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

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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).

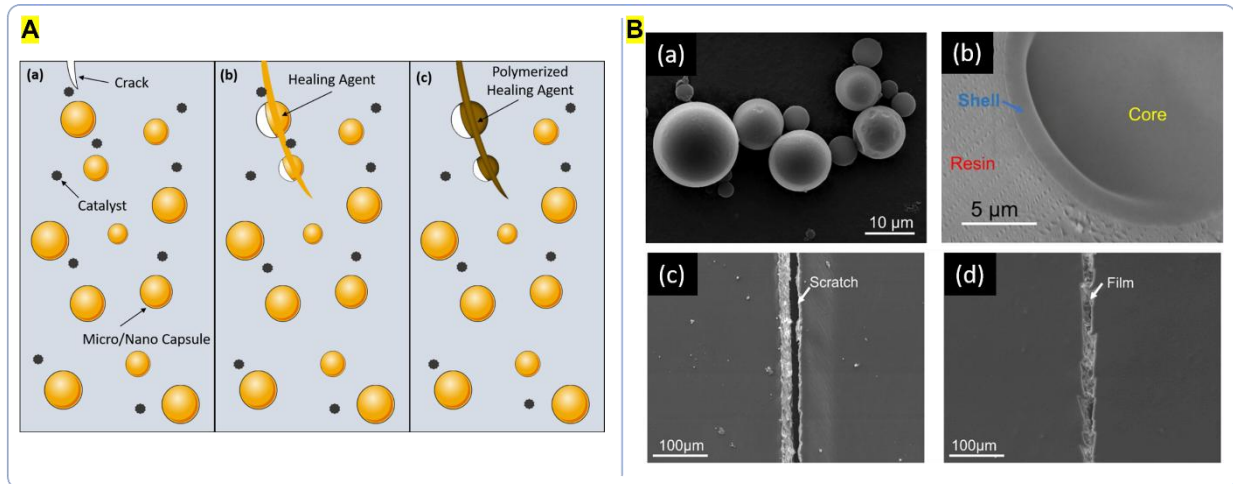


Fig. 1. A) Schematic diagram of capsule-based self-healing concept. (a) Crack forms in the material containing micro/nano capsules and catalysts, (b) Rupture of micro/nano capsules and release of healing agent, (c) Polymerization of healing agent stops the crack propagation.

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 $1\mu\text{m}$ (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 was 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 exhibit 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 preformed 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].

