Graphical Abstract

MICROPLASTIC

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Microplastic label in microencapsulation field
- consequence of shell material selection

Highlights

- MOFs provide CECs removal with high efficiency
- Incorporating MOFs into functional materials extends their application in CECs elimination
- MOFs as adsorbents, catalysts, membrane precursors can be considered in separation

Microplastic label in microencapsulation field - consequence of shell material selection

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KEYWORDS

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ABSTRACT

Plastics make our lives easier in many ways; however, if they are not appropriately disposed of or recycled, they may end up in the environment where they stay for centuries and degrade into smaller and smaller pieces, called microplastics. Each year approximately 42000 tonnes of microplastics end up in the environment when products containing them are used. According to the European Chemicals Agency (ECHA) one of the significant sources of microplastics are microcapsules formulated in home care and consumer care products. As part of the EU's plastics strategy, ECHA has proposed new regulations to ban intentionally added microplastics starting from 2022. It means that the current cross-linked microcapsules widely applied in consumer goods must be transformed into biodegradable shell capsules. The aim of this review is to provide the readers with a comprehensive and in-depth understanding of recent developments in the art of microencapsulation. Thus, considering the chemical structure of the capsule shell’s materials, we discuss whether microcapsules should also be categorized as microplastic and therefore, feared and avoided or whether they should be used despite the persisting concern.

Introduction

Plastics have become part of everyday human life for good. It is difficult to imagine life without them, not only in the broadly defined economy, but also in household uses which will be considered in more detail in this paper. Their wide use forces us to take great care in disposing of them properly or to replace them with more friendly solutions. Otherwise, they can be released into the environment and, owing to their durability, they can persist there, fragmented into smaller and smaller pieces down to the micrometre range [1]. These small pieces, called microplastics, are a significant ecological problem. On the other hand, the same small plastic particles can be deliberately produced, for example, in personal care and cosmetic products (PCCPs) as plastic glitters used in cosmetics for decoration purposes (nail art), exfoliating beads in body and facial scrubs, microbeads in toothpaste, hair shampoo, facial cleaner, shower gel [2–6] or household cleaners. [7,8] These intentionally added plastic particles are treated as primary sources, while those formed as a result of disintegration of larger pieces of polymers, e.g. from plastic packaging, bottles or bags, are treated as secondary sources (**Error! Reference source not found.Error! Reference source not found.**). Textiles made of synthetic fibres are a source of microplastics which can be found in the sewage sludge from household laundry and laundry dryers of clothing. [9–11] Studies have indicated that these fibres are one of the main sources of main microplastics in the environment (up to 35% of the global release into the oceans). [12] However, it is estimated that most microplastics in the environment originate from secondary sources. [7] Considerations of which aspects of microplastics (type of polymer, molecular structure, possible additives, physico-chemico-biological interactions and size) are mainly responsible for their deleterious effects remain inconclusive. [13] This issue is no longer considered only within the scientific community, [14–16] but is increasingly gaining public awareness. Microplastic is already a keyword that people associate with a health and life threat. However, it should be noted that the impact on the environment depends on the biodegradability of plastic. This issue will be discussed in more detail further in this paper.

Many years of research have clearly illustrated the problem of accumulation of microplastics from different sources in the environment, [17,18] including aquatic [19–22] and the less discussed terrestrial [23,24] and air [10,25] ecosystems (**Error! Reference source not found.**). It should be noted that these ecosystems cannot be treated separately. It is estimated that 80% of the microplastic pollution in the oceans comes from the land, mainly *via* rivers. [18] For example, it is assessed that between 1 and 4,200 kg of plastic waste per day is transported into the oceans *via* inland rivers (Hilo, Hi and Danube River, respectively) [21]. At the same time, research has shown that microplastic is also introduced into the environment with organic fertilizers from fermentation and composting of bio-waste, widely used in agriculture and horticulture. [26] Moreover, literature reports indicate that, as the size of microplastic particles decreases owing to degradation or as the intended effect in the production cycle, their presence and potential to accumulate in the food chain increases (**Error! Reference source not found.**). This means that microplastic is present in a variety of living organisms, including freshwater invertebrates, [27] fish, [20] penguins, [28] as well as plants. [29] In addition, recent literature reports indicate that the use of plastic food packaging can be the source of microplastics in human bodies. [30] As was presented by Li *et al.*,[31] such exposure may even occur in infants through consumption of food prepared in specialized polypropylene (PP) feeding bottles for infants. Studies have shown that the release of PP can reach 16.2 million particles per litre, and depends, among others, on how the bottle is sterilized. The examples presented clearly show that microplastics are virtually everywhere, from remote, uninhabited places to the water we drink and the food we eat, and finally the air we breathe. It is also worth noting that organic and inorganic contaminants can be adsorbed on the surface of plastic. [19,32–35] Therefore, microplastic can also be responsible for the transmission of pollutants in an ecosystem.

Figure 1

All these aspects are a reflection of the omnipresence of plastic and microplastic. Thus, is proper management of plastic waste a recipe for solving the problem of microplastic? Certainly, to a large extent, yes. A suitable waste management structure with expanded recovery systems and extended producer responsibility is crucial. Is it enough? Certainly not. Undoubtedly, it is correct to reduce the use of plastics from the secondary sources by, for example, minimizing the use of plastic bags in favour of durable textiles, and from the primary sources, by replacing plastic additives with their degradable substitutes. [13] This requires a high level of awareness among both manufacturers and consumers. The "microplastic-free formula" label, which is appearing more and more frequently on the PCCP packaging, clearly shows the increasing importance of the problem. Scientific innovation, new concepts and growing concern for the environment are the key to overcoming this crisis. It is, therefore, necessary to consider whether microcapsules, proposed for several years now in personal care and cosmetic products, as well as cleaner products, are the best available solution to this challenge.

