Materials Microencapsulation Applications in Oil Drilling and Production

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Abstract. Advancing the materials used in oil drilling and production has significantly augmented the industry’s efforts to improving the processes and preventing the operations failures. Presently, oil drilling and production demand that materials do not simply demonstrate better performance, but also possess some degree of intelligence. The intelligence is induced to the materials by preprogramming a certain response to a change in the surrounding conditions to trigger the function of the used materials. This improves the performance and prevents possible physical damage or mitigates negative changes in the downhole environment during production. Smart responsive microcapsules, with the ability to self-heal the materials, delayed and targeted active release, and could become a viable solution for the challenges the oil drilling and production industry is currently facing. This paper provides an overview of the benefits that a microencapsulation technique has demonstrated when applied to the materials involved in oil drilling and production. It outlines possibilities for improving the well drilling process when products containing microcapsules are applied. Several examples demonstrating the ability to perform downhole treatment seamlessly with pre-designed microcapsules are embedded. The paper puts emphasis on developing smart self-healing materials by integrating microcapsules into the cement sheath as well as the coatings of steel pipes to mitigate costly failures. Finally, the paper shows examples of some outstanding results of microencapsulated materials when applied to the most advanced research areas in the oil industry such as enhanced oil recovery (EOR) and hydraulic fracturing.

1. Introduction

Microcapsule is a small, typically diameter range of 1-1000 micrometres, sphere with a uniform wall around it. The material inside the microcapsule is referred to as the core, internal phase, or fill, whereas the wall is called a shell, coating, or membrane. There are several types of microcapsules morphologies that have been synthesized as shown in Figure 1. The general single-core microcapsule is made of the core and the shell around it, multi-core microcapsule has more than one core inside the shell, double- and sometimes multiple shell microcapsules have more than one shell around the core. Separate case is the microsphere with the core material equally distributed inside the matrix material without having well-defined shell encasing the entire sphere. There is a large variety of materials that could comprise the shell of a microcapsule: polymers, waxes, resins, polysaccharides, proteins, ceramics; while the core could be of three types of aggregation states: solid, liquid or solid dispersed in liquid. [1,2]
Microencapsulation is a process by which droplets or small particles are enclosed within a shell to produce microcapsules. Microencapsulation is used to ensure that the core material remains sealed without any interaction with the surrounding environment until it reaches the point where it should be released and begin functioning [1]. The principle reasons for microencapsulation can be summarized as follows:

1. Protecting the core materials from adverse environmental effects (pH, temperature, humidity, and other substances).
2. Controlling the active components for delayed (timed) release or long-acting (sustained) release.
3. Combining two incompatible components for a multifunctional structure.

Most used techniques to manufacture microcapsules could be divided into three groups: Physical, Chemical and Physical & Chemical, as shown in Figure 2. The most common techniques are described below.

1.1 Physical Microencapsulation Techniques

- **Spray–drying**
  Spray drying serves as a microencapsulation technique when an active material is dissolved or suspended in a melt or polymer solution and becomes trapped in the dried particle. The resulting material is the microsphere as pictured in the Figure 1. Spray drying is suitable for both thermolabile and thermostable materials and enables the production of uniform size particles. The main advantages are the ability to handle labile materials because of the short contact time in the dryer and the operation is economical. [2,3]

- **Fluidized-bed spray coating**
  Spray coating in a fluidized bed system allows for particles having different shapes and sizes are moved around in the fluidized bed and simultaneously coated with a fluidized material. The aqueous or organic
solution evaporates and the solids it contains form the coating layer. Originally developed as a pharmaceutical technique, fluidized-bed coating is now increasingly being applied in the food, automotive and other industries. Spray coating in a fluidized bed system produces an optimal surface coating through even application of a film material. [2,4]

- Electrostatically assisted spraying
  The method is based on using an electrostatic potential to pull droplets from a needle tip into a gelling bath. A voltage is applied between the needle feeding the alginate solution and an electro conductive solution underneath. The voltage forces the droplets to fall off the needle tip before it has grown to the point where it falls off due to its own weight. The beads are formed when droplets fall into the solution. The high voltage has been confirmed not to damage the encapsulated cells, proteins etc. [5,6]