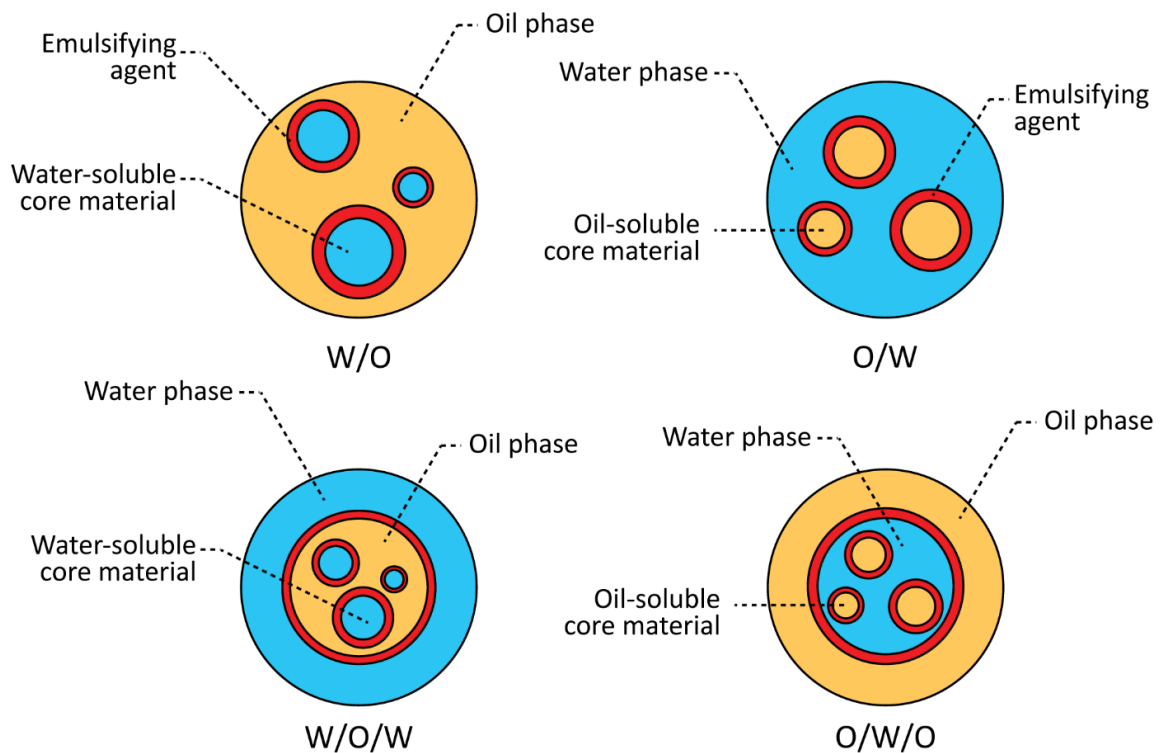


Fig. 2. Illustration of emulsion systems W/O, O/W, W/O/W and O/W/O.

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].

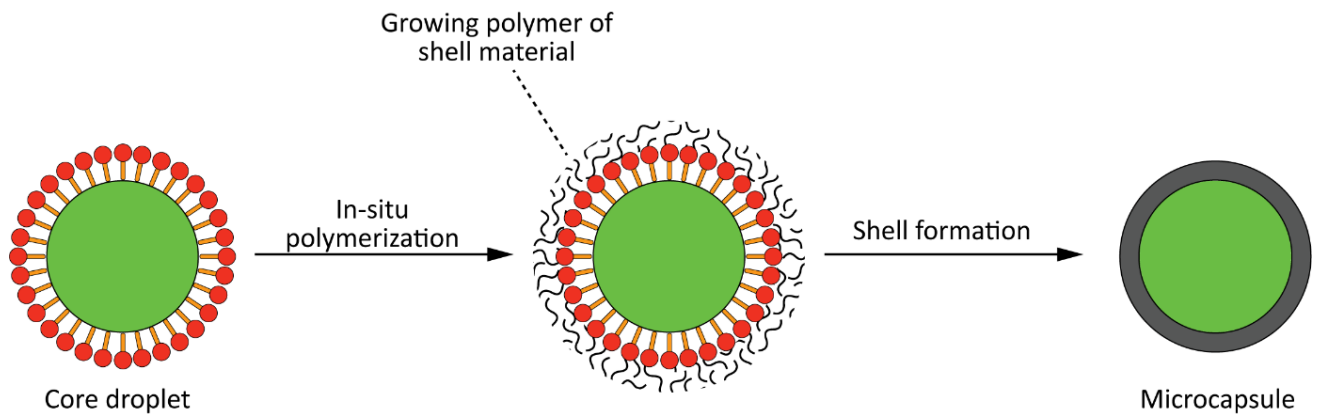


Fig. 3. Schematic diagram of microencapsulation by in situ polymerization.

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].

