Microencapsulation for chemical applications

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ABSTRACT: While encapsulation has been used industrially for decades, the public discovered microcapsules only recently. Based on a limited number of technologies, the processes of microencapsulation of chemicals have been very largely patented. Numerous applications have been proposed and developed while many new ones may appear in the next few years. Production may range from a few hundred kilograms for sophisticated applications to thousands of tons for some large scale industrial applications.

INTRODUCTION

Microencapsulation consists of embedding an active substance inside a microparticle. The resulting particle may have a different structure such as a solid sphere, a liquid core surrounded by a membrane, a coated solid core or a hydro gel bead. The purposes of encapsulation are diverse. For examples:

- Immobilisation of volatile materials;
- Isolation of reactive ingredients from the matrix;
- Protection of a fragile component during storage or processing;
- Controlled release over time or upon a trigger;
- Material structuration like conversion of liquid in powder;
- Improvement of powder flowing properties.

In fact, involving encapsulation into a process often results from a combination of such reasons. Different types of active substances enable multiple applications. As a result it leads that microencapsulation processes deriving from a few initial methods have to be adapted for each specific case.

SHORT HISTORY

The first reference to microencapsulation technologies dates back to the late 1800s (1), consisting of coating by spraying a solution onto particles in a rotating pan reactor. The coating was a first highly concentrated sugar, which was later replaced by a polymer solution. To avoid usage of organic solvents, polymer solutions are often replaced by a latex suspension. Complex formulations were developed combining polymers, surfactants, inert filler materials, and plastifiers to get an adequate release profile. For small particles (less than 1 mm), the pan coating has been generally replaced by a fluid bed to insure better mixing of the particles. Different designs have been proposed such as top spray fluid bed or Wurster process (promoting circulation of particle by inserting a central tube in the reactor). This technology has been especially developed in the pharmaceutical domain (2), but a large scale production of microencapsulated chemicals has been allowed by a continuous process. In 1932, spray drying (spraying of a polymer solution in a warm chamber to form small microspheres) has been first sold as a sealed-in volatile flavour in a gum Arabic microsphere (5). When trying to spray dry a fruit juice using isopropanol as a solvent, researchers from Robert and Co detected a strong taste of isopropanol in the resulting powder. They launched further experiments proved that volatile molecules could be entrapped by spray drying. This technology is still largely used in industrial applications, especially for food, but also to produce many other different types of powders. However, many authors consider that the first real industrial application of microencapsulation was initiated in 1954, when the National Cash Register (NCR) introduced the production of microcapsules for the carbonless copy paper. The project was the result of 15 years of research started by Barry Green (3). The first technology for producing liquid core microcapsules was based on coacervation, a phenomenon taking place in colloid systems, where macromolecular colloid rich coacervate droplets surround dispersed microcapsules cores in an emulsion, and form a colloid microcapsule wall, which is then solidified by a cross-linking agent. The main development of NCR carbonless copying paper was based on so-called complex coacervation, combining gelatine and acacia gum colloid solution (4). This process is still largely used today although the use of gelatine is sometimes restricted, and the cross-linking with glutaraldehyde

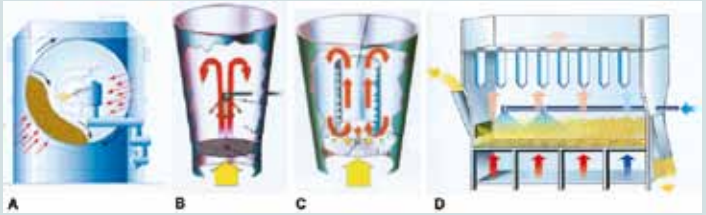

Figure 1. Coating process. A) Pan coater, B) Top spray fluid bed, C) Wurster fluid bed, D) Continuous process (http://www.glatt.de).

is needed to get strong and hard microcapsules. Researchers from du Pont have presented in 1959 at the American Chemical Society meeting a series of papers on interfacial polycondensation (6). These papers remain a key reference and lead to an extensive development of microencapsulation by interfacial polycondensation (7). In a process, two or more monomers polymerise around droplets in an emulsion and form a solid polymeric microcapsules wall. One of the monomers is initially dissolved in the aqueous phase, and the other one in a hydrophobic organic solvent, allowing a polymerisation taking place at the droplet interface. The selection of monomers and working conditions allows to get semi-permeable (also called artificial cells) (8) or impermeable membranes of polyamide, polyester or polyurea. The process was extended and modified to many technological sub-types and chemical variations, such as the *in situ* polymerisation of formaldehyde with either urea or melamin (9), where both monomers or precondensates are added only to the aqueous phase of the emulsion.