The aim of this work was to discuss whether microcapsules should also be categorized as microplastic, and therefore, feared and avoided, or whether they should be used despite the persisting concern.

Figure 2

Microcapsule and encapsulation technologies

The encapsulation technology (ET), protected and commercialized in 1956 by Dr Green and Dr Schleicher from the National Cash Register Company (Ohio, USA, US patent 2,730,457 [36]) is considered as one of the most interdisciplinary technologies invented in the last decades.[37] As shown in **Error! Reference source not found.**, the capsule is a small particle, which holds an active material surrounded by a shell (also called membrane, wall or coating). Depending on the morphology designed, capsules can be subcategorized as continuous shells/core capsules (**Error!**

Reference source not found.a), continuous core capsules with more than one layer of the capsule wall material (**Error! Reference source not found.**b), polycore capsules (**Error! Reference source not found.**c) or matrix capsules (also called spheres) (**Error! Reference source not found.**d). [38]

Figure 3

By selecting a suitable method of capsule preparation, such as: interfacial polymerization, *in situ* polymerization, coacervation, Layer by Layer, sol-gel encapsulation, suspension cross-linking, spray dryer, co-extrusion, phase inversion precipitation, capsules with different diameters can be manufactured as shown in **Error! Reference source not found.**. Capsules with a diameter of 1 nm to < 1 µm are called nanocapsules, those with a size ranging between 1 µm and < 1 mm are called microcapsules, while larger ones (≥ 1 mm) are called macrocapsules, respectively. There are multiple papers and patents which not only provide detailed information on the highlighted methods for capsule preparation, but also emphasize the advantages and disadvantages of these methods. [37–46]

Figure 4

The market for encapsulated technologies keeps on growing in volume thanks to the expanding range of applications. Synthetic microcapsules have become widespread in household and personal care products, such as cosmetics, perfume, rinse-off products and laundry detergent. [47–50] The Global Microencapsulation Market is expected to grow at a Compound Annual Growth Rate

(CAGR) of 11.7% from 2020 to 2027 and to reach $17.31 billion by 2027. The number of recent patents with micro-encapsulation and nano-encapsulation as a search word amounts to about 1200/year and has reached a total of approximately 30.000. [51] Perfume material-producing companies are investing in encapsulation technologies, as can be seen based on their patent activity. Companies such as IFF, Givaudan and Firmenich have invested in production plants in Europe. Perfume encapsulation approaches have been used in fabric enhancers, detergents and wash scent microcapsules to achieve a long-lasting scent. Encapsulation shells are polymeric materials that form a thin, flexible shell around the droplets of liquid fragrance oil. Such a solution provides a pleasant smell in our living space and has a positive effect on our emotional perception. [52] Fragrances are also beneficial in alleviating the physiological effects of mood and stress. [53] After the capsule shell ruptures upon use, it releases the liquid perfume content. According to the patent claims, the shells are not expected to be soluble in water and show limited biodegradability.[54] Their role is to increase deposition on textile garments and to permit a slow release of perfume through gradual diffusion or to break *via* friction when the garment is being worn. They thus allow the perfume to be perceivable in the garment for an extended period of time after wash, while decreasing the quantity of perfume used. [55] According to the International Fragrance Association (IFRA), the total volume of polymers used for all applications of fragrance encapsulation is at least 400 tons per year.[56] Moreover, the IFRA indicates that the use of fragrance encapsulation technologies, in terms of tonnage, is distributed principally to laundry detergents (50–55% of total volume) and fabric softeners (35–40%), with other products accounting for 5–15%. [57]

Furthermore, companies such as BASF and Syngenta have issued patent applications for encapsulation technologies for agriculture and construction industries. [58,59] The purpose of encapsulation is to enable a faster and more effective use of materials for extremely targeted delivery of active ingredients to specific places. It is achieved *via* protection of the load from aggressive environments and/or via controlled release within the time frame desired for the application. According to the International Fertiliser Society (IFS), fertilizer encapsulation has a significant impact on the increase in the efficiency of nutrient use, reduction of nutrient losses to the environment (‘run-offs’), prevention of nutrient-fixation in the soil, sustained/increased crop yield rates at a lower nutrient usage, improvement of the quality of plants that need a continuous supply of nutrients at a low rate, and reduction of labour. According to Fertilizers Europe, it is estimated that between 2016 and 2022, the average amount of 1,000–15,000 tons of microplastics per year will have been used for fertilizer encapsulation. According to a sector-wide study presented during the International Fertilizers Association (IFA) Conference on controlled-release fertilizers held in Dublin in 2019, the encapsulation market in Europe comprises approximately 50,000 tons per year.

