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Microencapsulation Technology and Applications

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ABSTRACT

Microencapsulation technology allows a compound to be encapsulated inside a tiny sphere known as microsphere/microcapsule, having an average diameter as small as 1 μm to several hundred micro meters. Many different active materials like drugs, enzymes, vitamins, pesticides, flavours and catalysts have been successfully encapsulated inside microballoons or microcapsules made from a variety of polymeric and non polymeric materials including poly(ethylene glycol)s, poly(methacrylate)s, poly(styrene)s, cellulose, poly(lactide)s, poly(lactide-co-glycolide)s, gelatin and acacia, etc. These microcapsules release their contents at appropriate time by using different release mechanisms, depending on the end use of encapsulated products. This technology has been used in several fields including pharmaceutical, agriculture, food, printing, cosmetic, textile and defence. In defence sector this technology has introduced the concept of self-healing composites as well as chemical decontaminating fabrics. This review paper highlights the major reasons behind microencapsulation, important techniques of microencapsulation and application of microencapsulated products in different areas of science and technology.

Keywords: Microencapsulation technology, microcapsule, release mechanisms, pharmaceuticals, polymers, stabilizers, emulsion

1. INTRODUCTION

Microencapsulation[1] is a technique by which solid, liquid or gaseous active ingredients are packaged within a second material for the purpose of shielding the active ingredient from the surrounding environment. Thus the active ingredient is designated as the core material whereas the surrounding material forms the shell. This technique has been employed in a diverse range of fields from chemicals and pharmaceuticals to cosmetics and printing. For this reason, widespread interest has developed in microencapsulation technology. Preparation of microcapsules dates back to 1950s when Green and Schleicher [2,3] produced microencapsulated dyes by complex coacervation of gelatin and gum arabic, for the manufacture of carbonless copying paper. To this day, carbonless copy paper is one of the most significant products to utilize microencapsulation technology, and is still produced commercially. The technologies developed for carbonless copy paper have led to the development of various microcapsule products in later years.

In the 1960s, microencapsulation of cholesteric liquid crystal by complex coacervation of gelatin and acacia was reported to produce a thermosensitive display material. J. L. Fergason developed nematic curvilinear aligned phase (NCAP), a liquid crystal display system by microencapsulation of nematic liquid crystal[4]. Encapsulation technology has provided the enlargement of display areas and wider viewing angles.

In defence applications this technology is used for fabrication of self-healing composites[5-10] which form an integral part of aerospace structures. Microencapsulation is also used for designing special fabrics for military personnel for their enhanced chemical protection against chemical warfare[11]. Thus, since the mid of 1970s, microencapsulation has become increasingly popular in pharmaceutical industry as well as for many other products and processes in daily use.

2. CLASSIFICATION

Microcapsules can be classified on the basis of their size or morphology.

2.1 Micro/Nanocapsules

Microcapsules range in size from one micron (one thousandth of a mm) to few mm. Some microcapsules whose diameter is in the nanometer range are referred to as nanocapsules to emphasize their smaller size.

2.2 Morphology Microcapsules

Microcapsules can be classified into three basic categories as monocored, polycored and matrix types as shown in Fig. 1. Monocored microcapsules have a single hollow chamber within the capsule. The polycore microcapsules have a number of different sized chambers within the shell. The matrix type microparticle has the active ingredients integrated within the matrix of the shell material. However, the morphology of the internal structure of a microparticle depends largely on the selected shell materials and the microencapsulation methods that are employed.

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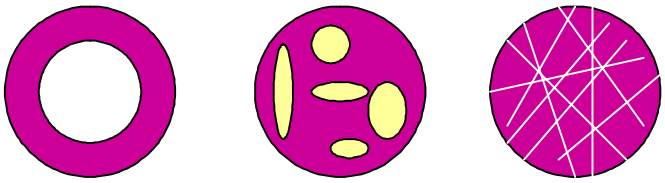


Figure 1. Different types of microcapsules.

3. IMPORTANT FEATURE OF MICROCAPSULES

The most significant feature of microcapsules is their microscopic size that allows for a huge surface area, for example, the total surface area of 1μm of hollow microcapsules having a diameter of 0.1 μm has been reported to be about 60 m^2. The total surface area is inversely proportional to the diameter. This large surface area is available for sites of adsorption and desorption, chemical reactions, light scattering, etc. More detailed features of microcapsules are summarised in books by Gutcho[12] and Arshady[13].