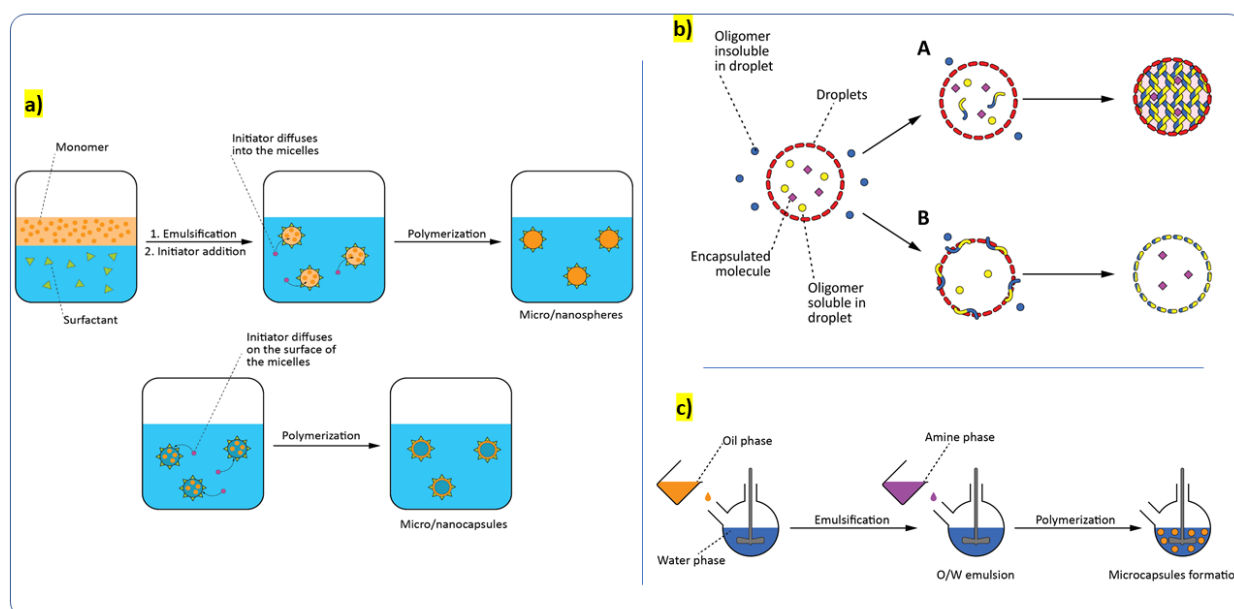


Fig. 4. a) Schematic diagram of microencapsulation by emulsion polymerization. **b)** Schematic diagram of microencapsulation by interfacial polymerization by two methods using: **(A)** Oligomer soluble in the droplet, **(B)** Oligomer insoluble in the droplet. **c)** Schematic diagram of polyurea microcapsules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

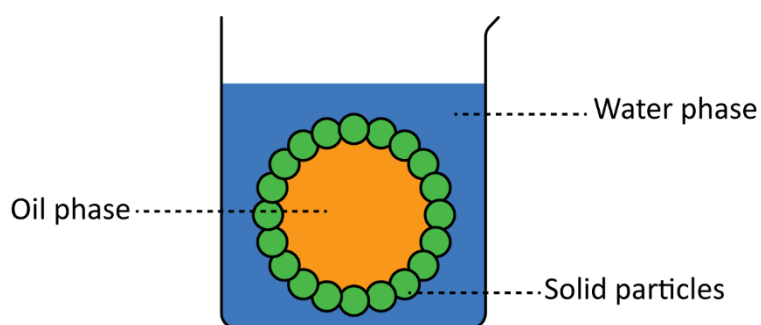


Fig. 5. Schematic diagram of a microcapsule prepared by Pickering emulsion process.

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.