Figure 5

Capsule shells are typically obtained by polymerization of different monomers through high levels of crosslinking of multifunctional monomeric materials, such as melamine. [60,61] Thus formed polymers used in commercially available capsule shells include melamine-formaldehyde (a), polyurea/polyurethane (c, d) and polyacrylate (e). Typical structures of such polymers are presented in **Error! Reference source not found.**. A detailed analysis taking into account both unbiodegradable and biodegradable polymers used for the production of microcapsules will be presented below in the following chapters. Crosslinked structures are necessary to avoid a premature release of the active compound in the formulated consumable product before its use. Unfortunately, these crosslinked polymeric capsule shells are not biodegradable, hence they are considered as microplastics. It should be emphasized that the formation of intermolecular covalent bonds during the crosslinking process [62] is the main factor causing the formation of comparatively hard and rigid capsule coatings. These irreversible covalent bonds are the main factor that determines the properties of such capsules, i.e. preservation of the cross-linked polymer structure despite stresses and various environmental factors. Additionally, crosslinked polymers, in contrast to biodegradable natural linear ones, are practically insensitive to single-bond breaks, and their highly compacted structure and high density result in low swelling and permeation tendencies.

It is important to note the definition of biodegradability. Following Li and et al., [63] biodegradability is the ability of polymeric materials to gradually decompose under the influence of specific biological processes conducted by microorganisms, such as fungi and bacteria, which can be tested according to ISO 17088:2012. [64] This definition is quite fluid, and depending on the conditions and microorganisms used, polymers that are generally not biodegradable, i.e. polyvinyl alcohol, polyurethanes or polyanhydrides, can also be degraded. [65–68] This is a perfect example of nature adapting to the prevailing conditions. Microorganisms evolve in conjunction with potential sources of valuable trace elements.

In order to demonstrate the significance of the problem of microplastic use in consumer goods, the European Commission in 2017 demanded that the European Chemicals Agency (ECHA) evaluate the scientific evidence for taking regulatory action at the EU level regarding microplastics purposely added to consumer products. In December 2020 and March 2021, the ECHA released two documents: (i) Restriction on formaldehyde and formaldehyde-releasing substances in articles [69] and (ii) Restricting the use of intentionally added microplastic particles to consumer or professional-use products of any kind.[70] According to these documents, the use of microcapsules with shells classified as microplastics in consumer goods is expected to be prohibited in the coming years.

Non-biodegradable microcapsules

Although synthetic polymers are a serious source of waste, their abolition in everyday life would be burdensome. Microencapsulation with a permanent synthetic polymer is used in sunscreens and cosmetic make-up products. This method enables the organic UV absorber to be isolated from the inorganic pigments, which helps to obtain the desired colour of the product. Otherwise, mixing the two components might cause the product to change colour over time, and direct contact of the UV absorber with the skin might cause an allergic reaction. [50] To effectively prevent the degradation of the active substance, it is encapsulated in a synthetic polymer such as acrylic polymer (**Error! Reference source not found.**f) or poly(vinyl alcohol) (**Error! Reference source not found.**g). [71] The polymer shell can protect the base substance from UV light, moisture and oxygen, e.g. extending the storage period in the case of volatile compounds. It can reduce the rate of evaporation or transfer of active material from the core to the medium, as well can prevent undesired chemical reactions. It is also an effective solution to the problem of agglomeration of fine powders. The polymer shell can improve the handling properties of sticky materials, control the release of substances and reduce toxicity or irritation. Microencapsulation can also ensure a controlled release and delivery of medicinal ingredients. The main beneficiaries of the encapsulation technology are the so-called “cosmeceuticals” which not only moisturize, revitalize and regenerate the skin, but are also a good complement to many treatments for skin diseases. The action of these products is mainly due to the content of vitamins, oils and therapeutic extracts that require processes to extend the stability. Microcapsules made of synthetic polymers can be used to encapsulate a wide variety of components, but there are still shortcomings in terms of effective retaining of the compacted/non-permeable structure of the polymer and in terms of its targeted delivery. For example, the leakage of active substances could occur due to capsule shell porosity. Various UV filters penetrate deep into the skin, causing photo allergic and phototoxic reactions, as well as skin irritation, creating an urgent need to develop safer sunscreen formulations. Encapsulation seems an ideal solution in order to reduce the penetration of the filter into the skin and maintain its effective concentration. A study involving the drug octinoxate (ethylhexyl methoxycinnamate, EHM) encapsulated in poly(methyl methacrylate) (PMMA, **Error! Reference source not found.**f) microspheres [72] showed that cream-based formulations exhibited different rates of drug release depending on the ratio of EHM to PMMA, with the fastest release observed for the 1:1 ratio and the slowest release observed for the 1:3 ratio. Moreover, after entrapping, the sunscreen activity was much higher than that of the sunscreen used in free form. PMMA microcapsules also improve photostability. This example perfectly illustrates how important the use of encapsulation is becoming in commercial solutions. On the other hand, the introduction of plastic should be accompanied by the development of techniques that would greatly minimize its subsequent release into the environment. Microspheres based on polymers can be also used alone as a synthetic pigment or as a shell for organic dyes. Both hollow and encapsulated microspheres show much higher colour uniformity and compatibility with other ingredients than, for example, a titanium dioxide-based dye.[73] As mentioned above, fragrance encapsulation is a fairly common technique used in cosmetics, home care products and beauty products. Synthetic polymers show the most attractive characteristics from the technological point of view, especially in terms of chemical and heat resistance. Moreover, their synthesis is already well developed and relatively simple (**Error! Reference source not found.**). They also allow controlled release of the different perfume components. Poly(urea-urethane) microcapsules, obtained by interfacial polyaddition of polyisocyanates and diamines, with poly(vinyl alcohol) as emulsifier, demonstrate sensitivity to light and release fragrance molecules upon irradiation. [74] Encapsulation of photo labile compounds in a poly(urea-urethane) shell and their dissolution in an oil core, enables fragrance release through mechanical breakage induced by rubbing. [75] Polyacrylate-based microcapsules have also been explored for prolonged release of fragrances; however, acrylates exhibit higher permeability to low-molecular weight fragrances, and the longevity of fragrance release is not as expected. [76,77] For example, crosslinked polyacrylate (PMMA)/paraffin microcapsules produced by polymerization of suspension in Pickering emulsion show high thermal resistance up to 184°C. Another example of thermally and chemically resistant polymers that can be easily opened by mechanical fracture as an efficient release mechanism are aminoplasts (urea-formaldehyde and melamine-formaldehyde polymers (**Error! Reference source not found.**a)). [78] Friable urea microcapsules with perfume are included in detergent compositions. [79] Stable liquid and sprayable compositions comprising aminoplast microcapsules containing fragrance have been designed by Firmenich S.A.[80] Fragrance can be also incorporated directly on textile, e.g. by imprinting the encapsulated fragrance onto textile through screen-printing. This method also allows the fragrance release by rubbing, as a consequence of the capsules breakage. [81,82]

