-O-C groups, and another broad peak at 1630 cm^{-1} is related to O=P-OH deformation vibrations. Moreover, the phosphorus content was confirmed by inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis and the modified EC contains 6.26 wt.% P.

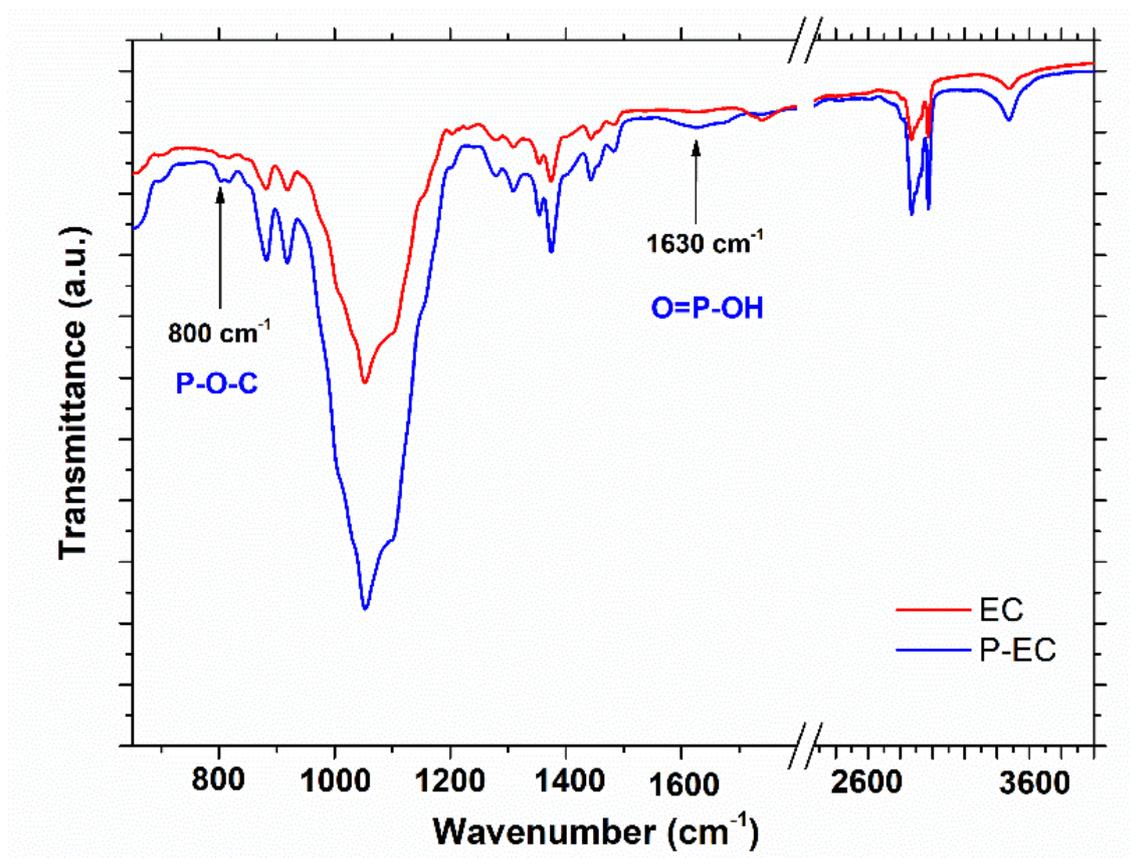


Fig. 2. FTIR spectra of ethyl cellulose (EC) and phosphorylated ethyl cellulose (P-EC).

Figure 3 shows the main characteristics of thermal degradation of native and phosphorylated ethyl cellulose, determined by thermogravimetric analysis.

As seen from (Fig. 3), native ethyl cellulose shows a maximum weight loss rate at $362\text{ }^{\circ}\text{C}$, whereas this appeared at $304\text{ }^{\circ}\text{C}$ for the phosphorylated ethyl cellulose. Thus, the introduced structures containing phosphorus catalyze the polymer's thermal degradation and carbonization, so that the main degradation process starts for phosphorylated ethyl cellulose at a temperature of $213\text{ }^{\circ}\text{C}$ compared to the corresponding native ethyl cellulose which starts at $273\text{ }^{\circ}\text{C}$ (Table 1). The phosphorylated ethyl cellulose loses 20 wt.% at $281\text{ }^{\circ}\text{C}$, whereas for the native ethyl cellulose, the same weight loss is observed at a higher temperature of $338\text{ }^{\circ}\text{C}$.

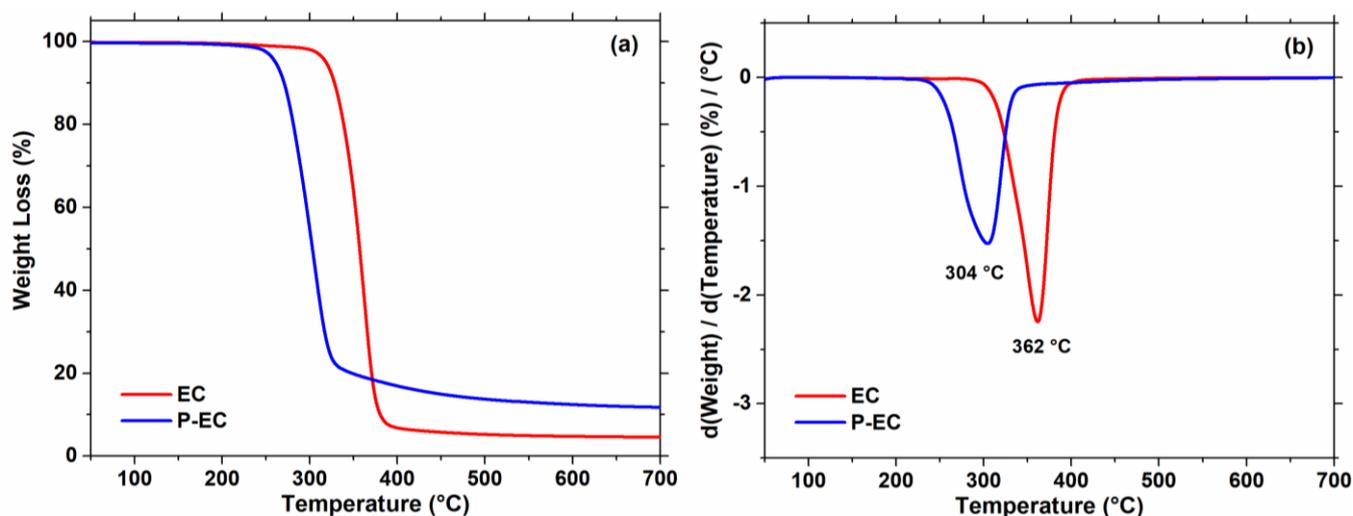


Fig. 3: Thermal degradation of native EC and P-EC. (a) TGA weight loss curves, and (b) weight loss first derivative curves.

It was noticed that, the weight loss of the P-EC is considerably lower compared to the native EC, and a difference of 17 wt.% was observed at 400 °C. The residue reaches 11.7 wt.% for the P-EC and 4.3 wt.% for native EC at 700 °C, which mean a difference of 7.4 wt.% (Table 1).

The native EC undergoes complete decomposition at 406 °C whereas the phosphorylated one underwent it at 350 °C. The observed thermal behavior of the P-EC is a clear indicator of a flame retardancy polymer material, where the phosphonate groups act as a promoter for more char residue at high temperature [38, 39]. Only 6.26 % weight amount of phosphorus in the P-EC induced a clear modification of its pyrolysis process reducing the flammable volatiles amount and increasing the carbonaceous residue formation which indicates its higher heat resistance.

Table 1. Specific surface area and thermal degradation characteristic properties of ethyl cellulose (EC) and phosphorylated cellulose (P-EC).

	Specific surface area*	Degradation temperature onset**	Degradation temperature**	Final weight residue**
	m ² g ⁻¹	°C	°C	%
EC	1.1	213	304	4.3
P-EC	21.4	273	362	11.7

* Determined by BET

** Measured by TGA

3.2 Microcapsules morphology and size distribution

Microcapsules based on ethyl cellulose (MC) and phosphorylated ethyl cellulose (P-MC) were prepared successfully. The content of the almond oil in the microcapsules was determined by extraction in n-hexane. The average oil content in the microcapsules was evaluated to be 58% and 61% for the MC and P-MC, respectively. Optical microscope images and SEM micrographs show that the obtained microcapsules have a spherical shape without any physical and strong inter-capsule bonding (Fig. 4).