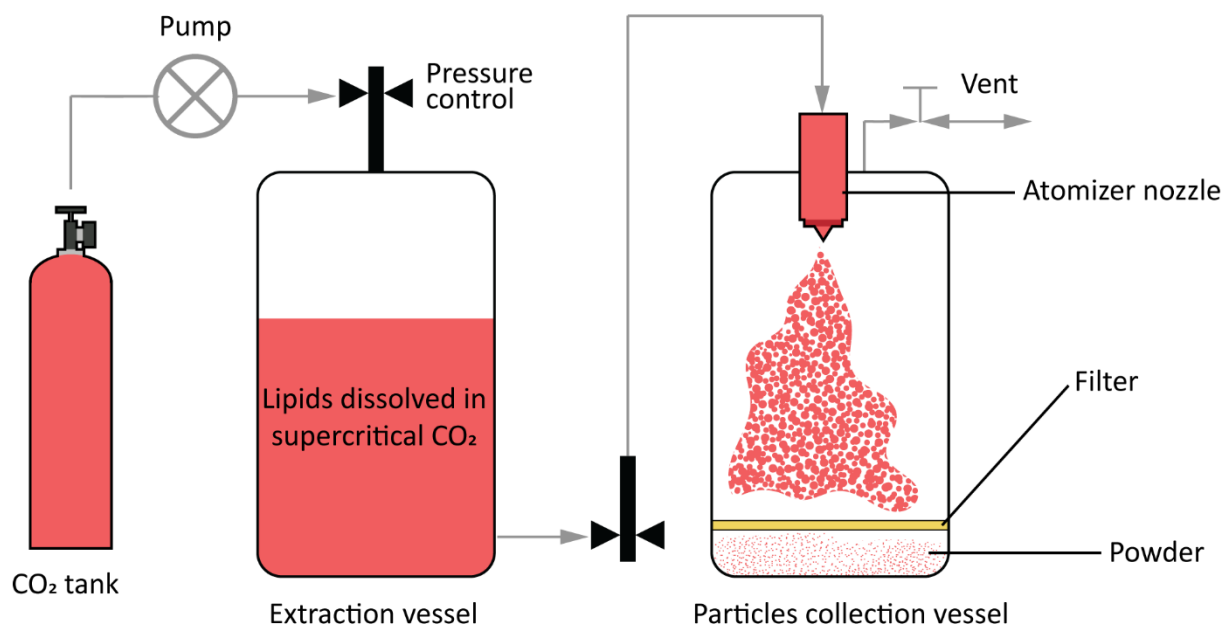


Fig. 6. Schematic diagram of supercritical fluid technology.

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].

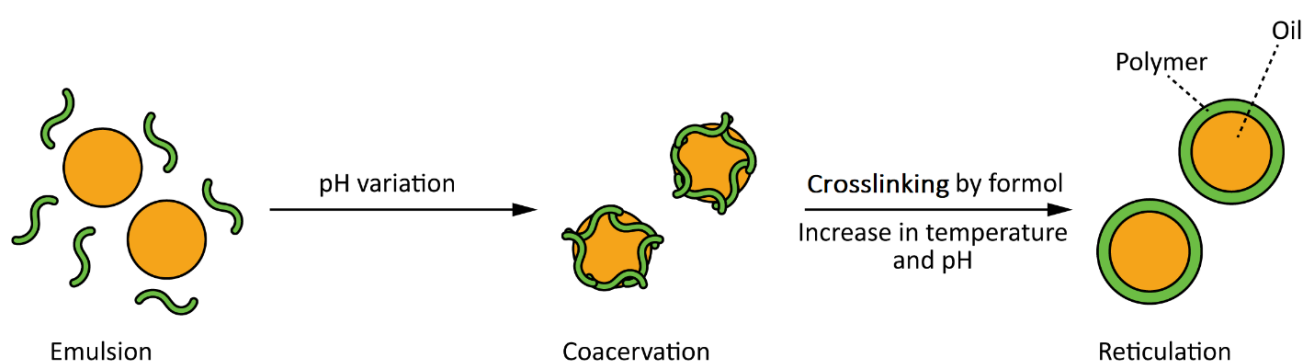


Fig. 7. Schematic diagram of encapsulation by complex coacervation process.

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].

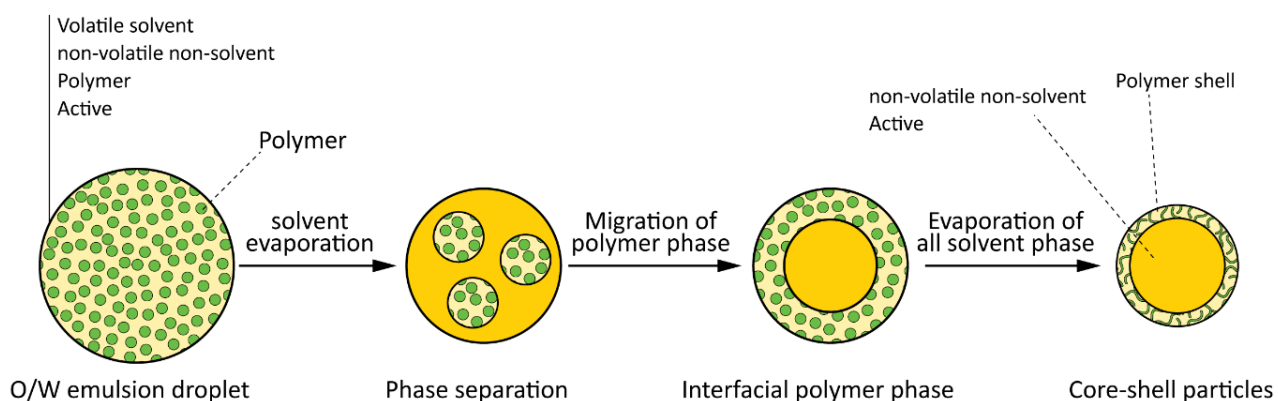


Fig. 8. Schematic diagram of microencapsulation by internal phase separation.