Figure 6

Using fragrance encapsulated in a polymer shell as a component of laundry products aims at decreasing the consumption of active compounds owing to reduced loss during storage and washing and prolonged release after deposition of the enclosed perfume on the clothes. Polymer shell can also work as a protective barrier from oxidants. [83] Most commercial laundry products contain fragrances encapsulated in aminoplast polymers, and thus the release of the active substances is achieved by a mechanical force acting on the rigid and brittle wall of the shell, which causes the capsule to burst on the textile. The mixture of volatile aroma substances encapsulated in a urea-formaldehyde or melamine-formaldehyde polymer can also be added into the fabric softener and cleaning products (solution used by the Procter & Gamble Company[75]). In addition to fragrance ingredients, water-soluble cleaning ingredients can be encapsulated in the polymer coating. Encapsulation in a polyacrylate (**Error! Reference source not found.**e) based polymer capsule limits the leakage of the components to 1–3%.

Another example of microencapsulation is the enclosing of the ingredients of hair shampoo, which has to meet various demands of today's consumers. Besides its washing action, shampoo should also improve hair condition, e.g. by its colouring, moisturizing and anti-dandruff action, as well as leave a pleasant fragrance. The only way to obtain these properties in one product is to encapsulate the appropriate agents in microcapsules. This has been recently achieved by encapsulation of anionic emulsifiers in a polyacrylic shell. The synergy observed between anionic emulsifiers and polyacrylate microcapsules allows the formation of anionic polyacrylate microcapsules. Such anionic microstructures show both fluid and elastic properties, as well as strong adhesion to the lipophilic surface of the hair or skin.[84] It has been found that a significant content of methacrylic acid monomer limits the diffusion of fragrance molecules through the polymeric shell. [85]

Flame-retardant fabrics is another application that uses microencapsulation in manufacturing.[86,87] The product suppresses the release of smoke or toxic fumes after ignition. Despite their key role, flame retardants also exhibit drawbacks, e.g. poor water resistance, poor compatibility with the fabric structure, toxicity, poor thermal degradation, most of which are mitigated by encapsulation. For example, red phosphorus is one of the most potent and widely used conventional flame-retardants. Unfortunately, despite numerous advantages, it also exhibits toxicity (releasing of highly toxic phosphine because of reaction with moisture), poor thermal stability and incompatibility with the polymer matrix. It has been shown that coating with melamine-formaldehyde resin is sufficient to achieve a higher ignition point, low release of toxic phosphine and prolonged storage time.[88] A much higher reduction of phosphine liberation (4 ppm at 280°C) can be obtained using a composite of urea-formaldehyde resin and silicon oxide as the microcapsule shell wall. [89] Ammonium polyphosphate is another flame retardant with a poor compatibility with textiles, which fails to meet the mechanical standards. It also tends to hydrolyse when exposed to moisture. For this compound, encapsulation by melamine-formaldehyde, and urea-formaldehyde faces certain problems, the most important of which is a loose encapsulated layer which is easily damaged. Moreover, this flame retardant has a low ignition point, and again poor compatibility with polymers.[90] Microencapsulation with polyurethane decreases retardant water leaching and increases its compatibility with the polyurethane matrix. Encapsulation of ammonium polyphosphate with a melamine-formaldehyde-*tris*(2-hydroxyethyl)isocyanurate resin results in an effective fire resistance of the flame retardant. [91] Microencapsulation of ammonium polyphosphate with a shell of epoxy resin ensures a much better compatibility with polypropylene matrix as well as high resistance to water. [92,93] The later feature, alongside thermal stability and a higher ignition point are also characteristic of ammonium polyphosphate microencapsulated by UV- curable epoxy acrylate resin. [94] Melamine phosphate is a typical halogen-free phosphorus flame retardant. It is a mixture of both melamine and phosphoric acids; therefore, its properties are also typical for components reagents. This retardant and fine dispersion particles (e.g. magnesium oxide, zinc borate) can be encapsulated with thermoplastic urethanes, improving the flammability behaviour of the polymer matrix, e.g. polyoxymethylene. [86,87,95] Such materials not only show flame retardancy and good mechanical performance, but also exhibit adsorption properties towards formaldehyde.