- Vibrational nozzle
  Core-shell encapsulation can be done using a laminar flow through a nozzle and an additional vibration of the nozzle or the liquid. A laminar jet of liquids falls apart into drops of equal size, if you superimpose a vibration with a wavelength, longer than the girth of the undisturbed jet on the liquid. The microcapsule is typically formed by physical cross-linking large polyelectrolyte molecules with metal ions, i.e., sodium alginate + calcium chloride. [7]

- Hot-melt extrusion
  Hot melt extrusion resembles vibrational nozzle method, with the exception that the shell-forming material is in the melted state. Depending on the device, a monocentric or concentric nozzle system is used, which produces different types of microcapsules, respectively, by extrusion and co-extrusion. The concentric system presents internal and external nozzles that allow the production of reservoir-type microcapsules. [8]

1.2 Physical & Chemical Microencapsulation Techniques

- Coacervation
  Coacervation involves the separation of a liquid phase of coating material from a polymeric solution and wrapping of that phase as a uniform layer around suspended core particles. The coating material is then solidified by means of heat, cross-linking, or solvent removal techniques. To optimize the process, some additives such as the stabilizer, coacervating agent, and crosslinking agent were added. Coacervation is a unique and promising microencapsulation technology, which can achieve high payloads (up to 99%). [2,9]

- Solvent evaporation
  Solvent encapsulation has been commonly used for encapsulation of epoxy, where epoxy and shell-forming polymer are dissolved in an organic solvent and dispersed in a water phase. After evaporation of the solvent, microcapsules with hard shells, which encase epoxy droplets, are obtained. The shells can be formed from a variety of polymeric materials such as poly(urea-formaldehyde), urea-formaldehyde, melamine-formaldehyde, polyetherimide, cellulose, and ethyl cellulose. Other shell materials include poly(ethylene glycol), poly(methacrylate), poly(styrene), poly(lactide), etc. [10]

- Layer-by-layer (LbL) adsorption
  LbL assembly method was for the first time reported by Caruso & Crusco and Möhwald in 1998. The method was based on the self-assembling of oppositely charged polyelectrolytes on the outer surface of colloidal particles. Taking LbL assembly of polyelectrolytes as an example, the construction process starts with a polyanion layer deposited on a positively charged surface followed by adsorption of a polycation reversing the surface charge. Consecutive adsorption of oppositely charged polymers results in formation of a stable polycation/polyanion complex in each cycle. Ultimately, a multilayer film is achieved, whose thickness can range from a few nanometres to several microns depending on the polyelectrolytes involved, the number of deposition cycles and the medium conditions. [11,12]

1.3 Chemical Microencapsulation Techniques

- Emulsion polymerization
  Emulsion polymerization is a polymerization process that also requires stabilizing the droplets of the immiscible liquids. It involves application of emulsifier to emulsify hydrophobic polymers through
aqueous phase by the emulsifier, then adding either a water or oil soluble the polymerization imitators to polymerize the monomers contained in the emulsified droplets. Resulting polymer-containing microspheres act as the microcapsules for the active that they held. [13,14]

- **Interfacial polycondensation**

  In interfacial polycondensation, the two reactants in a polycondensation meet at an interface and react rapidly. Under the right conditions, thin flexible walls form rapidly at the interface. Condensed polymer walls form instantaneously at the interface of the emulsion droplets. The two most popular amino resins for interfacial polycondensation of the core healing agent are urea-formaldehyde (UF) and melamine-formaldehyde (MF). [1, 2]

- **Interfacial cross-linking**

  Interfacial cross-linking is derived from interfacial polycondensation and was developed to avoid the use of toxic diamines, for pharmaceutical or cosmetic applications. When the reaction is performed at the interface of an emulsion, the acid chloride reacts with the various functional groups of the protein, leading to the formation of a membrane. The method is very versatile, and the properties of the microcapsules (size, porosity, degradability, mechanical resistance) can be customized. [1, 2]

Microcapsules are finding multiple opportunities to be applied for oil and gas drilling and production. The ways microcapsules bring the value to various operations in O&G industry are demonstrated below.