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].

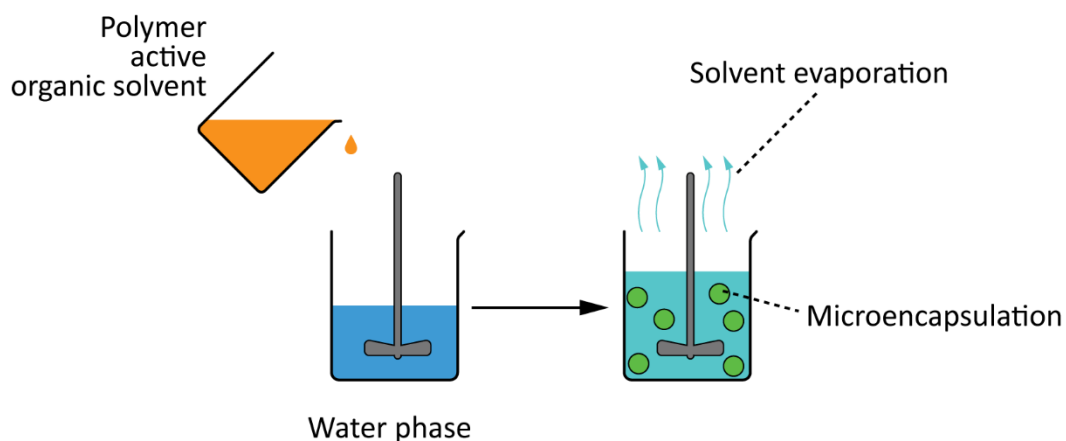


Fig. 9. Schematic diagram of microencapsulation by solvent evaporation. The organic phase containing the core and shell materials is emulsified in the water phase containing a surfactant. The solvent evaporates after emulsion stabilization induce the microcapsules formation.

In the studies of Abbaspour 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].

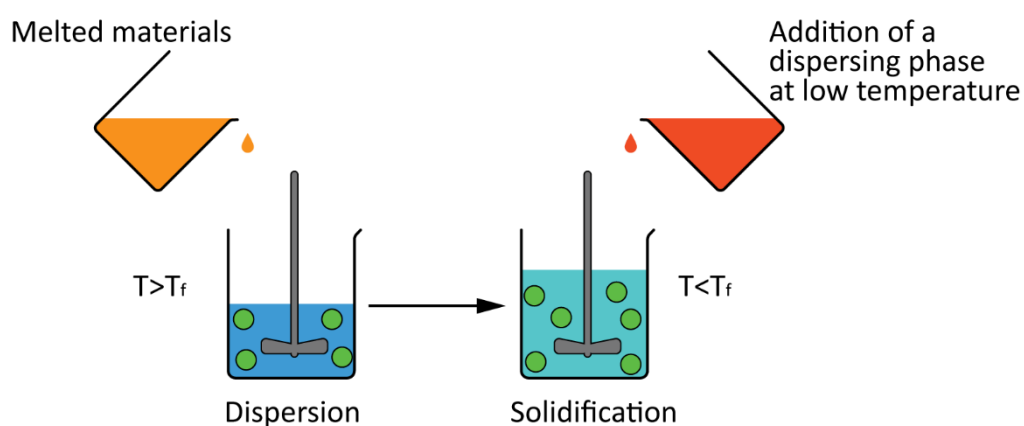


Fig. 10. Schematic diagram of microencapsulation by thermal gelation process. A mixture of melted shell and active material is dispersed in a liquid of opposite polarity. Then, a dispersing phase at low temperature is added to the emulsion to allow the capsules solidification and formation.

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).