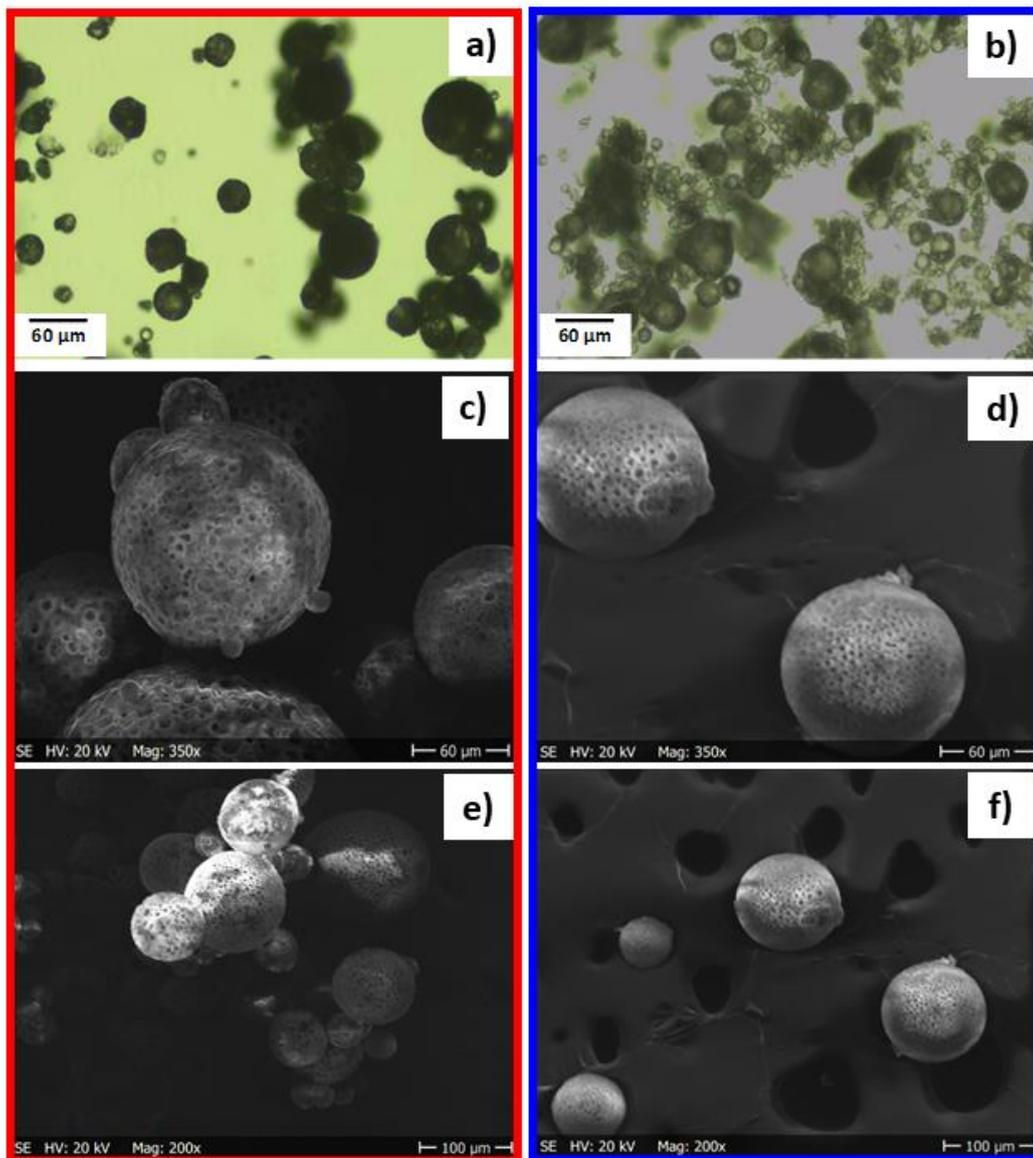


Fig. 4. Optical microscope images of almond oil-filled microcapsules using **(a)** EC and **(b)** P-EC as shell material. SEM micrographs of almond oil-filled microcapsules using **(c, e)** EC and **(d, f)** P-EC as shell material.

Moreover, microcapsules seem to have a rough shell surface with some residues on their top most likely due to agglomerations of the EC or P-EC which did not participate to the shell formation. Optical micrographs show the evidence of high dispersity of the size of the prepared microcapsules. In fact, the average diameter of almond oil microcapsules based native EC and phosphorylated EC is about 140 μm and 150 μm , respectively (Fig. 5).

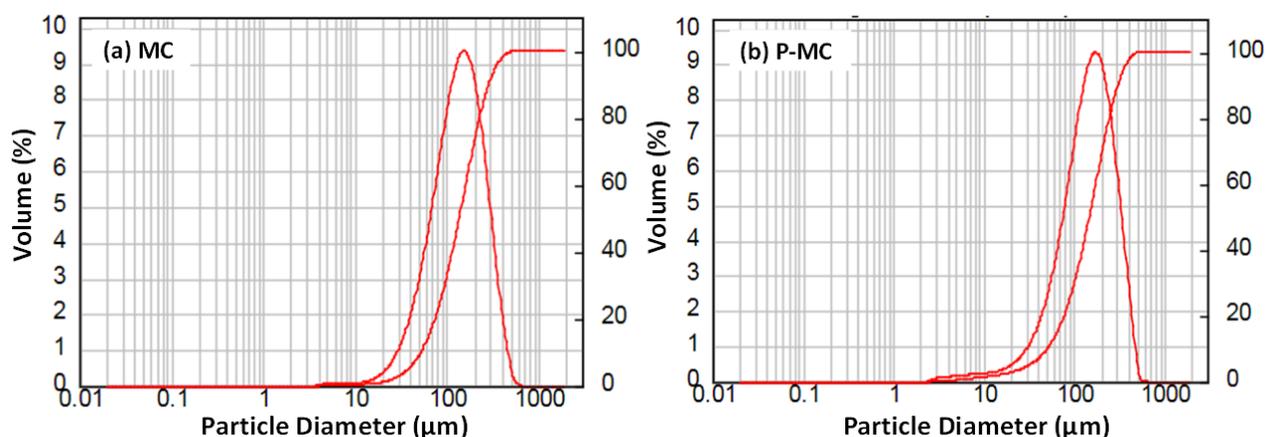


Fig. 5. (a) Size distribution of ethyl cellulose-based microcapsules (MC) containing Almond oil, and **(b)** Size distribution of phosphorylated ethyl cellulose-based microcapsules (P-MC) containing Almond oil.

The absence of almond oil around the microcapsules on the optical micrographs confirms the good oil encapsulation inside the shell material in both ethyl cellulose and phosphorylated ethyl cellulose. SEM micrographs did not show significant dissimilarity of surface morphology for microcapsules prepared using different shell materials, which makes clear the non-dependence of microcapsules features on shell material nature. Still, both non-phosphorylated and phosphorylated microcapsules have crater features on their surfaces and a golf ball-like morphology. The microcapsule morphology and final shape are depending on several parameters, e.g., core-shell materials, temperature, mixing mode, emulsifier and drying method. The lyophilization (freeze-drying) procedure is suspected to be the main factor responsible for the crater features observed on the surface of the obtained microcapsules. In fact, this drying method was previously pointed out to be the main cause of the porous structure on the surface of the obtained microcapsules [40]. This shape might affect self-healing efficiency and microcapsule's long-term stability. Hence, the craters will increase the exposition of the active ingredient encapsulated to the atmosphere, thus lowering the protection of the core material. Interestingly, the remaining microcapsules (i.e., MC and P-MC) were stable over several months inside a desiccator without any noticeable changes. The

same microcapsules were prone to agglomeration when left for a prolonged shelf exposure under ambient air humidity conditions. In fact, the hydrophilicity of the shell materials is promoting the increase of water content, hence the observed tendency to agglomeration.

3.3 Core-Shell Microcapsules FTIR Analysis

For chemical characterization of the core, shell and microcapsules, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was used (Fig. 6).