2. **Microcapsules for Drilling & Cementing the Well**

Drilling operations require smooth and consistent execution of the task without any interferences and stoppages. Drilling fluid is formulated to facilitate seamless process by removing the cuttings, lubricating, keeping the pressure and maintaining bore stability. With the development of deeper wells, several challenges such as corrosion prevention, higher torque and drag reduction between drilling tools are needed to be resolved, which require the discovery of more effective drilling fluids. Use of drilling fluid with lubricant additives is a simple and economical method. Many researchers have explored a huge variety of lubricant additives in water conditions to evaluate their tribological behaviours. The abilities on friction reduction and wear resistance could be improved by the addition of lubricant additives. Lubricant additives can aggregate with the drilling fluid constituents and lose their effectiveness. Therefore, microencapsulation could play important role to deliver the lubricant unaffected right to the point of friction.

Ji et al. created and tested microcapsules study the tribology behaviour of steel-steel contact under the lubrication of water-based drilling mud with different oleic acid-filled microcapsules as lubricant additives. Ball-on-disc tribometer was used to evaluate the lubrication properties of the steel-steel contact. Results show that the dependence of both friction and wear on the category of additives shares a consistent pattern. In contrast to oleic acid and empty microcapsules, oleic acid-filled microcapsules achieve the best tribological performance which is related to the lubricant effect of oleic acid and the isolation and rolling abilities of microcapsules. Experimental results reveal that the addition of oleic acid significantly reduced friction and wear compared to basic mud and empty microcapsule because of the lubrication effect of oleic acid. The microencapsulation of oleic acid significantly improved tribological behaviour of drilling mud, which is related to the rolling effect of microcapsule and its abilities in isolating, protecting the filled additives [15].

The trend toward drilling deeper and consequently hotter wells places increasing heat stability demands on the electronics in the bottomhole assembly (BHA). This could damage the heat-sensitive instrumentation for measuring while drilling in the BHA, which contains multiple electronics. For this reason, cooling the tools in the drillstring is very important function of drilling fluids. Other benefits of limiting the temperature of the drilling fluid include enhancing borehole stability and reducing bit temperature and subsequently, bit wear.

Monteiro et al. proposed to use encapsulated phase changing materials (PCMs) to cool down the drilling fluid, for the HPHT wells. PCMs can absorb or release latent heat when the temperature of the material increases or decreases beyond its melting point. The heat absorbed or released during a phase change (per unit mass) as latent heat is significantly higher than the sensible heat, and equally as important, the
heat absorption and release can be designed to take place at a temperature of interest. Two materials with liquid crystal phases were tested in this study: cholesteryl stearate and zinc stearate with the phase transition temperatures of 83°C and 128°C, respectively. It was concluded that the benefit of PCMs used for drilling would depend on the latent heat of the phase change as well as the phase change temperature with respect to the temperature profile of the fluid in absence of the PCM. There is an optimal phase change temperature that maximizes the decrease of fluid temperature at the bottom of the well. A challenge among the materials tested in the publication was the form stability, which is critical for PCM to find application in drilling fluids [16].

PCMs could also bring value when cementing the well. During the cementing operations of oil wells, there are many situations in which it is crucial to regulate the temperature of the slurry during and after its placement. Limiting the temperature rise of cement-based composite materials was traditionally achieved by reducing the heat of hydration of the composite (e.g., using supplementary cementitious materials or inert filling materials). The total amount of heat generated by a cement composite is primarily determined by the hydration extent of the cement that has a strong correlation with the composite’s strength development. Reducing the heat of hydration of oil well cement through chemical means typically results in lower strength of the material, especially during early ages.

Pang et al. investigated the application of microencapsulated phase-change material (MPCM) to regulate the temperature of oil well cement. The MPCM acted as the energy-storage medium. It was absorbing heat when the temperature of the cement reached the melting point of the phase-change material (PCM) and was releasing heat when the temperature dropped below its freezing/crystallization point. Two types of MPCM, supplied by Mikrotek Laboratories in a dry powder form were used. Paraffin was the core material for both, specified melting point for the first MPCM was 6°C and for the second it was 56°C. During this study, the heat evolution of cement slurries was investigated by both isothermal calorimetry and semiadiabatic tests. A similar amount of heat was generated by most slurries, as shown by isothermal calorimetry tests. Results from semiadiabatic tests and compressive-strength tests show that the slurry prepared with MPCM in a solid state exhibited least temperature rise and optimal mechanical properties (high strength and high-strain capacity), which can be attributed to desirable properties of the PCM including high latent heat and low Young’s modulus [17].