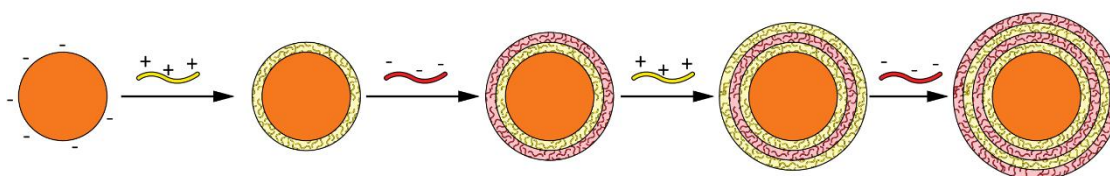


Fig. 11. Schematic illustration of microencapsulation via layer-by-layer process. After the preparation of a stable and negatively charged emulsion droplets, positively charged polyelectrolyte is adsorbed on the droplets to form a positively charged capsules. The process is repeated using another polyelectrolyte 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].

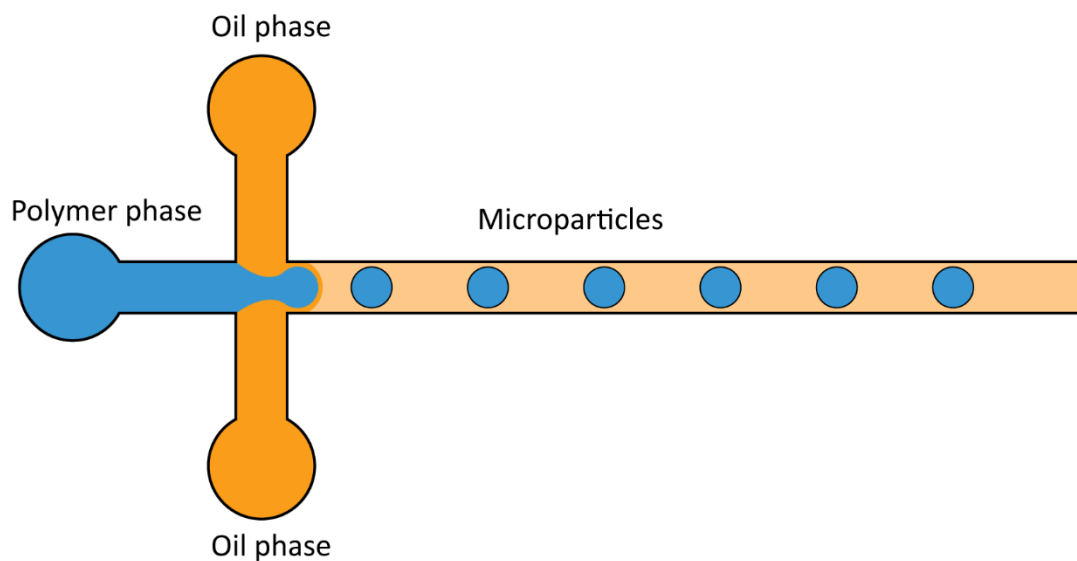


Fig. 12. Schematic diagram of microencapsulation by microfluidic encapsulation process. The junction allows the sharing of the aqueous phase by the oil phase which generates droplets.

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].