4. REASONS FOR MICROENCAPSULATION

Microencapsulation of materials is resorted to ensure that the encapsulated material reaches the area of action without getting adversely affected by the environment through which it passes. Amongst the principal reasons for encapsulation are:

1. Separation of incompatible components
2. Conversion of liquids to free flowing solids
3. Increased stability (protection of the encapsulated materials against oxidation or deactivation due to reaction in the environment)
4. Masking of odour, taste and activity of encapsulated materials
5. Protection of the immediate environment
6. Controlled release of active compounds (sustained or delayed release)
7. Targeted release of encapsulated materials

5. TECHNIQUES OF MICROENCAPSULATION

Although a variety of techniques have been reported for microencapsulation [14-24], they can broadly be divided into two main categories (Table 1)[25-83]. The first category includes those methods in which starting materials are monomers/prepolymers. In these methods chemical reactions are also involved along with microsphere formation. The second category consists of those methods in which starting materials are polymers. Hence, in these methods no chemical reactions are involved and only shape fabrication takes

Table 1. Major Microencapsulation methods

Microencapsulation methods	Materials Investigated Shell[core]	Applications	Refere-nces
Chemical methods			
Suspension Polymerization	Poly(styrene)[PCM]	Textile	25, 26
Emulsion Polymerization	Poly(alkyl acrylate)s[insulin]	Drug delivery	27, 28
Dispersion	Poly(2-hydroxyethyl-co-glycidyl methacrylate)[ferrofluid] , Poly (N-vinyl α-phenylalanine)[fluorescein isothiocyanate]	Biosciences	29, 30
Interfacial	Polyurea[insecticides, catalysts], Polyamide[oils], Polyurethane [insecticides], polyester[protein]	Crop protection, Catalysis, drug delivery	31-49
Physical/Mechanical methods			
Suspension crosslinking	Protein, Albumin[doxorubicin, magnetite], Polysaccharides	Drug delivery	50-52
Solvent evaporation/extraction	Poly(Lactide),Poly(Lactide-co-glycolide) [Drugs]	Drug delivery	53-61
Coacervation/phase separation	Protein, Polysaccharides, Ethyl cellulose, gelatin[Drugs]	Drug delivery	62-66
Spray drying	Polymers[Food ingredients]	Food Technology	67-70
Fluidized bed coating	Gelatin, carbohydrates, lipids	Food Technology	71-73
Melt solidification	Polyanhydride[insulin]	Food Technology	74
Precipitation	Phenolic polymers [enzymes]	Biocatalysis	75
Co-extrusion	Polyacrylonitrile[hepatocytes]	Biomedical	76, 77
Layer by Layer deposition	Polyelectrolytes[organic compounds]	Biosensor	78,79
Microencapsulation methods	Materials Investigated Shell[core]	Applications	Refere-nces
Supercritical fluid expansion	Poly(ethylene glycol)[felodipine]	Drug delivery	80, 81
Spinning disk	Paraffin	Food engineering	82, 83

place.

Generally the choice of the microencapsulation method depends on the nature of the polymeric/monomeric material used. Thus appropriate combination of starting materials and synthesis methods can be chosen to produce microencapsulated products with a wide variety of compositional and morphological characteristics. For example, poly (alkyl cyanoacrylate) nanocapsules are obtained by emulsion polymerisation[27], whereas reservoir type nylon microcapsules are usually prepared by interfacial polymerisation[48-49]. Similarly albumin microcapsules are prepared by suspension crosslinking[51], polylactide microcapsules by solvent evaporation/solvent extraction[53] and gelatin and related products by coacervation[63]. Some of the important and most common microencapsulation techniques are discussed in detail below.

5.1 Emulsion polymerisation

According to this technique[28] the monomer (alkyl acrylates) is added dropwise to the stirred aqueous polymerisation medium containing the material to be encapsulated (core material) and a suitable emulsifier. The polymerisation begins and initially produced polymer molecules precipitate in the aqueous medium to form primary nuclei. As the polymerisation proceeds, these nuclei grow gradually and simultaneously entrap the core material to form the final microcapsules. Generally lipophilic materials (insoluble or scarcely soluble in water) are more suitable for encapsulation by this technique. Insulin loaded poly (alkyl cyanoacrylate) nanocapsules[27] have been synthesised by using this technique. In addition to the entrapment of drug during microcapsule formation, drug loading can also be accomplished by incubation of cyanoacrylate nanocapsules (empty nanocapsules) with the dissolved or finely dispersed drug.