Biodegradable microcapsules

As was mentioned above the use of synthetic plastics causes several environmental problems Consequently, the use of non-biodegradable microplastics in PCCPs has been prohibited in the United States, Canada and several European countries, such as France and the United Kingdom. [96,97] Regulations introduced in these countries include the possible ways of improvement of the available encapsulation technologies to curb microplastic contamination *via* development of natural substitutes and production of new biodegradable plastic. [98,99] Biodegradable materials, either natural or synthetic, can be used as encapsulation materials for PCCPs; however, their production remains complex and expensive, and their physicochemical properties are not as good as those of conventional microcapsules. [50,100–102]

Biodegradable polymers exhibit a high susceptibility to natural enzymatic degradation.[63] Furthermore, their degradation end-products are non-toxic and biocompatible (including water, carbon dioxide, biomass, etc.). [103] Generally, the shell of biodegradable capsules can be made of organic or inorganic materials (**Error! Reference source not found.**).

Figure 7

The formation of microcapsules based on inorganic materials is more complex in comparison with organic-based microcapsules. There are many intrinsic limitations for the production of inorganic capsules associated with their low mechanical strength, limited functionalization, and high shell permeability. [104] One of the most common manufacturing methods of inorganic microcapsules is template-direct synthesis, which involves a hard or soft template. [105,106] A hard template can be used to achieve core-shell structures and hollow spheres with well-defined wall thickness and narrow size-distribution. However, this method requires removal of the hard template by either dissolution in strong acid (or organic solvents) or calcination at high temperatures (500–1200°C). The removal of the template leads to a high porosity of the outer shell, which may limit the encapsulation efficiency. On the other hand, even these methods have been reported in the scientific papers, their application in a consumer-oriented market is quite impossible – most of encapsulated materials are not stable under mentioned conditions. Hollow spheres can be also obtained using soft templates, including emulsion droplets, gas bubbles, surfactants or hydrogels (**Error! Reference source not found.**). [107–109] The template is removed by evaporation. However, owing to the low stability of soft templates, evaporation of the liquid may result in a collapse of the hollow structures. [109]

Figure 8

Despite several technical gaps related to the formation of inorganic shells, inorganic microcapsules might offer several benefits for the PCCP and textile industry. [110] For instance, Morgan *et al.* demonstrated the encapsulation of an organic fluorescent dye (Cy3 Amidite) in non-toxic and well-dispersed calcium phosphate nanoparticles. [111] Their pH-dependent solubility provided a controlled release of organic dye and gradual degradation of the inorganic shell. The results indicate that biodegradable calcium carbonate capsules could serve as efficient vehicles for various textile dyes and pigments. Petrov *et al.* reported that calcium carbonate microparticles may act as a protein adsorber and simultaneously as a template for layer-by-layer polyelectrolyte shell formation. [112] The authors highlighted that the content of proteins captured by $CaCO_3$ microparticles can be easily controlled, and the presented approach may be used for encapsulation of various macromolecules and bioactive compounds, such as enzymes (including detergent enzymes). Recently, preparation of inorganic capsules based on silica nano-/microstructures has attracted great attention owing to several of their features, especially high surface area, tuneable pore size and biocompatibility. [113,114] Zhang *et al.* investigated the encapsulation of n-octadecane (used in the production of detergents) within silica shell material. [113] The silica shell ensured good phase-change performance, as well as collapse resistance of the capsule shell, thanks to its excellent anti-osmosis properties. Silica materials can be used in the coating of dyes and pigments to improve their dispersion capability, stability in aqueous solutions, colour intensity and heat resistance. [115] Encapsulated organic pigments are widely used in cosmetics (e.g. lipstick, pressed powder, blush, mascara), plastics, paints and textile industries. [116–118] Yuan *et al.* reported encapsulation of the benzidine yellow G pigment by nano-silica particles. [115] The authors demonstrated that the nano-silica shell enhanced thermal stability, wettability and dispersibility of organic pigment in an aqueous system. Moreover, the nano-silica shell prevented the exposure of the tested pigment to UV radiation.

Furthermore, according to recently published papers and patents cosmetics, rinse-off products and detergents could contain micro-/nanocapsules with the capsule shells formed by synthetic biodegradable polymers, such as poly(ε-caprolactone) (PCL, **Error! Reference source not found.**j), poly(2-hydroxypropionic acid), commonly known as polylactic acid (PLA, **Error! Reference source not found.**m), poly (L-lactic acid) (PLLA), poly(lactide-co-glycolide) acid

(PLGA, **Error! Reference source not found.**l) or poly(glycolic acid) (PGA, **Error! Reference source not found.**n). [50,119–124] However, natural or semi-synthetic polymers can be also selected as shell materials in the manufacture of capsules for PCCPs. For instance, gelatine (**Error! Reference source not found.**k), chitosan (**Error! Reference source not found.**h), hyaluronic acid (HA) or various polypeptides might be successfully employed as shell materials. [125–129] The choice of materials for encapsulation determines the chemical and physical properties of the final capsules. Several factors should be taken into account prior to the selection of shell material, including stability, reactivity, biocompatibility, flexibility, strength and optical properties. [130] These features significantly affect the release kinetics, stability and fabrication method of the encapsulated substance. [131]