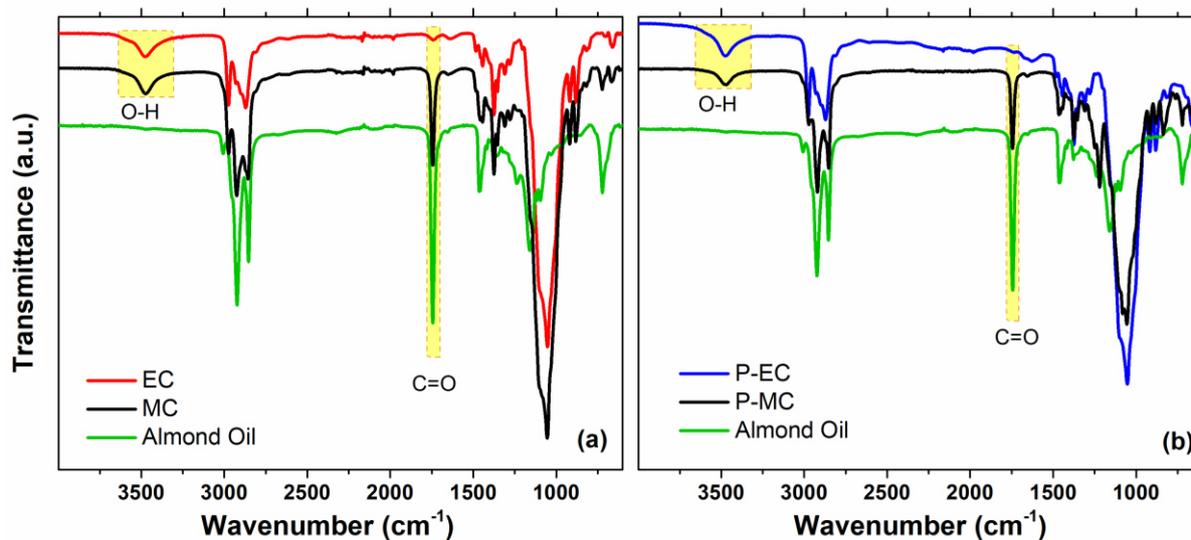


Fig. 6. (a) FTIR spectra of ethyl cellulose microcapsules (MC), almond oil and ethyl cellulose (EC). **(b)** FTIR spectra of phosphorylated ethyl cellulose microcapsules (P-MC), almond oil and phosphorylated ethyl cellulose (P-EC).

The infrared spectra of almond oil showed sharp peaks at 2921 cm^{-1} , 2849 cm^{-1} , 1462 cm^{-1} and 723 cm^{-1} related to the methylene groups. Peaks corresponding to the methyl group vibration were observed at 1464 cm^{-1} and 1375 cm^{-1} . The characteristic peak of olefinic double bonds is seen at 3009 cm^{-1} . The triglyceride ester groups appeared at 1743 cm^{-1} , 1235 cm^{-1} , 1159 cm^{-1} and 1095 cm^{-1} [41-43]. The phosphorylated microcapsules FTIR spectra reveal the appearance of new small peaks at 810 cm^{-1} and 1630 cm^{-1} corresponding respectively to P-O-C and O=P-OH group, due to the presence of the phosphorus in the P-EC shell.

The microcapsules infrared spectra contain all the characteristic peaks of the core material (Almond oil) and shell material (in yellow in fig.7). This gives a clear confirmation that the microencapsulation was correctly carried out using both ethyl cellulose and phosphorylated ethyl cellulose as shell materials. Moreover, no bands related to SDS were observed either for the MC and P-MC based microcapsules, hence, the efficiency of the cleaning procedure during the preparation step is proved.

3.4 Thermal Analysis

The thermal stability of the prepared microcapsules was investigated by thermogravimetric analysis (TGA) and the obtained results are presented in Fig. 7. The prepared microcapsules (phosphorylated and non-phosphorylated) exhibit two stages of weight loss. The almond oil microcapsules show two stages at 206–290 °C and 290–450 °C, which correspond to the decompositions of ethyl cellulose shell and the almond oil core, respectively. The thermal degradation shows an overlapping temperature range of the core and shell materials which limits the accurate determination of the percentage of each component.

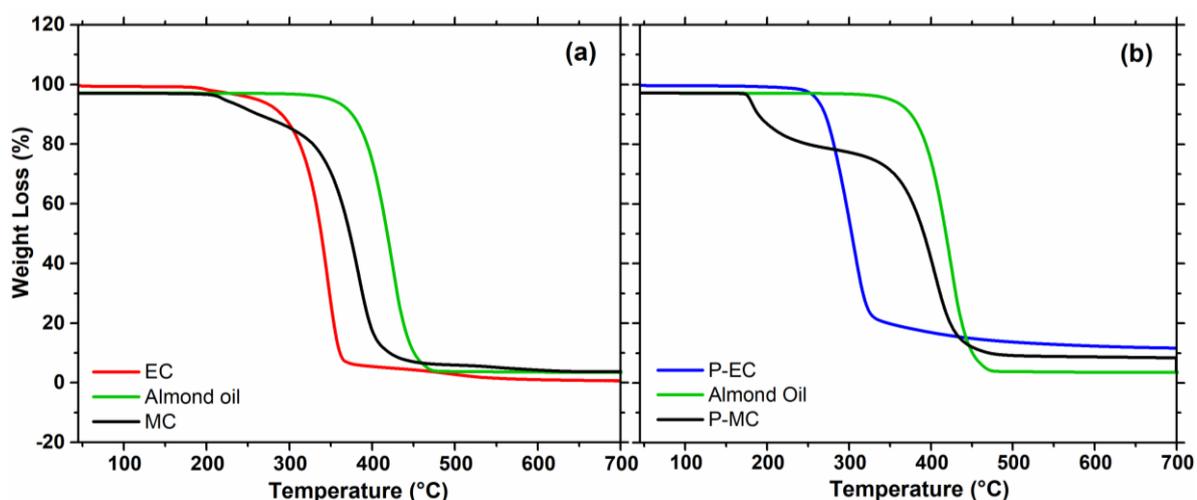


Fig. 7. (a) TGA weight loss curves of native ethyl cellulose (EC), almond oil and full microcapsules (MC). **(b)** TGA weight loss curves of phosphorylated ethyl cellulose (P-EC), almond oil and full phosphorylated microcapsules (P-MC).

The phosphorylated microcapsules thermogram shows an initial stage weight loss at 180-290 °C related to the decomposition of phosphorylated ethyl cellulose. The second stage weight loss supporting the decomposition of almond oil was observed between 290 °C and 500 °C. It is worth to note that the thermal degradation of the MC and P-MC microcapsules resulted in a final residue of 0.5 % and 5.2%, respectively. The TGA study confirmed the absence of the SDS material within the MC and P-MC microcapsules, which is typically characterized by an onset degradation temperature around 162 °C and a maximum degradation temperature around 218°C. It is worth commenting that the flame retardancy character of the used P-EC is still clearly observed for the resulting prepared microcapsules. Even at a small percentage, the phosphorus in the microcapsule shell induced and increase of the carbonaceous residue formation.

3.5 Salt spray test results

To evaluate the self-healing abilities and corrosion resistance of the prepared microcapsules, a salt spray test was performed on metallic substrates. The visual aspect progression during the study of the scratched areas on coated blank, MC and P-MC based samples is shown in (Fig. 8). To begin with, both scratched microcapsules loaded coatings showed a marked effectiveness in preventing corrosion compared to blank epoxy coating during the first week of test. However, all samples showed corroded zones at different stages across the scratched region after 28 days of the spray test using the 3.5 wt.% NaCl solution. In fact, the corroded zone was more evident on the pure epoxy resin coated sample compared to samples coated with epoxy resin loaded with microcapsules. In the case of blank samples, the rust was already propagated upon most of the scratch area after only 7 days of salt spray exposure and continued to develop until the end of the test. Moreover, it was clearly visible that the corrosion was spreading even more in between the coating and the metal surface at the end of the test. While in the case of samples containing non-phosphorylated microcapsules (MC), the corrosion emerged on the scratch center starting from day 7 and continued to progress showing a better anti-corrosion resistance compared to the blank samples. The study showed also that, the corrosion process did not visibly occur in the sample containing phosphorylated microcapsules (P-MC) until day 28, which reveals a better anti-corrosion resistance in comparison to both blank and MC containing samples. Considering the component of the P-MC compared with the MC, the phosphonate group is playing a crucial role in the observed anticorrosion performances. It is well known that phosphorus-containing compounds promote the anti-corrosion effects owing mostly to their excellent adhesion ability [44]. In addition to the strong interfacial interactions of phosphonate groups with the metal substrate, additional interactions are expected with the functional groups of the fatty acids of the core materials. Thus, there is a synergic effect between the phosphonate groups and the fatty acids of the almond oil integrated within the prepared coatings. In optimal conditions, a strong interaction between the $P-O^-$ functional groups and the metal ions M^{n+} from the metal substrate is occurring [44]. Furthermore, the hydroxyl and phosphonate groups on the P-EC can interact via hydrogen bonding with the triglycerides constituted of fatty acids.