5.2 Interfacial polycondensation

As the term "interfacial" implies, this technique involves the polycondensation (condensation polymerization) of two complementary monomers at the interface of a two phase system [31-34]. For the preparation of microcapsules, this two-phase system is mixed under carefully-controlled conditions to form small droplets of one phase (dispersed phase) in the other one (continuous phase/suspension medium). The material to be encapsulated must be chosen in such a way as to be present (dissolved or dispersed) in the droplets. It is also necessary to use a small amount of a suitable stabilizer to prevent droplet coalescence or particle coagulation during the polycondensation process and capsule formation. Interfacial polycondensation can be utilized to produce both monocore type or matrix type microcapsules, depending on the solubility of the polycondensate in the droplet phase. The two basic mechanisms leading to the formation of both types of microcapsules are schematically depicted in Fig. 2[84]. Thus if the polymer is soluble in the droplets, matrix type microcapsules are formed. On the other hand, if the polymer is not soluble, it precipitates around the droplets and leads to the formation of monocore type microcapsules. Preparation of microcapsules

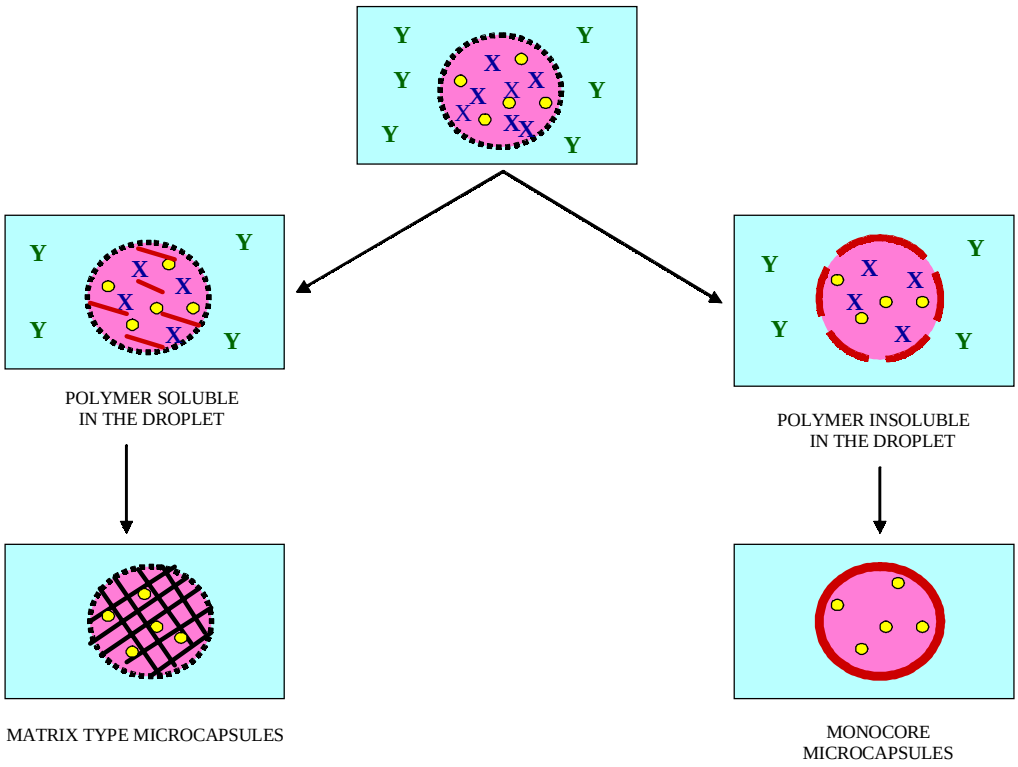


Figure 2. Mechanism of matrix type or monocore type microcapsule formation by interfacial polymerization (X and Y are bifunctional monomers).

by interfacial polycondensation is applicable to a large number of polymers including polyamides [35-37], polyureas [38-41], polyurethanes[42-45] and polyesters [46,47]. In either case, the process can be adopted to produce micrometer or nanometer size particles. Polyurea microcapsules encapsulating osmium tetroxide have been synthesised by using this technique[39].

5.3 Suspension crosslinking

Suspension crosslinking is the method of choice for the preparation of protein and polysaccharide micro-capsules[50,51]. Microcapsule formation by this technique involves dispersion of an aqueous solution of the polymer containing core material in an immiscible organic solvent (suspension/dispersion medium) in the form of small droplets. The suspension medium contains a suitable stabilizer to maintain the individuality of the droplet/microcapsules. The droplets are subsequently hardened by covalent crosslinking and are directly converted to the corresponding microcapsules. The crosslinking process is accomplished either thermally (at >500 C) or by the use of a crosslinking agent (formaldehyde, terephthaloyl chloride, etc). Suspension crosslinking is a versatile method and can be adopted for microencapsulation of soluble, insoluble, liquid or solid materials, and for the production of both micro and nanocapsules. Albumin nanocapsules containing doxorubicin and magnetite particles have been synthesised by using this technique[52].

5.4 Solvent Evaporation/Solvent Extraction

Microcapsule formation by solvent evaporation/solvent extraction [53-60] is very similar to suspension crosslinking, but in this case the polymer is usually hydrophobic polyester.