Huo et al. demonstrated the possibility to control the heat evolution by MPCM through physical means. It was shown that heat evolution of cement slurry system was successfully controlled by the synthesized MPCM. Compared with conventional cement slurry system CB, the maximum temperature and temperature rise of sample CM-III were reduced by 6°C and 4.5°C, and the hydration heat of 24 and 48 hours was reduced by $1.5 \times 10^4$ and $1.4 \times 10^4$ J [18].

Self-healing cement creation is another direction where microencapsulation can deliver significant value to the oil and gas industry. Self-healing in cement or concrete can be broadly classified into two categories: autogenic and autonomic healing as shown in Figure 3. Autogenic healing is an intrinsic material healing property which is triggered with the hydration of unhydrated cement remaining in the matrix resulting in formation of calcium carbonates or hydroxides (Figure 3 (a)). Autonomic healing on the other hand is the use of components which normally are not present in cement-based composites. This category typically refers to different types of materials incorporated into the matrix usually in the form of encapsulated additions, that could be based on the bacteria (Figure 3(b)) or adhesive material (Figure 3 (c)). Self-healing is triggered upon crack formation which results in the rupture of the encapsulated system and the subsequent release of the healing compounds. Microcapsules represent an ideal solution for creating autonomic self-healing cement. The microencapsulated healing agent utilizes stress as a trigger for self-healing to occur. During damage, the capsules are ruptured which activates the release and reaction of healing agents in the region of damage. Healing agents work in four different ways: (1) they can either react with moisture, air or heat; (2) reaction with the cementitious matrix itself; (3) reaction with a second component, which is present in the matrix; and (4) reaction with provided by additional capsules [19].
Figure 3. Self-healing mechanisms: (a) autogenous; (b) autonomous bacteria-based; and (c) autonomous capsule-based.

In-situ interfacial cross-linking using amino resins is the most common method to make capsules for creating self-healing cement. Urea-formaldehyde (UF) and melamine-formaldehyde (MF) are the two most popular amino resins. In preparing the microcapsules, UF can be cross-linked to form hard shells that protect the healing agent in the cores. During the preparation process, a low-molecular weight oligomer is first formed from the condensation of urea and formaldehyde. Subsequently, the oligomer becomes attached onto the surface of the dispersed core material and gradually polymerizes to form the shell [20].

Single-component healing agents are the best to be utilized for self-healing cement. One of the well-studied healing agents is sodium silicate also known as liquid glass. The self-healing solutions based on it have been well-explored by different researchers and demonstrated the ability of the cement and concrete to heal the cracks autonomously [21–23].

The other well-known self-healing agent is isocyanate-based chemistry, that has very strong adhesive properties. Du et al. created microcapsules with toluene-di-isocyanate (TDI) as core and paraffin as shell for self-healing of concrete using melt condensation method. He studied the effects of preparation temperature, agitation rate and paraffin/TDI mass ratio on core fraction of microcapsules. The mortars with the microcapsules showed more favourable self-healing capacity. The optimum content of the microcapsules is 3% by mass of the cement. Compared to the control mortar, the pre-damage mortar with 3% microcapsules obtained much higher compressive strength reserved ratio after 48 h self-healing. The cracks with a width of less 0.4 mm on the mortar with 3% microcapsules were self-healed in 6h [24].

Epoxy-based chemistry is another adhesive that could be microencapsulated and added to the cement mixture to make it self-healing. Epoxy chemistry could also be reinforced with nanosized fillers, for instance with the carbon nanotubes (CNT). The resulting self-healing effect for these actives is very promising to be tested for oil and gas cementing works [25,26].

3. Microcapsules for Well Completion

Self-healing coating made of non-metallic materials is yet another topic where microcapsules could be of great support. Self-healing functionality can be imparted by the presence of nano/micro containers of polymer and inorganic origin in the coating structure. Self-healing effect could be based on different principle: capsule, vascular and intrinsic. While capsule and vascular types of self-healing rely on the contained adhesive, intrinsic type is inherent withing the material and it could work numerous times since there is no limitation of the encapsulates [27].