Samples coding	Salt spray exposure time (day)			
	1 day	7 days	14 days	28 days
a) Blank				
b) MC				
c) P-MC				

Fig. 8. Optical photographs of scratched coated mild steel samples (a,b,c) after various exposure times (1, 7, 14 and 28 days) to salt spray with 3.5 wt.% NaCl solution. a) blank, without microcapsules b) coating with ethyl cellulose based microcapsule (MC) c) coating with phosphorylated ethyl cellulose microcapsules (P-MC).

4. Conclusions

Phosphorylated ethyl cellulose was successfully obtained through a phosphorylation reaction using phosphoric acid in the presence of molten urea. ICP-OES analysis confirm a content of 6.26 wt.% of phosphorus in the structure of P-EC. The functionalization of the EC promoted its flame retardancy behavior as revealed by the TGA analysis. Moreover, the specific surface area of P-EC showed an increase by a factor of 20 compare to that of native EC. The almond oil encapsulation was carried out successfully and the microcapsules showed a practical thermal stability window for the targeted application. The self-healing and anti-corrosion properties of prepared microcapsules were evaluated by a salt spray test on scratched epoxy-based coatings. The results revealed that the coating containing phosphorylated

microcapsules had a higher corrosion resistance compared to both blank coating and the coating loaded with non-phosphorylated microcapsules over a 4 weeks test. The phosphorylated microcapsules formulated in this work are presented as a proof of concept. To the best of our knowledge, this is the first attempt to prepare almond oil microcapsules using ethyl cellulose and phosphorylated ethyl cellulose as shell materials. These microcontainers approach seems to be promising and could potentially be used in different green and sustainable applications to enhance materials properties such as durability, biodegradability, metal chelating and flame retardancy. Further investigations and tests on the influence of the degree of phosphorylation on the performances of these materials are currently in progress and should be the subject of a forthcoming publication.

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Chapter 4

Preparation and application of phosphorylated microcapsules in self- healing Anti-Corrosion epoxy Coating

Introduction to chapter 4

L'application de revêtements organiques a été largement adoptée pour la protection des métaux en raison de leurs propriétés de barrière physique contre l'humidité et les ions corrosifs. Cependant, ces revêtements sont sujets à des micro et macro-dommages. Par conséquent, les revêtements intelligents, et en particulier les revêtements auto-cicatrisants, qui peuvent s'adapter intelligemment et de manière autonome pour récupérer les dommages sans intervention externe et retrouver leurs performances de barrière, sont hautement souhaitables. Ainsi, de nombreux efforts ont été faits pour développer des revêtements auto-cicatrisants efficaces contre la corrosion. Diverses approches ont été développées pour produire des matériaux auto-cicatrisants. Parmi ces approches, celle de l'encapsulation est un moyen privilégié pour développer des revêtements auto-cicatrisants. Cette technique consiste à encapsuler les agents de cicatrisation en utilisant un polymère comme matériau d'enveloppe, puis à incorporer les microcapsules préparées dans la matrice. Lorsqu'un dommage mécanique se produit, les capsules se brisent et libèrent les agents de cicatrisation contenus pour remplir les fissures et développer un film de revêtement. Dans la littérature, différents polymères tels que l'urée-formaldéhyde et les résines époxy ont été fréquemment utilisés comme matériaux d'enveloppe pour la préparation de capsules contenant des agents de cicatrisation.

Dans ce chapitre, des microcapsules à base d'éthylcellulose phosphorylée contenant de l'huile d'amande ont été préparées par la méthode d'encapsulation par évaporation de solvant afin de développer des revêtements auto-cicatrisants et anti-corrosion. Les tensioactifs utilisés pour la préparation des microcapsules ont été variés et les effets de cette variation sur les microcapsules et les revêtements préparés ont été étudiés. Les microcapsules obtenues ont été caractérisées. En outre, la résistance à la corrosion et les performances d'auto-cicatrisation des revêtements époxy contenant des microcapsules remplies d'huile d'amande ont été étudiées dans un milieu corrosif de 3,5 % en poids de NaCl. L'effet de deux microcapsules différentes préparées avec des surfactants différents sur la résistance à la corrosion et les propriétés auto-cicatrisantes des revêtements préparés est l'objectif principal de ce travail.

Ce dernier chapitre, intitulé « Preparation and application of phosphorylated microcapsules in self-healing Anti-Corrosion epoxy Coating » est présenté sous la forme d'un article qui sera publié dans un journal international.

Preparation and application of phosphorylated microcapsules in self-healing anti-corrosion epoxy coating

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Abstract

In this study, almond oil-filled microcapsules were prepared by solvent evaporation method using phosphorylated ethyl cellulose (P-EC) as shell material for end use in anti-corrosion self-healing coatings. Two surfactants sodium dodecyl sulfate (SDS) and n-Dodecyl phosphonic acid (DDPA) were used for the preparation of the microcapsules. The effects of these surfactants on the microcapsules and the prepared coatings were studied. The shape and morphology of the obtained microcapsules were investigated using Scanning Electron Microscopy (SEM) and Optical Microscopy (OM). The results showed the spherical shape-like of the microcapsules with diameters range from 20 μm to 160 μm . FTIR spectroscopy and TGA analysis were involved to prove the oil presence in microcapsules and to verify the absence of any strong chemical interaction between core and shell materials. The prepared microcapsules were dispersed into epoxy matrix coatings. To investigate the anti-corrosion properties and the self-healing ability of the epoxy-based samples on a mild steel substrate, salt spray tests and electrochemical impedance spectroscopy (EIS) were performed. The results showed that the coatings containing microcapsules had a better performance compared to the blank samples in terms of corrosion resistance and self-healing after 28 days of exposure to the conditions of salt spray test. The samples containing the P-EC-based microcapsules improved the corrosion resistance and act as smart self-healing coatings.

1. Introduction

The application of organic coatings has been widely adopted for the protection of metals due to their physical barrier properties against humidity and corrosive ions. However, these coatings are prone to micro and macro damages. Alternatively, smart coatings and especially self-healing coatings that can intelligently adapt autonomously to recover the damages without external interventions to regain their barrier performances are highly desirable. Thus, many efforts have been made to develop effective self-healing anti-corrosion coatings [1–3]. Variety of approaches to generate self-healing materials have indeed been developed. Within these approaches, the encapsulation approach is a preferred way for developing self-healing coatings [4,5]. This technique consists of the encapsulation of the healing agents using a polymer as shell material then embed the prepared microcapsules into the matrix. When mechanical damage occurs, the capsules break and release the contained healing agents to fill the cracks and develop a coating film [6]. In the literature, different polymers such as urea-formaldehyde [7,8] and Polyurethane [9,10] were frequently used as shell materials for the preparation of capsules containing healing agents

However, the use of biopolymers as shell materials for the encapsulation of active healing agent still not predominant for the applications of self-healing materials, and rarely reported in the literature.

The use of biopolymers as shell materials for encapsulation is mostly known for medical applications, especially for the preparation of different drug release systems. Ethyl cellulose (EC) is one of these polymers, used generally to cover and protect active agents to prepare capsules for drugs application. Ethyl cellulose has been recently used for the encapsulation of vegetable oils as healing agents to prepare anti-corrosion self-healing coatings [11].

The EC was used in different research studies to prepare microcapsules, the focus of these studies was generally oriented to optimize the capsules properties and the preparation conditions. Thus, the preparation of EC based capsules for the application in anti-corrosion self-healing coating has received less attention. For instance, EC was used to develop linseed oil-filled micro/nano capsules, which were subsequently embedded in polyurethane coatings to examine their properties [12].

In this study, phosphorylated ethyl cellulose-based microcapsules containing almond oil were prepared via solvent evaporation encapsulation method in order to develop anti-corrosion self-healing coatings. The surfactants used for the preparation of the microcapsules were

varied and the effects of this variation on the microcapsules and the prepared coatings were studied. The obtained microcapsules were characterized. Besides, corrosion resistance and self-healing performance of the epoxy coatings containing almond oil-filled microcapsules were investigated in a corrosive medium of 3.5 wt.% NaCl. The effect of two different microcapsules prepared with different surfactants on the corrosion resistance and self-healing properties of the prepared coatings is the main target of this work.