PCL is one of the most popular synthetic biodegradable polymers. It can be hydrolysed into alcohol and carboxylic acid in water and body fluids; however, its degradation is slower in comparison with other biodegradable polymers. [132] PCL is widely utilized for the encapsulation of essential oils, such as citronella oil, menthol, thymol and eucalyptol. [123,133–135] For instance, citronella essential oil exhibits mosquito (or other insects) repellent action, and thus can be applied as an additive to sprays and candles, but also to various cleaning products, such as household cleaners and detergents. [136,137] PCL-encapsulated essential oils may be also used for finishing textile fabrics to make them more attractive to the consumer. [138] Generally, most essential oils are labile and volatile, which greatly limits their applications. Encapsulation of essential oils allows extending their longevity, prevents their evaporation and prolongs their release. [137] Zhu *et al.* investigated the encapsulation of thymol oil in PLGA. [139] The authors highlighted that PLGA encapsulation enhanced the thermal stability of thymol oil and allowed its slow and sustained release. Moreover, owing to the excellent antibacterial activity of thymol, the essential-oil microcapsules exhibit great potential for use as antibacterial additives. [139] Some essential oils, such as red thyme and clove bud oils, exhibit acaricidal activities, and thus can be utilized as alternative acaricides in the prevention of sensitization to house dust mite allergens. [140] However, these oils release a strong odour, and thus are not suitable for long-term application. Kim *et al.* suggested encapsulation of thyme and clove bud oils in gelatine (natural organic polymer) to prevent their rapid and uncontrolled evaporation. It was proven that gelatine-encapsulated clove bud oil can serve as a natural eco-friendly acaricide to effectively reduce the population of house dust mites. [141]

Polymer microcapsules/microbeads made of natural polymers offer a promising alternative for non-biodegradable ones. Bea *et al.* fabricated Ca-alginate (**Error! Reference source not found.**i) microbeads that can be used as scrubbing additives in cosmetics, such as peeling, soap or toothpaste. The alginate microcapsules easily degraded in the seawater, as a result of a reversible ion-exchange reaction between calcium ions in the capsules and sodium in the seawater. [125] Another example of a biodegradable polymer that may act as shell material is bio-derived poly-3-hydroxybutyrate (PHB). [142] PHB and its copolymers are produced by microalgae, such as *Spirulina platensis*. Nanocapsules made of PHB, owing to their excellent antibacterial and antioxidant properties, can be used in the PCCP industry (in creams, scrubs, masks, nutricosmetics), as well as the polymer industry, for the manufacture of smart packaging. [143–146]

The main drawback of natural polymers in the encapsulation technology is their low mechanical strength and high permeability. To overcome this problem, the polymer matrix can be reinforced by various additives, such as natural organic, inorganic or synthetic copolymers (**Error! Reference source not found.**). For instance, Wang *et al.* improved the mechanical properties of

PLGA and alginate microspheres using silk fibroin coatings. [126] Moreover, they showed that the silk shell prevented the aggregation and decomposition of the PLGA capsules. [126]. Konuklu *et al.* formulated chitosan-gelatine microcapsules containing caprylic acid. [147] Both chitosan and gelatine are non-toxic, biocompatible and biodegradable; however, the presence of chitosan provides the final product with antibacterial properties. Caprylic acid is a well-known fatty acid that can be found in coconut oil. It is a popular ingredient of cosmetics, such as creams or emollients, as well as disinfectants, lubricants and perfumes, It possesses moisturising, anti-inflammatory, and antibacterial properties. [148–150] Encapsulation of fatty acids allows protection and a controlled release of core substances. [147] Chitosan is a commonly used encapsulation material. However, it is insoluble in most solvents at pH > 6.5, so its uses in the encapsulation of active components, such as enzymes, can be limited. Jiang *et al.* examined the ionic complexation of chitosan with alginate to formulate microcapsules for amylase encapsulation.[143] Amylase, alongside lipase and protease, is used in the formulation of detergents to enhance their detergency. [151] Encapsulated detergent enzymes facilitate the control of active component release and exhibit high efficiency in hard water and high temperature. [152] Even though biodegradable materials have been extensively studied, they are still far from up-scaled production. A number of scientific reports and patents discuss the limitations of the industrial production of biodegradable materials used in the encapsulation technology. Such biodegradable, natural-based materials are often used as additives in conventional plastic production. However, the combination of the functional properties of commonly used polymers and biodegradability is still far from being achieved.

Perspectives and challenges in encapsulation chemistry/final conclusions

In light of the above considerations regarding both the production of microcapsules and their use in household conditions, as well as their possible release into the environment, it is necessary to assess their durability and mechanical properties. Depending on the setting, achieving both the required durability during use and the release of the desired components in due time can be expected.

The tunability of mechanical characteristics allows the formation of customizable and flexible microcapsules that can be adapted to the required flow patterns in a broad range of applications, such as oil recycling, chemical reactor feed streams, red blood cell flow and chemically targeted delivery, as well as in household and personal care products. [153,154] Microcapsules with known and customizable mechanical properties can be produced using advanced, highly regulated synthesis methods. such as droplet microfluidics. These methods allow controlling the size of the microcapsule and membrane thickness by precise regulation of the liquid flow rate. In particular, capillary glass microfluids provide flexible and selectable materials offering different mechanical characteristics. [155,156]

Micromanipulation is a technique used to study the mechanical properties of microcapsules. The principle of this technique is to exert a compressive stress on single microcapsules placed between two parallel surfaces. [157,158] The specific mechanical properties of microcapsules, such as yield strength, Young's modulus, relaxation time, Poisson's coefficient can be evaluated by mathematical simulation and micromanipulation measurements. Compression between two plates is recognized as one of the available break-strength tests that describe the mechanical strength of microcapsules. A sufficient number of microcapsules are placed on a glass plate and then covered with another glass plate. Subsequently, the glass plates are placed between the two rubber plates to guarantee an even mass uniformity. A defined quantity of the mass is then gently applied to the upper plate for a certain period time to tear the microcapsules. The ratio of the active substance released from the broken microcapsules to the total amount of active substance is used to determine the percentage of broken microcapsules and, consequently, the mechanical strength of the microcapsule population.