The polymer is dissolved in a water immiscible volatile organic solvent like dichloromethane or chloroform, into which the core material is also dissolved or dispersed. The resulting solution is added dropwise to a stirring aqueous solution having a suitable stabilizer like poly (vinyl alcohol) or polyvinylpyrrolidone, etc. to form small polymer droplets containing encapsulated material. With time, the droplets are hardened to produce the corresponding polymer microcapsules. This hardening process is accomplished by the removal of the solvent from the polymer droplets either by solvent evaporation (by heat or reduced pressure), or by solvent extraction (with a third liquid which is a precipitant for the polymer and miscible with both water and solvent). Solvent extraction produces microcapsules with higher porosities than those obtained by solvent evaporation. Figure 3 shows a schematic representation of microencapsulation by solvent evaporation technique. Solvent evaporation/extraction processes is suitable for the preparation of drug loaded microcapsules based on the biodegradable polyesters such as polylactide, poly (lactide-co-glycolide) and polyhydroxybutyrate[61].

5.5 Coacervation/Phase separation

Coacervation [62] (or phase separation) is widely employed for the preparation of gelatin[63,64] and gelatin-acacia[65] microcapsules, as well as for a large number of products

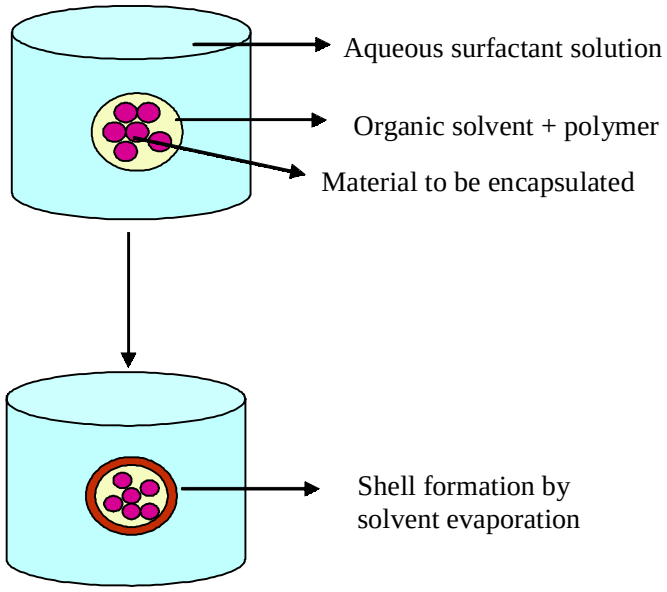


Figure 3. Schematic representation of microencapsulation by solvent evaporation technique.

based on cellulose derivatives and synthetic polymers[66]. Phase separation processes are divided into simple and complex coacervation. Simple coacervation involves the use of a single polymer such as gelatin or ethyl cellulose, in aqueous or organic media, respectively. Complex coacervation involves two oppositely charged polymeric materials such as gelatin and acacia, both of which are soluble in aqueous media. In both the cases, coacervation is brought about by gradual desolvation of the fully solvated polymer molecules. Microencapsulation by coacervation is carried out by preparing an aqueous polymer solution (1-10 %) at 40-50 °C into which the core material (hydrophobic) is also dispersed. A suitable stabilizer may also be added to the mixture to maintain the individuality of the final microcapsules. A suitable desolvating agent (coacervating agent) is gradually introduced to the mixture, which leads to the formation of partially desolvated polymer molecules, and hence their precipitation on the surface of the core particles. The coacervation mixture is cooled to about 5-20 °C, followed by the addition of a crosslinking agent to harden the microcapsule wall formed around the core particles. Gelatin microcapsules loaded with carboquone[64] as well as gelatin acacia microcapsules loaded with sulfamethoxazole[65] have been produced by coacervation.

5.6 Other Techniques

In addition to the microencapsulation techniques described above, microencapsulation can also be carried out by spray drying[67-70], fluidised bed coating[71-73], melt solidification[74], polymer precipitation[75], co-extrusion[76, 77], layer-by-layer deposition[78, 79], supercritical fluid expansion[80,81], and spinning disk[82,83].

Microencapsulation by spray drying is a low cost commercial process, which is mostly used for the encapsulation of fragrances, oils and flavors. In this process, an emulsion

is prepared by dispersing the core material, usually an oil or active ingredient immiscible with water, into a concentrated solution of wall material. The resultant emulsion is atomized into a spray of droplets by pumping the slurry through a rotating disc into the heated compartment of a spray drier. There the water portion of emulsion is evaporated, yielding dried capsules containing core material. Lycopene has been microencapsulated inside gelatin microcapsules by using this technique[70].

Fluidised bed coating[71-73] is used for encapsulation of solid core materials including liquids absorbed into porous solids. This technique is used extensively to encapsulate pharmaceuticals. Solid particles to be encapsulated are suspended in a jet of air and then covered by a spray of liquid coating material. The capsules are then moved to an area where their shells are solidified by cooling or solvent vaporization. The process of suspending, spraying and cooling is repeated until the capsule walls are of the desired thickness. Ascorbic acid has been microencapsulated in polymethacrylate as well as ethyl cellulose by using this technique[72].