Most of the self-healing solutions are made for polymer coatings, they could as well be used for the composite materials such as pipes, casings or liners by incorporating the adhesive-carrying container in the body of the product. Composite materials could also be prepared with the vascular-type network that
can self-repair larger-sized scratches or cracks. The review below highlights the publications that are the most relevant to oil and gas applications.

Significant number of publications were devoted to inducing self-healing properties to the epoxy-based coatings with the help of microcapsules. This material has broad applicability to the oil and gas production as it was presented in the previous part of publication, so making it self-healing could benefit stability of crude resources’ production. The most efficient self-healing actives for oil and gas would be the ones that can react upon exposure to moisture due to the downhole environment. One example of this material could be silyl esters do not require catalysts or cross-linking for polymerization (or solidification) because, in their case, barrier formation is based on the hydrolysis process. Silyl esters show good reactivity with both water and metal; this allows them to form an adhered-to-metal barrier that can prevent corrosive materials from encountering the underlying metal [28]. García et al. fabricated an epoxy matrix composite, wherein 100-μm urea-formaldehyde microcapsules filled with silyl ether were embedded in the epoxy. The results of the impedance and current density measurements obtained in the case of the microcapsule-embedding composite confirmed that it provided for anticorrosion performance as compared to that of the bare samples [29].

Isocyanates represent another excellent candidate for self-healing for epoxy-based products in downhole conditions. As silyl ethers they also react with water and form protective layer on the metal’s surface. The water-friendly properties of the isocyanate group can cause issues during encapsulation in a shell polymer, given its high reactivity. In order to prevent these possible issues, Wu et al. fabricated polyurea/silica hybrid microcapsules for encasing isocyanate-based healing agents by combining interfacial polymerization and an in-situ sol gel process. The hybrid structure of the microcapsules resulted in improvements in the thermal and chemical properties of the microcapsules. As a result, during a corrosion test, wherein the samples were immersed in a 10 wt% NaCl solution for 48 h, the hybrid-microcapsule embedding epoxy resulted in a completely rust-free substrate [30]. Following the same research rout, Sun et al. fabricated 88-μm double-layered polyurea microcapsules. They could successfully encase an isocyanate-based healing agent within microcapsules. The resulting microcapsules demonstrated impressive stability in non-polar solvent as well as when exposed to the elevated temperatures. Both conditions very well represent the environment in the downhole [31].

Another option to induce self-healing to non-metallic coatings and composites is by embedding micro- or nanosized fibers filled with adhesive inside the nonmetallic matrix material. This technological approach is called vascular-type self-healing. The fibers could be made by several methods, one of the most frequently used for nanofibers (NF) synthesis is electrospinning. Electrospinning is the method that allows to fabricate networks of core-shell nano- and microfibers that are filled with enough healing agent. As the example of this technology, core-shell nanofiber coatings were prepared on steel substrate with dimethyl siloxane (DMS) as self-healing agent and dimethyl-methyl hydrogen-siloxane (as curing agent) separately in the cores via the dual emulsion electrospinning method. DMS and dimethyl-methyl hydrogen-siloxane were both encapsulated in polyacrylonitrile (PAN) shells. These dual nanofibers were deposited onto a steel substrate. Finally, the nanofiber mats were intercalated with poly (dimethyl siloxane) (PDMS) matrix. The corrosion experiments that were conducted on the manually damaged nanofiber coating proved the self-healing efficiency and corrosion resistance of these coatings [32].

Apart from emulsion electrospinning method, co-electrospinning was also proved to be an efficient method for fabricating encapsulated nanofiber mats [33]. In co-electrospinning, two syringes were simultaneously used to electrospin the dimethylvinyl-terminated dimethyl siloxane (resin) encapsulated PAN and methylhydrogen dimethyl siloxane (curing agent) encapsulated PAN nanofibers, which were collected by a drum to get intertwined nanofiber mat. This nanofiber mat embedded transparent PDMS coating over steel surface efficiently acted as a corrosion barrier via the healing process by the release of the resin monomer from the fiber cores to heal the corrosion.