2. Experimental

2.1 Raw materials

To synthesize the microcapsules containing the healing agent, ethyl cellulose powder (viscosity 10 cP, measured as a 5 % vol in toluene/ethanol 80:20 (vol), extent of labeling: 48 % ethoxyl), sodium dodecyl sulfate (SDS), n-Dodecyl phosphonic acid (DDPA), Span 80, urea powder, almond oil to be used as a core material for microcapsules, epoxy resin and hardener were supplied from Sigma Aldrich chemicals. The ethyl acetate (EA) was purchased from Somaprol. The orthophosphoric acid (85 %) and methanol were ordered from Merck KGaA. The sodium hydroxide from VWR. All chemicals were analytical reagents grade and were used as received.

2.2 Preparation of oil-filled microcapsules

In this research work, phosphorylated microcapsules were prepared by the promoted two-stages solvent evaporation method [13]. Before starting the encapsulation, the ethyl cellulose was phosphorylated under homogeneous conditions using phosphoric acid in molten urea following the procedure described elsewhere [13,14]. The obtained phosphorylated ethyl cellulose (P-EC) was used as shell material for the microcapsules. The encapsulation starts firstly with the oil phase preparation, it consists of dissolution of the phosphorylated ethyl cellulose powder in ethyl acetate (90 wt.%) for two hours under magnetic stirring at room temperature. After that, the almond oil was added gradually to the solution containing the P-EC. Then, the mixture was stirred at room conditions for further half an hour. Secondly, the water phase was prepared, it consists of two solutions of different surfactant. The first aqueous solutions contain 1 wt.% sodium dodecyl sulfate (SDS) and 0,05 wt.% of Span 80 instead of 1 wt.% n-Dodecyl phosphonic acid (DDPA) and 0,05 wt.% of Span 80 for the second solution.

The prepared oil phase was added drop wise to the water phase containing surfactant (1 wt.% SDS or 1 wt.% DDPA) under mechanical mixing at 60 °C. After 90 minutes, the solvents were evaporated and phosphorylated microcapsules (P-MC) containing almond oil were formed. The obtained mixtures were washed with deionized water, then filtered to remove the remaining surfactant and generate the final microcapsules. The obtained microcapsules based on SDS and DDPA surfactants are designated by MC-sds and MC-ddpa, respectively.

2.3 Characterization of microcapsules

The surface morphologies of phosphorylated ethyl cellulose (P-EC) and the obtained microcapsules were examined by scanning electron microscopy (SEM, Quanta FEG 250). The prepared microcapsules were observed by an optical microscopy using a LEICA DM 2000 LED with a LEICA MC 120 HD camera. The distribution of phosphorus (P) in the P-EC was investigated by Energy Dispersive X-ray spectroscopy (EDX) using IDFix software by SAMx attached to the Quanta FEG 250 electron microscope. Raw materials, phosphorylated ethyl cellulose and obtained microcapsules were analysed separately using Fourier Transform Infrared (FTIR) Spectroscopy using a PerkinElmer FTIR spectrophotometer (Wellesley, MA, United States), collecting 16 scans in the 4000-600 cm^{-1} range with 4 cm^{-1} resolution.

Inductively coupled plasma optical emission spectrometry method (ICP-OES), was used to measure the phosphorus (P) content of the P-EC, using the Agilent 5110 ICP-OES Instrument. The thermal behaviour of raw materials and the prepared microcapsules was investigated by means of thermogravimetric analysis (TGA) technique using a thermogravimetric analyser (Model –TGA 5500, Discovery series, TA Instruments, United States). The typical experimental tests were performed under nitrogen atmosphere, the samples were heated from room temperature to 700 °C using a heating rate of 10 °C/min.

2.4 Preparation and application of coating samples loaded with microcapsules

To prepare the epoxy-based self-healing coatings, the following procedure was adopted. 15 wt.% of microcapsules were gently dispersed into the epoxy resin under manual mixing using spatula. A stoichiometric amount of the hardener was then added to the mixture. Mild steel substrates with a dimension of 1 cm^2 were ground up to 2000 grit with abrasive paper and followed by polishing with diamond paste, degreased in acetone, and dried in air. The coatings were applied on degreased and polished steel substrates using a manual film applicator. The

coated steel panels were dried overnight in a fume hood at room temperature. The average thickness of dry film samples was measured as $400 \pm 20 \mu\text{m}$.

2.5 Characterization of coating

In order to study the corrosion inhibition performances of the prepared coatings, EIS measurements were carried out. A three-electrodes cell system including a platinum rod (counter electrode), an Ag/AgCl electrode (reference electrode), and the sample (working electrode) was used for all electrochemical tests. In order to prepare the panels for the electrochemical experiments, the samples were scratched and exposed to the electrolyte. EIS measurements were examined at ambient temperature ($25 \pm 1 \text{ }^\circ\text{C}$) in a 3.5 wt.% NaCl solution. The perturbation amplitude of the AC voltage was $\pm 10 \text{ mV}$ (peak to zero), and scanning frequencies ranged from 100 kHz to 0.01 Hz. EIS measurements were carried out by VoltaLab 10 PGZ100 and its associated software was utilized to analyze the obtained data from the EIS study. The scratched surface area was considered as the actual area of the working electrode in all calculations.

Standard salt spray test was carried out to evaluate the anti-corrosion resistance of the coated samples. After curing, a scratch was formed on the sample surface using a scalpel blade and the cross-cut specimens were left at room temperature for about 24 h. The back and edges of the specimens were covered with wax. The visual aspect progression during the study of the scratched areas on coated blank coating and coatings containing microcapsules was for 28 days.

3. Results and discussion

3.1 Optical microscopy and SEM studies

The oil-filled microcapsules based on phosphorylated ethyl cellulose (MC-sds and MC-ddpa) were prepared successfully. The n-hexane extraction method was used to determine the almond oil content of the prepared microcapsules, results revealed that MC-sds and MC-ddpa contain 62% and 65% of almond oil, respectively. Fig. 1 displays the prepared microcapsules morphology. The optical microscope images (Fig. 1c, Fig. 1d) and SEM micrographs (Fig. 1d, Fig. 1e) exhibit the spherical shape of the microcapsules. The SEM micrographs show the compact aspect of the microcapsules with some roughness on the surface due to the preparation method. The rough surface may induce a better interfacial bonding and adhesion between the epoxy resin and the microcapsules.