Biodegradable microcapsules are also produced by the solidification of molten polymer droplets[74] or by polymer precipitation[75]. A dispersion of the drug in molten polymer is stirred in silicone oil to produce small droplets of the polymer drug mixture. The suspension mixture is then cooled, and the resulting solidified microcapsules are separated from the oil. Insulin has been microencapsulated in polyanhydride[74] by using this technique. In the polymer precipitation process, an aqueous solution of the polymer containing the drug is dropped into a stirred solution, which acts as the precipitating medium. Here, the polymer droplets precipitate immediately and are thus converted into the drug loaded microcapsules. Enzymes have been encapsulated in conjugated phenolic polymers by using this technique[75].

The co-extrusion process[76,77] also possess a number of commercial applications. In this process a dual fluid stream of liquid core and shell materials is pumped through concentric tubes and forms droplets under the influence of vibration. The shell is then hardened by chemical crosslinking, cooling or solvent evaporation. Hepatocytes have been encapsulated in polyacrylonitrile[77] by using this technique.

One important method of microencapsulation is layer-by-layer deposition [78,79]. In this process polyelectrolyte multilayers are prepared by sequentially immersing a substrate in positively and negatively charged polyelectrolyte solutions in a cyclic procedure. Core shell particles with tailored size and properties are prepared using colloidal particles as the core material that serves as a template onto which multilayers are fabricated. Hollow capsules of organic, inorganic or hybrid particles can be obtained by dissolving the core material. This technique is both versatile and simple, with the multiplayer film thickness being controlled precisely by varying the total number of layers deposited. In this way the final properties can be tuned. Glucose oxidase has been microencapsulated by alternate deposition of polyallylamine and polystyrene sulfonate layers[78].

Microencapsulation has also been carried out by rapid expansion of supercritical fluid[80,81]. Supercritical fluids are highly compressed gases that possess several advantageous properties of both liquids and gases. Most widely used ones are supercritical CO_2, alkanes (C_2 to C_4) and nitrous oxide (N_2O). Supercritical CO_2 is widely used for its low critical temperature value in addition to its non-toxic and non-flammable properties. It is also readily available, highly pure and cost effective. It has found applications in encapsulating active ingredients by polymers. Different core materials such as pesticides, pigments, pharmaceutical ingredients, vitamins, flavors and dyes have been encapsulated by using this method. A wide variety of shell materials that either dissolve (paraffin wax, acrylates, polyethylene glycol) or do not dissolve (proteins, polysaccharides) in supercritical CO_2 are used for encapsulating core substances. In this process, supercritical fluid containing the active ingredient and the shell material are maintained at high pressure and then released at atmospheric pressure through a small nozzle. The sudden drop in pressure causes desolvation of the shell material, which is then deposited around the active ingredient (core) and forms a coating layer. Felodipine has been encapsulated in poly(ethylene glycol) by using this technique[81].

In the spinning disc[82,83] method the microencapsulation of suspended core materials is carried out by using a rotating disc. Suspensions of core particles in liquid shell material are poured into a rotating disc and due to the spinning action of the disc, the core particles become coated with the shell material. The coated particles along with the excess shell material are then cast from the edge of the disc by centrifugal force, after which the shell material is solidified by external means (usually cooling). This technology is rapid, cost effective, simple and has high production efficiencies. Paraffin microbeads have been synthesized by using this technique[82].

6. RELEASE MECHANISMS

Different release mechanisms of encapsulated materials provide controlled, sustained or targeted release of core material. Generally there are three different mechanisms by which the core material is released from a microcapsule - mechanical rupture of the capsule wall, dissolution or melting of the wall, and diffusion through the wall. Less common release mechanisms include ablation (slow erosion of the shell) and biodegradation. The release mechanism depends on the nature of application, for example, carbonless copy paper, scratch and sniff perfumes, and self healing structures rely on mechanical rupture of shell to release the core contents. The rupture may be caused by pressure as in case of carbonless copy paper and scratch and sniff perfumes or due to propagation of cracks as for self-healing structures. In the self-healing structures microcapsules act as means of storing and delivering an *in situ* glue, to prevent the spread of cracks. Thus a microencapsulated healing agent and a catalyst known to trigger polymerization in the chosen agent is embedded in a composite matrix. Rupture of any

microcapsules by an approaching crack defect releases the healing agent into the crack plane by capillary action. When the released healing agent comes in contact with the catalyst, the resulting polymerization bonds the crack face closed, stopping the defect in its track. For example urea formaldehyde microencapsulated dicyclopentadiene (DCPD) healing agent and Grubb's Ru catalyst have been incorporated into an epoxy matrix to produce a polymer composite capable of self healing [85].