Encapsulation of corrosion inhibitors is another approach that can deliver self-healing properties to coatings and composites. This method represents interest to the downhole applications. There is a wide variety of corrosion inhibitors that were tested for this approach, including phosphates, nitrites, molybdates, tungstates, vanadates, borates and rare earth salts and the organic corrosion inhibitors such
as benzotriazole (BTA), mercaptobenzothiazole (MBT), imidazoline, 8-hydroxyquinoline (8-HQ) and aliphatic amines. In this method of self-healing, inhibitors can suppress anodic dissolution and cathodic reactions occurring in the coating. Inhibition of anodic dissolution can be achieved using inhibitors that can passivate the oxide layer of the metal surface. Cathodic reactions are slowed down by inhibitors that precipitate oxide and hydroxide at cathodic sites. There are also mixed-type inhibitors that are composed of many organic molecules. These inhibitors can slow down both the anodic and cathodic corrosion reactions by physical adsorption or a chemical reaction or complexation on metal substrates [34].

One of the recent publications demonstrates the possibility of encapsulating the BTA corrosion inhibitor into the mesoporous silica nanocapsules with the shell made of the highly branched polyethyleneimine (PEI). These nanocapsules demonstrated excellent anti-corrosion performance with induced pH-sensitive release of the active in the epoxy-based coating [35].

4. Microcapsules for Hydraulic Fracturing

Hydraulic fracturing and fracture acidizing are techniques commonly utilized to stimulate the production of oil and gas from subterranean formations of low permeability. In carrying out such techniques, high viscosity gelled aqueous fluids and water-hydrocarbon emulsions have been utilized as fracturing and fracture-acidizing fluids, which can form the suspension of propping agent without excessive settling, and bring about the opening of one or more fractures in the formation to a greater width. Thus, to recover from the formation through the well bore, the fracturing fluid seeps into the formation or back-flows out from the fractures, and it is desirable to utilize a breaker to convert the gel or emulsion to a low viscosity. The microencapsulation of breakers achieves the delayed release of active, which allows the breaker to be temporarily isolated from the fracturing fluid. Thus the breaking system tends to release over a desired period of time, followed by the relatively rapid release of the inner phase, which improves its performance, reduces the residue of the fracturing fluid, and does no harm to the initial viscosity of the fracturing fluid [1]. Many kinds of chemicals have been utilized to fabricate the special microcapsule structure. The most shared core materials are persulfate oxidizers, such as sodium peroxydisulfate and ammonium peroxydisulfate, which can be used at high temperatures.

Zuo et al. developed microcapsules containing water-soluble ammonium persulfate (APS) cores as gel breakers that offer controlled burst release, are become increasingly important in improving the gel breaking efficiency of fracturing fluids in oil fields. To date, microcapsules with various control slow release behaviors have been thoroughly investigated, but microcapsules with burst release properties are rarely studied. Here, we reported a novel inverse emulsion polymerization method to exploit this new type of microcapsule. The encapsulated cores offer controlled burst release from the microcapsules and their beginning time of burst release could be delayed up to 42 h. All the cores could be completely released within 1 h from the microcapsules. The temperature, pH, and salt concentration change could stimulate the release [36].

Ma et al. demonstrate the possibility of encapsulating oxalic acid (OA) using coacervation of ethyl cellulose induced by polydimethylsiloxane method. Oxalic acid-containing microcapsules were used to delay an in-situ exothermic reaction between ammonium chloride (NH4Cl) and sodium nitrite (NaNO2) during hydraulic gel fracturing for oil extraction. The as-prepared OA microcapsules possessed perfect core-shell structures, uniform diameters, tunable sizes, adjustable sustained-release performances, and excellent catalytic performances for in-situ exothermic hydraulic gel fracturing systems [37].

5. Conclusion

In this review it was demonstrated that oil and gas industries could benefit significantly in different areas if they were to be using microencapsulated active materials. As it was described, microcapsules could bring tribological improvement during drilling process, as well as better thermal stability for drilling and cementing at the HPHT conditions. Cementing as well as completion could gain significant value by creating self-healing effect in the cement and non-metallic coatings for production pipes using microcapsules filled with different adhesive materials. Hydraulic fracturing could also go more seamlessly when utilizing microcapsules filled with the gel breaker materials.
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