Figure 2. Interfacial coacervation process and resulting capsules © D. Poncelet.

During the 1970's, technologies have been developed based on the solvent removal. After a polymer has been dissolved in a volatile organic solvent, the solution is dispersed into an aqueous phase. The organic solvent is removed by extraction or evaporation at atmospheric or reduced pressure, resulting in the solidification of droplets as polymeric microspheres. The method was developed and widely used in the pharmaceutical field. However, the importance and applicability of microencapsulation of chemicals is reducing due to the cost and the problem of solvent toxicity. More recently, technologies emerged based on dripping either from nozzles (10) or through a spinning device (11). Resulting droplets are solidified by cooling of a melt material, or by gelation of the polymer solution (10). The productivity of such processes has increased over years to allow the production of hundreds to thousands tons per year of capsules with a very narrow size distribution.

Figure 3.Dripping processes: A) vibrated nozzles (http://www.brace.de) B) rotating nozzles (http://www.swri.org).

SOME APPLICATIONS OF ENCAPSULATED CHEMICALS

The first important application was the carbonless copy paper. In the typical multiple copy paper form, the back side of a paper (CB) is coated with a microencapsulated leuco dye in an organic solvent (microcapsules are transparent, 5 – 10 µm in diameter). The front side of paper (CF) contains a layer of colour developer. Upon pressure of a pen, microcapsules burst open, leuco dye reacts with the colour developer, and a coloured product a copy is produced by a chemical reaction between the leuco dye and a colour developer. The system has been widely used for example for cash register receipts, official documents, forms, bank mailers, etc. Historically, pressure-sensitive copying papers remain the largest industrial product containing microcapsules. However, the importance of this technology has decreased with the development of computers and fast laser printers.

Figure 4. Carbonless copy paper: A) principle B) example.

Interfacial polymerisation and coacervation have been widely used for agrochemical encapsulation, such as insecticides, fungicides, insect repellents or preservatives, allowing a long-lasting effect or targeted release of active compounds. Interfacial polymerisation has been the main technology for microencapsulation of adhesives or catalysts with a mechanical release. One typical example is the coating of screws with microcapsules containing a glue, allowing a secure sealing of the screw without the need of a ring.


Figure 5. Screw coated with encapsulated glue (blue colour).

Several temperature management systems have been developed with microencapsulated phase change materials. For instance, BASF has developed a microencapsulated paraffinic phase change material to be incorporated in the building walls within the concrete or plaster matrix structure. When temperature increases, the core material melts, absorbing the energy. When the temperature drops, the material solidifies and gives back the stored energy. The heat capacity of a 15 mm panel with such microcapsules provides buffered temperature behaviour equal to a 7 cm concrete. Phase change material microcapsules may also be used in textiles, e.g. for winter clothes and garments for extreme working conditions. Most actives ingredients included in dishwasher or laundry detergents are included in microcapsules, either for their protection or for a controlled release. This is especially important for the enzymes, where the regulations are very strict, particularly regarding the concentration in the air. Major companies, such as DSM or Genencor, sell encapsulated enzymes in production quantities of thousands tons per year.

The structure of the microcapsules became quite complex, with multiple layers containing different active ingredients. Genencor runs the largest plant for microencapsulation consisting of fluid beds with eighty spray nozzles and has developed a processes running for more than 8 hours.
Microcapsules are also incorporated in photographic papers, computer screens and other liquid crystal displays, biosensors, crash detector systems, tooth pasts and cosmetics. The number of applications is increasing every day.

CONCLUSIONS

The number of patents on microcapsules has increased quickly during the last three decades. New inventions are often derivates or improvements of previously described techniques. Microencapsulation became a fashion, a high-tech field and many products are marketed by claiming the use of microcapsules. Several companies, such as IBM, Kodac, BASF, 3M, Rhone-Poulenc, Danisco, DSM, etc. have developed industrial processes and products based on microencapsulation, ranging from a few tons to thousands of tons per year. This contribution could only present an introduction to the large domain of microencapsulation.
For more information, including list of books on microencapsulation, you may consult the Bio encapsulation Research Group web site (http://bioencapsulation.net).

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