Detergent industry utilises dissolution of shell wall of powder detergents for release of encapsulated protease enzyme in order to remove bloodstains from the clothing. In food industry baking mixes encapsulated in fat are released after shell melting (when proper temperature is reached) to react with food acid to produce leavening agents, which gives baked goods their volume and lightness of texture. In food industry some ingredients such as nutrients are encapsulated to mask taste, and flavorings are encapsulated due to their volatile nature, that would other wise evaporate out and be lost as in chewing gum.

Pesticides are microencapsulated to be released over time, allowing farmers to apply the pesticides less often rather than requiring very highly concentrated and toxic initial applications. Similarly, in pharmaceutical industry microencapsulated products are designed for sustained/ controlled release by either biodegradation of the shell, or by diffusion through the shell. Aspirin, for example provides effective relief from fever, inflammation and arthritis, but direct doses of aspirin can cause peptic ulcers and bleeding. The drug is, therefore, encapsulated in ethyl cellulose or hydroxypropylmethyl cellulose and starch. In this way the aspirin diffuses through the shell in a slow, sustained dose rather than being released all at once. Insulin has also been encapsulated in biodegradable polylactic acid microcapsules for its controlled release into the body[86].

One of the important diffusion controlled defence application is novel clothing fabric, which contains microcapsules composed of chemical decontaminants encapsulated within semipermeable polymers. The polymer being selectively permeable to toxic chemical agents but impermeable to the decontaminating agents, thereby allowing the toxic chemicals to diffuse into the microcapsules where they undergo irreversible detoxifying chemical reactions[11].

7. APPLICATIONS

7.1 Agriculture

One of the most important applications of microencapsulated products is in the area of crop protection[87-93]. Nowadays insect pheromones are becoming viable as a biorational alternative to conventional hard pesticides. Specifically, sex-attractant pheromones can reduce insect populations by disrupting their mating process. Hence small amounts of species- specific pheromone are dispersed during the mating season, raising the background level of pheromone to the point where it hides the pheromone plume released by its female mate[91,93]. Polymer microcapsules, polyurea[92], gelatin and gum arabic[93] serve as efficient delivery vehicles to deliver the pheromone by spraying the capsule dispersion. Further, encapsulation protects the pheromone from oxidation and light during storage and release.

7.2 Pharmaceutics

One of the major applications area of encapsulation technique is pharmaceutical/ biomedical for controlled/sustained drug delivery[94-103]. Potential applications of this drug delivery system are replacement of therapeutic agents (not taken orally today like insulin)[104,105], gene therapy[106-109] and in use of vaccines for treating AIDS[110-112], tumors[113,114], cancer[115] and diabetes[116-118]. Protein such as insulin, growth hormone[119,120], and erythropoietin[121,122] (used to treat anemia) are example of drugs that would benefit from this new form of oral delivery. The delivery of corrective gene sequences in the form of plasmid DNA[123] could provide convenient therapy for a number of genetic diseases such as cystic fibrosis[124,125] and hemophilia[126]. The spheres are engineered to stick tightly to and even penetrate linings in the gastrointestinal track before transferring their contents over time into circulatory system[127].

Based on this novel drug delivery technique, Lupin has already launched in the market worlds first Cephalexin (Ceff-ER) and Cefadroxil (Odoxil OD) antibiotic tablets for treatment of bacterial infections. Aspirin controlled release version ZORprin CR tablets are used for relieving arthritis symptoms. Quinidine gluconate CR tablets are used for treating and preventing abnormal heart rhythms. Niaspan CR tablet is used for improving cholesterol levels and thus reducing the risk for a heart attack. Glucotrol (Glipizide SR) is an anti diabetic medicine used to control high blood pressure.

7.3 Food Industry

Currently there is a trend towards a healthier way of living, which includes a growing awareness by consumers for what they eat and what benefits certain ingredients have in maintaining good health. Preventing illness by diet is a unique offering of innovative so called "functional foods", many of which are augmented with ingredients to promote health. However simply adding ingredients to food products to improve nutritional value can compromise their taste, colour, texture and aroma. Sometimes they slowly degrade and lose their activity, or become hazardous by oxidation reactions. Ingredients can also react with components present in the food system, which may limit bioavailability. Microencapsulation is used to overcome all these challenges by providing viable texture blending, appealing aroma release, and taste, odour and colour masking [128-133]. The technology enables food companies to incorporate minerals, vitamins, flavours and essential oils. In addition, microencapsulation can simplify the food manufacturing process by converting liquids to solid powder, decreasing production costs by allowing batch processing using low cost, powder handling equipment. Microcapsules also help fragile and sensitive

materials survive processing and packaging conditions and stabilize the shelf life of the active ingredient[134].