Yet another technique to estimate the mechanical properties of microcapsules is the shear breakage test. The shear impact on the microcapsules and their subsequent mechanical resistance to shear forces up to breakage of such microcapsules can be tested in a turbine reactor. [159] The microcapsules break down by mixing with glass balls of the prescribed diameter. The breakage of the microcapsules causes the release of the encapsulated active substance. By measuring the concentration of this substance before and after shear rupture, the fraction of undamaged microcapsules is estimated. Mechanical damage is a complicated function of the capsule properties such as diameter and mean shear rate. [160]

An osmotic pressure test [161,162] was used as a quick method to evaluate the mechanical strength of semi-permeable microcapsules. Van Raamsdonk and Chang [163] used this test to determine the quantitative strength of alginate microcapsules by treating them with a number of hypotonic solutions of different osmolarity and then evaluating the percentage of damaged microcapsules. This test is a straightforward and precise method to quickly determine the strength of a high number of microcapsules. Still, it is limited to microcapsules with semi-permeable surfaces and is only applicable for measuring the mechanical stability of semi-permeable microcapsules with reasonably small mechanical endurance.

Atomic force microscopy, micropipette aspiration, texture analysis and micromanipulation are the most popular techniques to measure the mechanical properties of single microcapsules. In the early days, colloidal AFM sensors were used to measure the adhesion force between a flat surface and a single colloidal particle. [164] In further studies, it was adapted to investigate strain by compression of single particles with a large radius of curvature between a colloidal particle and a flat surface. [165] AFM was also used to measure the strain and deformation of microcapsules under applied load. [160,165–168] The deformation forces measured are usually in the range from pN to μN. [169] This technique is also used to determine Young modulus through nanoindentation. [170] The aim of this technique is to estimate the local Young modulus, limited to the most loaded area in the capsule wall. The local value of Young modulus can be an order of magnitude higher than that of the neighbouring area. [171]

Another method is the micropipette aspiration technique, which can be used to measure the deformability of individual microcapsules. [172] This technique involves pulling a part of the microcapsule into a micropipette and recording the difference in pressure between the inside and outside of the pipette. The major drawbacks of the micropipette aspiration technique are the stress concentration on the edge of the pipette and the friction between the surface of the micropipette and the wall of the capsule, which can hinder the calibration process and interfere with the mechanical response of the capsule during aspiration. [173,174]

Texture analysis is a technique using a piston penetrometer – a texture analyser additionally equipped with a stress sensor. For the compression of individual capsules, a piston with an appropriate diameter should be used. [175,176] Typical texture analysers are used for particles of several hundred micrometres to several millimetres in diameter, [177] but their application to particles of a few micrometres in size is significantly hampered by the required measurement precision.

Micromanipulation is a technique, which is able to counteract the constraints of the methods described above, in particular the size limitation of the microcapsules tested. The technique consists of compressing single microcapsules between two parallel surfaces using flat-ended and flat-ended glass probe. [178] Micromanipulation appears to be quite suitable to characterize microcapsules with a fractional micrometre diameter. This technique is effective for testing the elastic and plastic properties of microcapsules [179] and for characterizing and comparing their mechanical strength. [157] Micromanipulation is used in a broader sense to characterize the mechanical properties of other particles such as pollen grains,[180] microspheres, [181] hydrogels [182] and multi-molecular polymers such as methacrylic acid copolymers. [183] The technique of micromanipulation is to some degree limited by the time of the experiment and the smallest force with which the measurement can be performed for one micronutrient. In particular, this technique is not suitable for measurements of microcapsules of the size range below 1 micrometre.

The ubiquity of microplastics in the environment will continue to be an issue for many years to come, both for scientific consideration and in the public consciousness. Therefore, the sustainable development of materials that can significantly minimize the amount of waste generated is highly justified. Obviously, removing plastics altogether and lumping every polymer together is not feasible – it is necessary to take a rational look at the properties of the end products obtained, including their application, durability and routes of release into the environment. The increasing knowledge of the synthesis of biodegradable plastics is contributing to the possibility of using such solutions where it can make sense. Moreover, it is possible to find other eco-friendly polymers. A classification can be made for these polymers, according to the categorization presented in the literature, [184] such as: bio-based plastics (from biological resources), compostable plastics (subclass of those biodegradable plastics which can be decomposed in compost facilities) or recyclable plastics (from which monomers or oligomers can be recovered). As a final remark, we should underline the need of an objective insight into the entire life cycle of microcapsules to address the possible concerns and risks, while taking into account the benefits of encapsulation. Thus, materials for microencapsulation have to fulfil all or at least some of the following requirements: (i) good rheological properties at high concentrations (if needed) and good workability during the encapsulation; (ii) no reactions with the material to be encapsulated; (iii) seal and hold of the active material within its structure during processing or storage; (iv) complete release of solvent or other materials used during encapsulation under drying or other solvent-removing conditions (if applicable); (v) maximum protection of the core against the environmental conditions; (vi) inexpensive; and (vii) food-grade and legal qualification. Tuning novel materials for microencapsulation while taking into account all these aspects, represents the real challenge for researcher in this field in the forthcoming years.