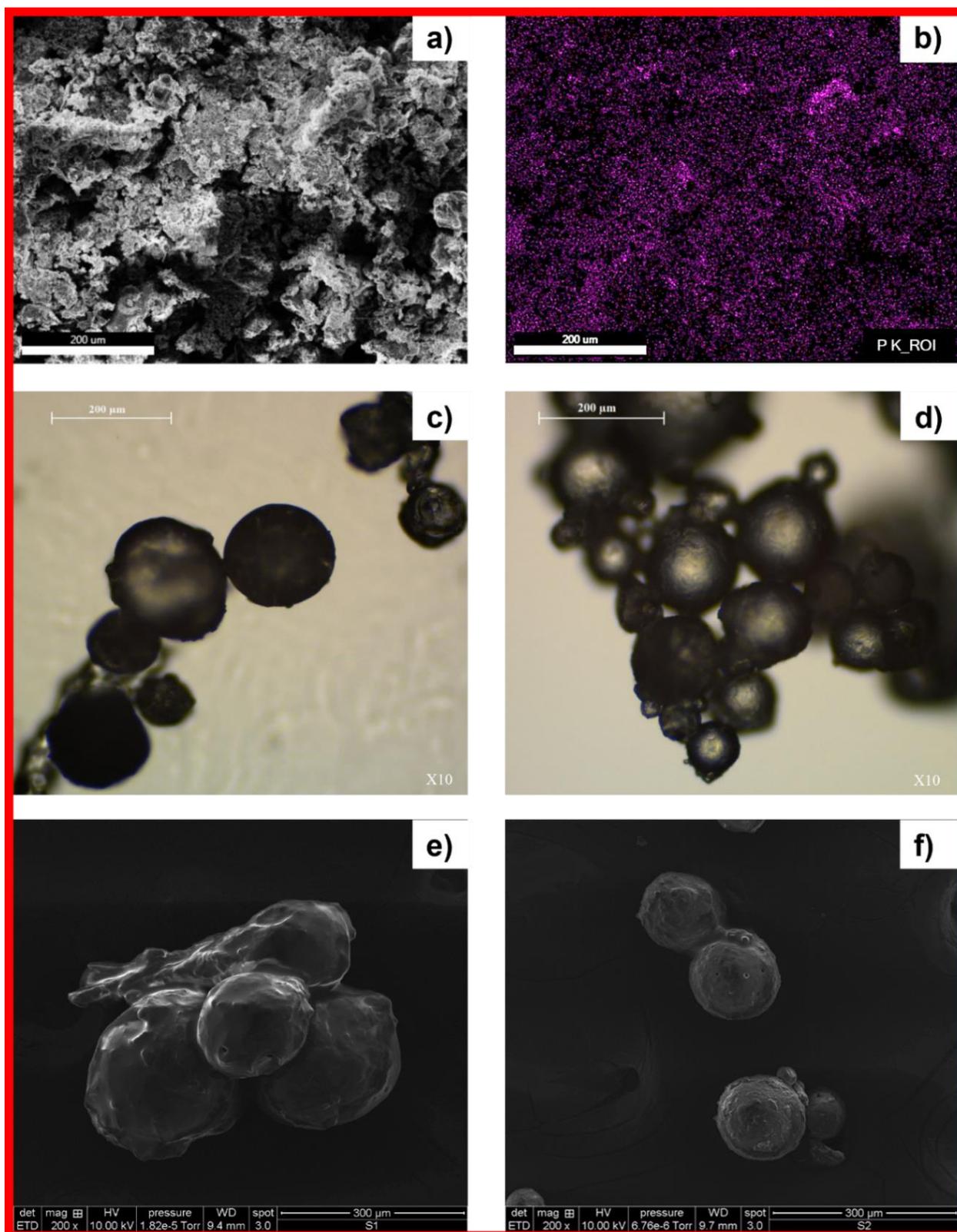


Fig. 1. (a) SEM micrograph of phosphorylated ethyl cellulose (P-EC). (b) Mapping of phosphorus element for phosphorylated ethyl cellulose (c). Optical microscope images of almond oil-filled microcapsules using (c) SDS and (d) DDPA as surfactants. SEM micrographs of almond oil-filled microcapsules using (e) SDS and (f) DDPA as surfactants.

3.2 Microcapsules characterization (FTIR and TGA)

The thermal stability of the prepared microcapsules is considered as a key parameter for the targeted applications as well as for the storage and vitality of the microcapsules. TGA was used to evaluate the thermal properties of the prepared microcapsules (MC-sds and MC-ddpa), almond oil, and phosphorylated ethyl cellulose (PEC). Almond oil has a high thermal stability, with practically no mass loss below a temperature of 290 °C (Fig. 2). Two stages of weight loss were observed for the prepared microcapsules. The MC-sds microcapsules exhibit two stages of weight loss at 197–290 °C and 290–500 °C related to the decompositions of PEC shell and almond oil core, respectively. The thermogram of MC-ddpa microcapsules shows a first stage of weight loss at 176–290 °C corresponding to the PEC decomposition. The second stage of weight loss ranging from 290 °C and 520 °C is related to the decomposition of almond oil. As a result, we can conclude that the almond oil microcapsules were successfully prepared and can be used and stored under a temperature of 197 °C and 176 °C for MC-sds and MC-ddpa respectively.

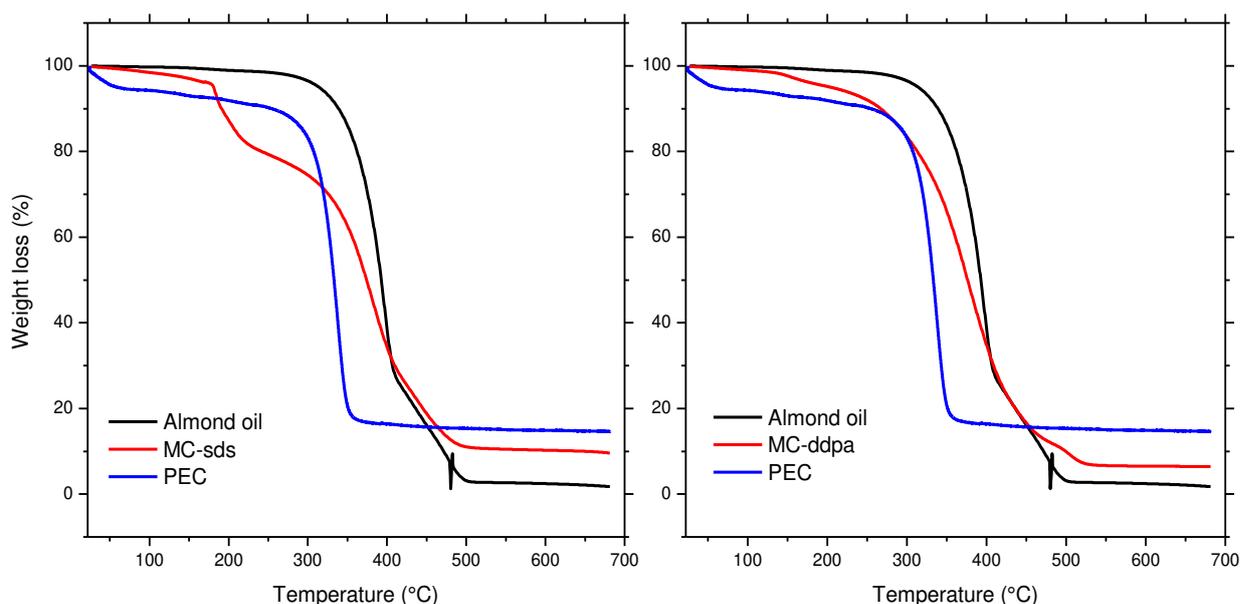


Fig. 2. (a) TGA weight loss curves of phosphorylated ethyl cellulose (PEC), almond oil and full microcapsules (MC). **(b)** TGA weight loss curves of phosphorylated ethyl cellulose (P-EC), almond oil and full phosphorylated microcapsules (P-MC).

In order to have a good knowledge of the chemical structure of the prepared microcapsules, FTIR tests of almond oil, PEC shell and PEC containing almond oil microcapsules (MC-sds and MC-ddpa) were adopted and the spectrum are demonstrated in Fig. 3. The peaks assigned to the methylene groups of almond oil were observed at 723 cm^{-1} , 1462 cm^{-1} , 2849 cm^{-1} and 2921

cm^{-1} . The peaks at 1375 cm^{-1} and 1464 cm^{-1} were related to the methyl group. The characteristic peak related to the olefinic double bonds was revealed at 3009 cm^{-1} . The peaks at 1095 cm^{-1} , 1159 cm^{-1} , 1235 cm^{-1} and 1743 cm^{-1} were attributed to the triglyceride ester groups [15–17].

The small new peaks appeared at 810 cm^{-1} and 1630 cm^{-1} in the FTIR spectra of the microcapsules were assigned to P-O-C and O=P-OH groups respectively, thanks to the presence of phosphorous in the modified ethyl cellulose used as shell material. All the characteristic peaks related to the shell material (PEC) and the core material (Almond oil) are in the FTIR spectra of the prepared microcapsules (in yellow in Fig. 3), which confirm clearly that the encapsulation of the oil was correctly done using the phosphorylated ethyl cellulose as shell materials [13].

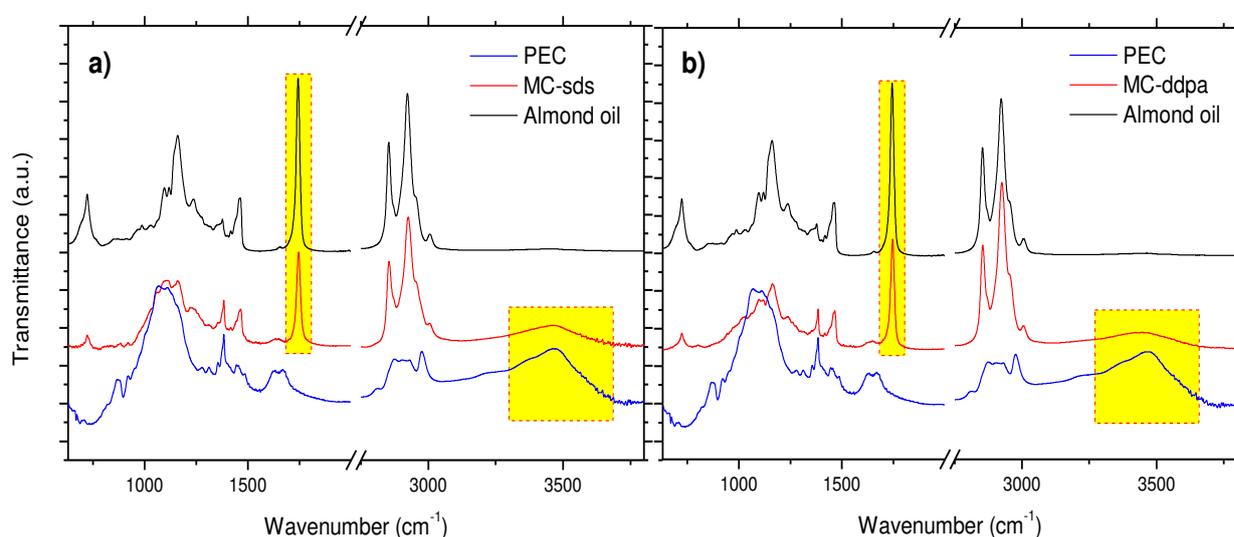


Fig. 3. (a) FTIR spectra of the oil-filled microcapsules (MC-sds), almond oil and phosphorylated ethyl cellulose (PEC). **(b)** FTIR spectra of the oil-filled microcapsules (MC-ddpa), almond oil and phosphorylated ethyl cellulose (PEC).