7.4 Energy Generation

Hollow plastic microspheres loaded with gaseous deuterium (a fusion fuel) are used to harness nuclear fusion for producing electrical energy[135]. The capsules are multilayered. The inner layer, which compresses the fuel, is a polystyrene shell about 3 μm thick. Next is a layer of poly(vinyl alcohol) about 3 μm thick, that retards diffusion of deuterium out of the capsule. The outer layer (the ablator) is about 50 μm thick and consists of a highly crosslinked polymer made from 2-butene. During the fusion experiments, energy from high powered laser beams is absorbed by the surface of the microcapsule shell. As the outside of the shell (called ablator) burns off, the reaction force accelerates the rest of the shell inward, compressing and heating the deuterium inside. This results in high densities and temperature in the centre of the capsule leading to the fusion of deuterium nuclei to give tritium, helium and other particles releasing an enormous amount of energy. This process has been named as inertial confinement fusion (ICF). Such ICF targets made of organic microcapsules have been in use since 1980s.

7.5 Catalysis

Transition metal based catalytic processes are of vital importance to pharmaceutical, agrochemical and fine chemical industries. A vast proportion of such catalytic metal species are often expensive and toxic, thereby making operational handling potentially hazardous. Microencapsulation has recently been recognized as a useful alternative strategy to enable safe handling, easy recovery, reuse and disposal at an acceptable economic cost. Polyurea microcapsules due to their insolubility in aqueous and organic solvents, and resistance towards degradation have been used for encapsulation of different catalysts. Metal species such as palladium (II) acetate and osmium tetroxide have been encapsulated in polyurea microcapsules and used successfully as recoverable and reusable catalysts without significant leaching and loss of activity[39,40]. It is thought that the urea functionality, which forms the backbone of the polymer, ligates and retains the metal species with in the polymeric matrix. Futuristic trend is towards incorporation of other chelating and ligating functional groups within the polyurea framework to study rate enhancement in such reactions, and trying other polymers for encapsulation.

7.6 Defence

One of the important defence applications of microencapsulation technology is in self-healing polymers and composites[136-142]. They possess microencapsulated healing agents embedded within the matrix and offer tremendous potential for providing long-lived structural materials. The microcapsules in self-healing polymers not only store the healing agent during quiescent states, but provide a mechanical trigger for the self-healing process when damage occurs in the host material and the capsules rupture. The microcapsules posses sufficient strength to remain intact during processing of the host polymer, yet rupture when the polymer is damaged. High bond strength to the host polymer combined with a moderate strength microcapsule shell are required. To provide long shelf life the capsules must be impervious to leakage and diffusion of the encapsulated healing agent for considerable time. These combined characteristics are achieved with a system based on the *in situ* polymerisation of urea-formaldehyde microcapsules encapsulating dicyclopentadiene healing agent[143]. The addition of these microcapsules to an epoxy matrix also provides a unique toughening mechanism for the composite system. Such microcapsules have tremendous application in aerospace area for making self-repairable spacecrafts. Such self-healing spacecrafts open up the possibility of longer duration missions by increasing the lifetime of a spacecraft.

Microencapsulation is also used for designing special fabrics for military personnel, for their enhanced chemical protection against chemical warfare[11]. For this purpose special reactive microcapsules have been developed which can be applied to fabrics or finished garments to provide reactive sites for neutralisation of chemical reagents. This involves microencapsulation of conventional decontamination chemicals that are currently effective for deactivation of toxic mustard blistering agents (H agents) and toxic nerve agents known conventionally as G agents, for example isopropylmethyl phosphonofluoridate (GB, sarin) and the V agents, and formulation of the microcapsules in a resin finish that can be uniformly applied to fabric substrates. The preffered microcapsules containing a decontaminating agent were obtained by organic phase separation with ethyl cellulose microcapsules containing a solid decontamination agent consisting of sym-bis (N-chloro-2,4,6-trichlorophenyl) urea and *ZnO*. The microcapsules were then bonded to the fabric with an acrylic binder emulsion. The very thin walls (1 to 10 microns) of microcapsules allow for rapid agent permeation for optimum decontamination and thus protect the wearer from toxic chemical agents.

8. STATUS OF MICROENCAPSULATION RESEARCH IN DMSRDE

Defence Materials and Stores Research and Development Establishment, Kanpur is actively working in this area since last four years and has developed expertise in microencapsulation technology by using two techniques. One is solvent evaporation and the other one is interfacial polymerisation. Characterisation of all the synthesised microcapsules was done by using optical microscope (OM, Leica) and scanning electron microscope (SEM, Zeiss).