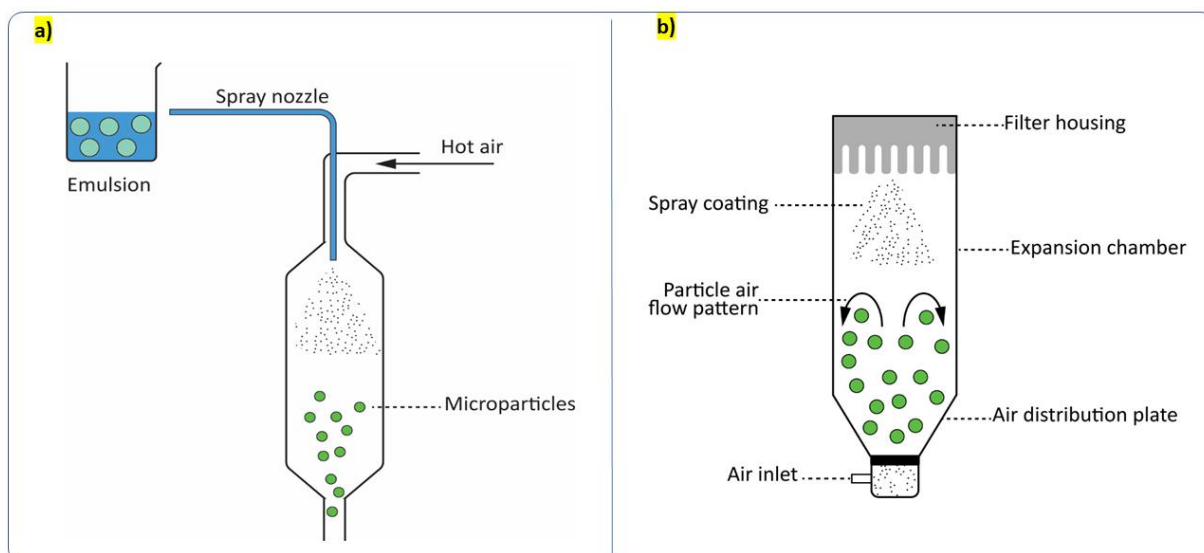


Fig. 13. a) Schematic illustration of microencapsulation by spray-drying process. The emulsion is sprayed through the nozzle to generate small droplets, which are transformed into dry particles by evaporation of the organic solvent caused by the heated dry air flow. Thereafter, the particles are collected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

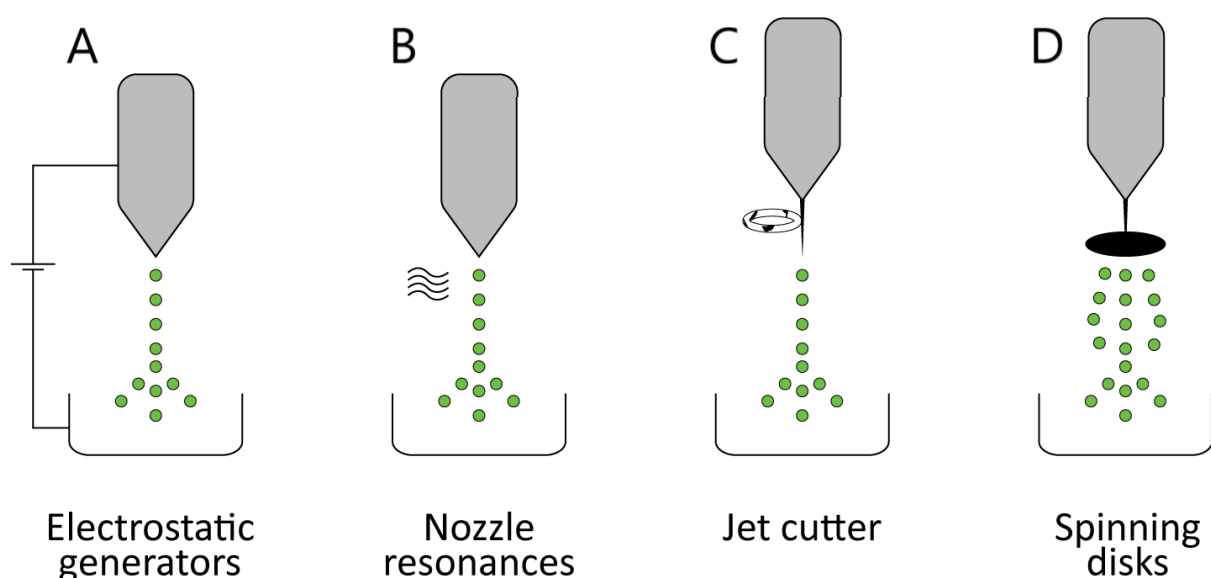


Fig. 14. Schematic illustration of different configurations of prilling microencapsulation process. (A) Electrostatic generator: Charges accumulate on the surface of the droplets by applying an electrostatic potential cause the opposition of the surface tension, allowing the formation of capsules. (B) 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]

[illegible]

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	58-260µm	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	300 µm	Polyurethane	Corrosion protection coatings	[38]
			Nanocapsules	150 nm	coatings		
Solvent evaporation	Almond oil	Ethyl cellulose and Phosphorylated Ethyl	Microcapsules	140 and 150 µm	Epoxy coating	Corrosion protection coatings	[42]

		cellulose					
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]

[illegible]

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]
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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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