3.4 Salt spray study

Self-healing materials have become an essential part of smart materials that mimic the method of self-repairing behaviour of natural materials. They automatically heal damages induced by external forces, therefore extending the service life of materials. Microcapsule-based self-healing materials have received the most attention among self-healing materials [18]. In this study, self-healing epoxy coatings were obtained by adding microcapsules into epoxy resin. Salt-spray testing was used to investigate the corrosion resistance of the coatings with both microcapsules MC-sds and MC-ddpa. The observations are depicted in Fig. 4. After

7 days in the corrosive medium, a clear indication of rust can be seen at the scratched area of the control sample. Corrosion grew more severe as the exposition time increased. In comparison, self-healing coatings containing microcapsules exhibited no indication of visible rust after 7 days. After 14 days, MC-sds microcapsules loaded coatings demonstrated slight corrosion, while the MC-ddpa loaded coating is nearly free of corrosion.

After 28 days, the coatings exhibited various degrees of corrosion, although the corrosion was considerably less apparent than in the neat epoxy coatings (blank sample). As a result, it is possible to infer that the coatings containing microcapsules have a good resistance to corrosion, and the corrosion resistance is very close when using the MC-ddpa microcapsules or the MC-sds microcapsules.

Samples coding	Salt spray exposure time (day)			
	1 day	7days	14 days	28 days
a) Blank				
b) MC-sds				
c) MC-ddpa				

Fig. 4. Optical photographs of scratched coated mild steel samples (a,b,c) after various exposure times (1, 7, 14 and 28 days) to salt spray with 3.5 wt.% NaCl solution. **a)** blank, without microcapsules, **b)** coating with MC-sds microcapsules, **c)** coating with MC-ddpa microcapsules.

3.5 EIS measurements

The anti-corrosion behavior of the samples was examined using the EIS technique after exposing the samples to a 3.5 wt. % NaCl spray test for 1, 7, 14, and 28 days. Bode-Modulus plots for different samples are shown in Fig. 5. The $|Z|$ in low frequency ($|Z|_{lf}$) is a key factor to examine the total resistance of the samples that is deduced from Bode plot. The obtained $|Z|$ values at low frequencies of about 0.01 Hz for all the samples are exposed in Table 1.

Table. 1. Electrochemical data obtained from EIS test results.

Samples coding	$ Z _{0.01 \text{ Hz (ohm. cm}^2)}$			
	Immersion time			
	1 day	7 days	14 days	28 days
BLANK	1.18×10^2	9.47×10^2	4.43×10^2	1.75×10^2
MC-sds	2.23×10^4	2.68×10^4	0.31×10^3	7.54×10^4
MC-ddpa	11.05×10^4	5.71×10^4	8.07×10^4	0.95×10^4

According to the results presented in Table 1, the obtained $|Z|_{lf}$ values after 1 day, for the blank sample and the epoxy coating samples containing microcapsules (MC-sds, MC-ddpa) are 1.18×10^2 , 2.23×10^4 and 11.05×10^4 (ohm. cm^2), respectively. There is no significant difference in values of $|Z|_{lf}$ between the samples containing microcapsules due to the short exposure time in saline solution and the low penetration of electrolytes through the coating bulks. It worth to note that the $|Z|_{lf}$ values of the blank sample was lower compared to the coatings containing microcapsules during all the period of tests since there was no healing agent or corrosion inhibitor for the protection of the metallic substrate from the corrosive media. After 28 days of immersion in the corrosive medium, the MC-sds containing sample (7.54×10^4 ohm. cm^2) revealed a small advantage in terms of resistance compared with the MC-ddpa containing sample (0.95×10^4 ohm. cm^2). This behavior agrees with the results of salt spray test. The better performance of the capsules containing samples could be justified by the inhibitory action of almond oil in the presence of 3.5 wt.% NaCl solution, which has been investigated in previous work [13].

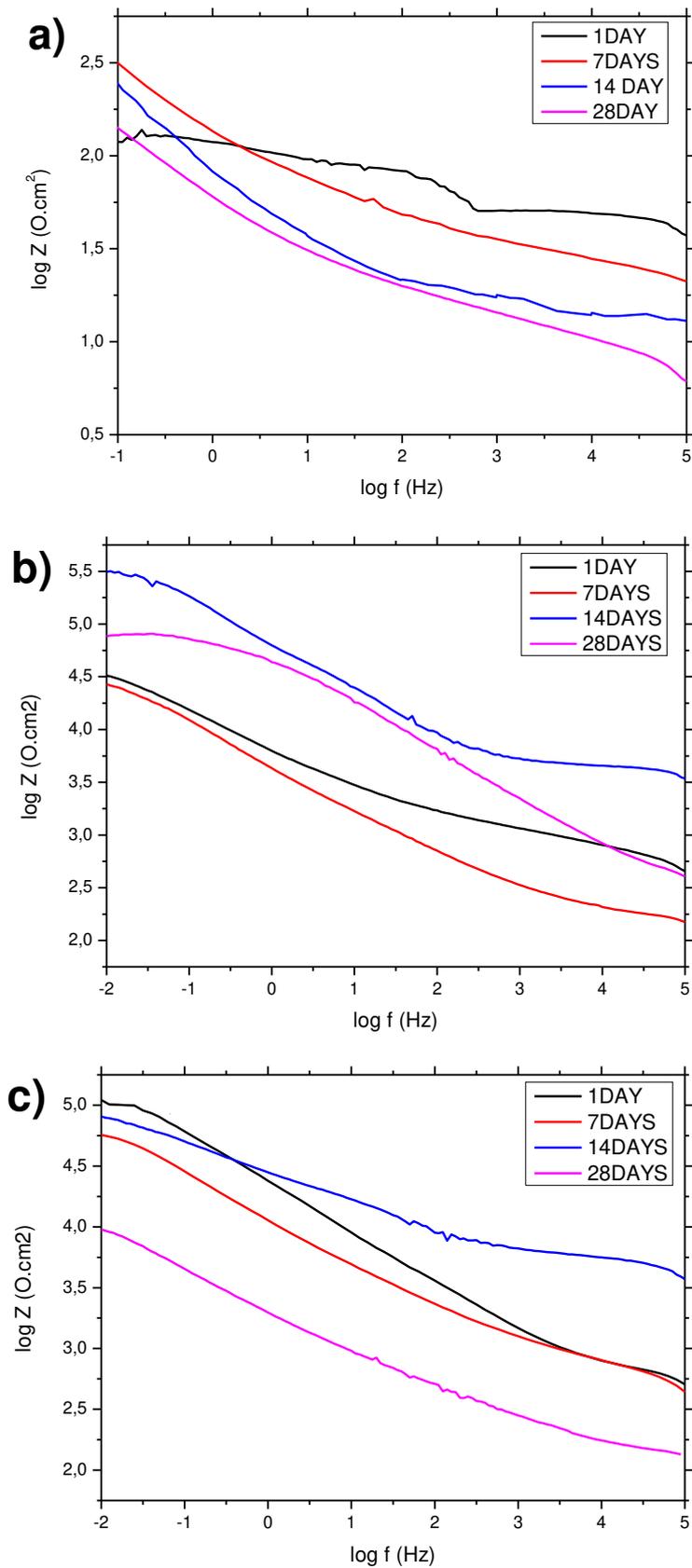


Fig. 5. Bode-Modulus plots for different coating samples: **a)** Blank, **b)** MC-sds, **c)** MC-ddpa, during various immersion times (1, 7, 14, and 28 days) in 3.5 wt% NaCl solution.