Polymethylmethacrylate (PMMA) was selected as the polymer for encapsulation using solvent evaporation technique. Different materials like carbon nanotubes (CNTs), polyaniline, carbon microcoils (CMCs) and magnetic nanoparticles have been successfully encapsulated inside PMMA microcapsules. In a typical synthesis for encapsulation of polyaniline,

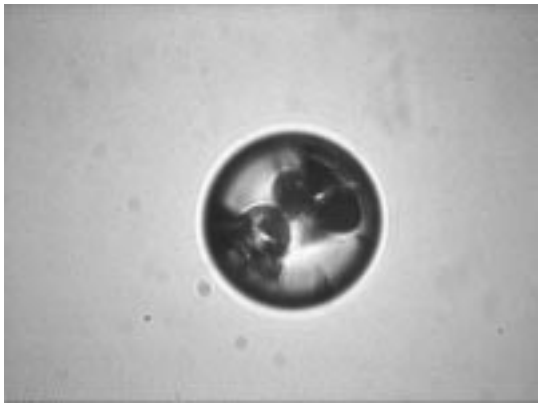
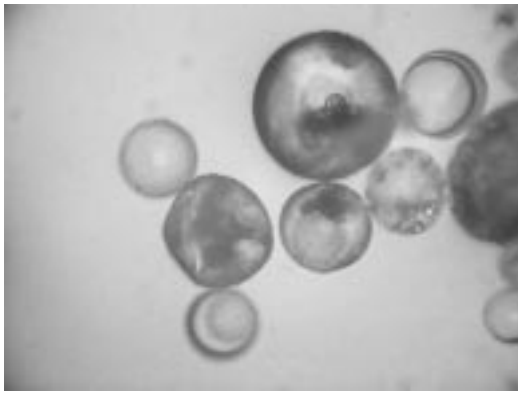
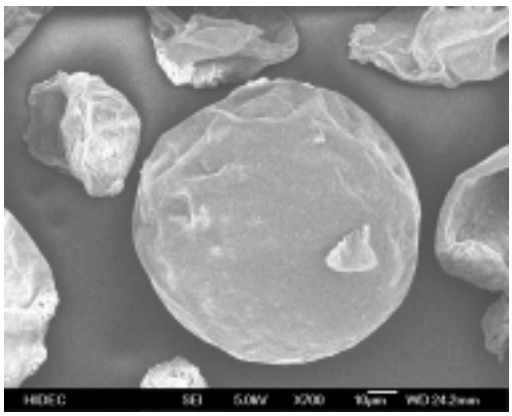


Figure 4. Optical micrograph of polyaniline encapsulated PMMA microcapsule.

PMMA was first dissolved in a low boiling solvent like dichloromethane/chloroform with the help of magnetic stirring. Polyaniline was added into the stirring solution. This solution was then added dropwise to a stirring emulsifier (polyvinyl alcohol/polyvinyl pyrrolidone) solution. The mixture was kept stirring till the evaporation of the solvent. After that, the polyaniline encapsulated PMMA microcapsules were collected by filtration, washed with water and dried. Figure 4 shows the optical micrograph of polyaniline encapsulated PMMA microcapsules. The formation of microcapsule is clearly evident from the micrograph. A perfect sphere is seen with the presence of green polyaniline inside the sphere. Using the same procedure microencapsulation of other materials was also carried out.



(a)



(b)

Figure 5. Optical (a) and SEM (b) micrographs of ferrofluid coated *ZnO* nanoparticles encapsulated polyamide microcapsules.

For microencapsulation of materials by utilising interfacial polymerisation technique, polyamide was selected as the polymer. Two types of materials, ferrofluid coated *ZnO* nanostructures and ferrofluid were encapsulated inside the polyamide microcapsules. For carrying out the microencapsulation, terephthaloyl chloride was dissolved in toluene followed by addition of the core material. This mixture was then added dropwise to a stirring polyvinyl alcohol emulsifier solution. After 15 min. the diamine/triamine monomer diluted with water was added to initiate the polymerisation. Few drops of *NaOH* solution was added, which acts as acid scavenger and neutralises the liberated HCl. The reaction was complete within 4 to5 h. After completion of reaction the microcapsules were filtered, washed with water and freeze dried. The optical and SEM micrographs (Fig. 5) show clearly the presence of material inside the microcapsules as well as the formation of spherical microcapsules respectively. In addition to carrying out the microencapsulation of various materials inside polyamide microcapsules, hollow polyamide microcapsules were also synthesized by using the same technique of interfacial polymerisation[144].

9. CONCLUSIONS

The research in the area of microencapsulation has huge potential to give raw materials advantageous traits resulting in superior products. Periodically new developments in this area have led to new products, e.g. the first remarkable product was carbonless copy paper, the second was controlled release of drugs. At present, paper-like displays, self- healing structures and chemical decontaminating fabrics are receiving much attention.

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