4. Conclusion

The spherical microcapsules filled with almond oil as healing agent for anti-corrosion coatings were prepared by solvent evaporation method. Two surfactants (SDS and DDPA) were used to prepare different microcapsules. The diameters of the obtained microcapsules ranging from 20 μm to 160 μm and the oil content of MC-sds and MC-ddpa was 62% and 65%, respectively. Meanwhile, FTIR proves that almond oil was successfully encapsulated into the phosphorylated ethyl cellulose (PEC) shell because all the characteristic peak of core material (almond oil) and shell material (PEC) were existing in the spectra of the microcapsules. The phosphorylated ethyl cellulose used as shell material of the microcapsules shows an excellent thermal behaviour leading to a good thermal stability of the microcapsules with an initial decomposition temperature of 197 °C and 176 °C for MC-sds and MC-ddpa respectively. After 28 days, the EIS results shows that the resistance of the coatings containing microcapsules is more than 104 $\Omega\cdot\text{cm}^2$, which is much higher than 102 $\Omega\cdot\text{cm}^2$ of the oxide layer of the neat epoxy coating. The salt spray test results confirm the corrosion protection ability of the self-healing coating in accordance with the EIS results.

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Chapter 5

Conclusions and further work

1. Conclusions

Les matériaux auto-cicatrisants sont des matériaux intelligents utilisés dans différentes applications telles que les matériaux de construction, les batteries et les revêtements. Le développement de matériaux auto-cicatrisants se fait selon deux scénarios : le développement de matériaux ayant des propriétés auto-cicatrisantes intrinsèques, ou la préparation de matériaux auto-cicatrisants extrinsèques contenant des ajouts tels que des microcapsules remplies d'agents cicatrisants. Actuellement, la technique d'autocicatrisation extrinsèque est la plus étudiée et la plus appliquée. La préparation de microcapsules est une étape clé pour le développement de matériaux extrinsèquement auto-cicatrisants. À cette fin, une variété de procédés d'encapsulation ont été rapportés dans la partie bibliographique de cette étude.

L'objectif était de présenter les procédés d'encapsulation utilisés pour développer des microcapsules pour des revêtements auto-cicatrisants anticorrosion. Pour chaque méthode d'encapsulation, la description comprend les matériaux de noyau et d'enveloppe utilisés, la taille et la morphologie des capsules, certaines techniques de caractérisation et les applications visées. En se basant sur notre revue de littérature, la méthode d'évaporation du solvant a été choisie comme technique d'encapsulation pour le reste des études expérimentales menées dans notre étude afin de développer un revêtement auto-cicatrisant et anticorrosion. Le choix de la méthode d'encapsulation était basé sur différents facteurs tels que les matériaux à utiliser pour l'encapsulation, la taille et la morphologie des capsules ciblés. Le travail expérimental portant sur la préparation des microcapsules contenant des huiles par la méthode d'évaporation du solvant a été réalisé avec succès. L'éthylcellulose native et l'éthylcellulose phosphorylée ont été utilisées comme matériaux polymères d'enveloppe pour encapsuler quatre huiles différentes (huiles de lavande, de graines noires, de figues de barbarie et d'argan). C'était la première fois que l'on encapsulait ces huiles en utilisant de l'éthylcellulose phosphorylée comme polymère formant l'enveloppe. La composition des microcapsules a été évaluée par FTIR, et les résultats obtenus ont prouvé que les microcapsules étaient uniquement composées de l'huile étudiée (huile de lavande, de graines noires, de figue de barbarie ou d'argan) et de l'enveloppe (éthylcellulose ou éthylcellulose phosphorylée). L'analyse thermogravimétrique (ATG) a été utilisée pour étudier la stabilité thermique des microcapsules préparés, elle a confirmé la propriété de retardation de flamme induite au P-MC grâce à l'utilisation du P-EC comme matériau d'enveloppe. La teneur en huile

a été déterminée pour les microcapsules obtenues. Les images du MEB ont confirmé l'efficacité de la méthode de préparation et ont montré la forme sphérique des microcapsules avec une gamme de taille de particules de 10-170 μm . L'objectif principal de cette première partie de l'étude était de prouver le concept d'encapsulation d'huile en utilisant le P-EC comme enveloppe.

L'éthylcellulose phosphorylée utilisée pour préparer les microcapsules a été obtenue avec succès par une réaction de phosphorylation utilisant de l'acide phosphorique en présence d'urée fondue. L'analyse ICP-OES confirme une teneur en phosphore de 6,26 % en poids dans la structure de la P-EC. La fonctionnalisation de l'éthylcellulose a favorisé son comportement de retardateur de flamme comme le révèle l'analyse ATG. De plus, la surface spécifique du P-EC a augmenté d'un facteur 20 par rapport à celle de l'éthylcellulose natif.

Dans la deuxième partie de l'étude, l'accent a été mis sur l'encapsulation de l'huile d'amande qui a été réalisée avec succès. Les microcapsules obtenues ont montré une stabilité thermique pour l'application ciblée. Les propriétés auto-cicatrisantes et anti-corrosion des microcapsules ont été évaluées par le test de brouillard salin sur des revêtements à base de résine époxy rayés. Les résultats ont révélé que le revêtement contenant des microcapsules phosphorylées présentait une résistance à la corrosion supérieure à celle du revêtement vierge et du revêtement chargé de microcapsules non phosphorylées sur une période de test de 4 semaines. C'était la première tentative de préparer des microcapsules d'huile d'amande en utilisant de l'éthylcellulose et de l'éthylcellulose phosphorylée comme matériaux d'enveloppe. La troisième partie de notre étude a été consacrée à l'amélioration des propriétés des microcapsules d'huile d'amande préparées. Pour cela, nous avons fait varier les tensioactifs utilisés pour la préparation des microcapsules. Les effets de cette variation sur les microcapsules et les revêtements préparés ont été étudiés. Les microcapsules obtenues ont été caractérisées par FTIR, ATG, MEB... En outre, la résistance à la corrosion et les performances d'auto-cicatrisation des revêtements époxy contenant des microcapsules à base d'huile d'amande ont été étudiées dans un milieu corrosif de 3,5 % en masse de NaCl. L'effet des deux types de microcapsules préparées avec des tensioactifs différents sur la résistance à la corrosion et les propriétés auto-cicatrisantes des revêtements était l'objectif principal de ce travail. Les mesures EIS ont montré que les revêtements contenant les microcapsules phosphorylées contenant de l'huile d'amande ont une meilleure performance contre la corrosion en comparaison avec ceux sans capsules.

2. Further work

Les revêtements anticorrosion et auto-cicatrisants présentent de grand potentiel pour le développer des revêtements anticorrosion à usage industriel intensif. Toutefois, pour que le concept fonctionne, un certain nombre de facteurs doivent être pris en compte et étudiés de manière approfondie en étroite collaboration entre les chimistes, les ingénieurs et spécialistes en sciences des matériaux et revêtements. Actuellement, il est toujours nécessaire de trouver de nouvelles méthodes d'auto-cicatrisation qui peuvent être appliquées aux systèmes industriels et à grande échelle, ainsi qu'étudier l'impact des capacités d'auto-cicatrisation sur d'autres caractéristiques du revêtement. Le présent travail peut être poursuivi par une étude plus approfondie des revêtements contenant des microcapsules, et d'explorer davantage l'effet des propriétés des huiles sur les capsules finales.

L'approche des revêtements auto-cicatrisants contenant des microcapsules est très prometteuse et pourraient potentiellement être utilisés dans différentes applications écologiques et durables pour améliorer les propriétés des matériaux telles que la durabilité, la biodégradabilité, la chélation des métaux et la retardation de flamme. Des recherches et des tests supplémentaires sur l'influence du degré de phosphorylation sur les performances de ces matériaux sont très intéressants et doivent être étudiés. D'autres efforts doivent être consacrés à la préparation de capsules contenant des matériaux anticorrosifs adaptés à l'utilisation industrielle. Ainsi, les essais de corrosion de longue durée présentent un intérêt particulier.

Il convient de tenter d'établir un modèle permettant de simuler la quantité d'un agent cicatrisant à ajouter au revêtement pour obtenir le degré de cicatrisation souhaité, la répartition des capsules dans les revêtements, la taille minimale et maximale des fissures qui peuvent être cicatrisées, ainsi que l'effet du diamètre et de la concentration des microcapsules sur l'efficacité de la cicatrisation du revêtement.