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Notes

ET is a consumer-driven technology, which has been used by industry players (Procter & Gamble, Henkel, Unilever, BASF) to launch new products or to enhance the existing ones with improved properties. Moreover, encapsulation has been employed by pharmaceutical and healthcare companies for masking taste and odour, and to protect the activity of the encapsulated active materials (which act as drug/herbal functional ingredients). It has also been explored by manufacturers of consumer goods for perfume delivery in home care and rinse-off personal care products, including but not limited to detergents, toothpaste, bath products, and facial scrubs.

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References

[1] R.C. Thompson, Y. Olson, R.P. Mitchell, A. Davis, S.J. Rowland, A.W.G. John, D. McGonigle, A.E. Russell, Lost at Sea: Where Is All the Plastic?, Science (1979). 304 (2004) 838. https://doi.org/10.1126/science.1094559.

[2] C. Guerranti, T. Martellini, G. Perra, C. Scopetani, A. Cincinelli, Microplastics in cosmetics: Environmental issues and needs for global bans, Environ Toxicol Pharmacol. 68 (2019) 75–79. https://doi.org/10.1016/j.etap.2019.03.007.

[3] Q. Sun, S.Y. Ren, H.G. Ni, Incidence of microplastics in personal care products: An appreciable part of plastic pollution, Science of the Total Environment. 742 (2020) 140218. https://doi.org/10.1016/j.scitotenv.2020.140218.

[4] R.Z. Habib, M.M. Salim Abdoon, R.M. Al Meqbaali, F. Ghebremedhin, M. Elkashlan, W.F. Kittaneh, N. Cherupurakal, A.H.I. Mourad, T. Thiemann, R. Al Kindi, Analysis of microbeads in cosmetic products in the United Arab Emirates, Environmental Pollution. 258 (2020) 113831. https://doi.org/10.1016/j.envpol.2019.113831.

[5] X. Wang, N. Bolan, D.C.W. Tsang, B. Sarkar, L. Bradney, Y. Li, A review of microplastics aggregation in aquatic environment: Influence factors, analytical methods, and environmental implications, J Hazard Mater. 402 (2021) 123496. https://doi.org/10.1016/j.jhazmat.2020.123496.

[6] A. Piotrowska, O. Czerwińska-Ledwig, M. Serdiuk, K. Serdiuk, W. Pilch, Composition of scrub-type cosmetics from the perspective of product ecology and microplastic content, Toxicol Environ Health Sci. 12 (2020) 75–81. https://doi.org/10.1007/s13530-020-00051-9.

[7] L. An, Q. Liu, Y. Deng, W. Wu, Y. Gao, W. Ling, Sources of Microplastic in the Environment, in: Handbook of Environmental Chemistry, Springer, Cham, 2020: pp. 143–159. https://doi.org/10.1007/698_2020_449.

[8] F. Laborda, C. Trujillo, R. Lobinski, Analysis of microplastics in consumer products by single particle-inductively coupled plasma mass spectrometry using the carbon-13 isotope, Talanta. 221 (2021) 121486. https://doi.org/10.1016/j.talanta.2020.121486.

[9] B. Henry, K. Laitala, I.G. Klepp, Microfibres from apparel and home textiles: Prospects for including microplastics in environmental sustainability assessment, Science of the Total Environment. 652 (2019) 483–494. https://doi.org/10.1016/j.scitotenv.2018.10.166.

[10] S. O'Brien, E.D. Okoffo, J.W. O'Brien, F. Ribeiro, X. Wang, S.L. Wright, S. Samanipour, C. Rauert, T.Y.A. Toapanta, R. Albarracin, K. V. Thomas, Airborne emissions of microplastic fibres from domestic laundry dryers, Science of The Total Environment. 747 (2020) 141175. https://doi.org/10.1016/j.scitotenv.2020.141175.

[11] J.P. da Costa, Micro- and nanoplastics in the environment: Research and policymaking, Curr Opin Environ Sci Health. 1 (2018) 12–16. https://doi.org/10.1016/j.coesh.2017.11.002.

[12] F. De Falco, E. Di Pace, M. Cocca, M. Avella, The contribution of washing processes of synthetic clothes to microplastic pollution, Sci Rep. 9 (2019) 1–11. https://doi.org/10.1038/s41598-019-43023-x.

[13] D.M. Mitrano, W. Wohlleben, Microplastic regulation should be more precise to incentivize both innovation and environmental safety, Nat Commun. 11 (2020) 1–12. https://doi.org/10.1038/s41467-020-19069-1.

[14] Y. Zhang, S. Pu, X. Lv, Y. Gao, L. Ge, Global trends and prospects in microplastics research: A bibliometric analysis, J Hazard Mater. 400 (2020) 123110. https://doi.org/10.1016/j.jhazmat.2020.123110.

[15] F. Qin, J. Du, J. Gao, G. Liu, Y. Song, A. Yang, H. Wang, Y. Ding, Q. Wang, Bibliometric Profile of Global Microplastics Research from 2004 to 2019, Int J Environ Res Public Health. 17 (2020) 5639. https://doi.org/10.3390/ijerph17165639.

[16] T. Gouin, R.A. Becker, A.G. Collot, J.W. Davis, B. Howard, K. Inawaka, M. Lampi, B.S. Ramon, J. Shi, P.W. Hopp, Toward the Development and Application of an Environmental Risk Assessment Framework for Microplastic, Environ Toxicol Chem. 38 (2019) 2087–2100. https://doi.org/10.1002/etc.4529.

[17] Q.T. Birch, P.M. Potter, P.X. Pinto, D.D. Dionysiou, S.R. Al-Abed, Sources, transport, measurement and impact of nano and microplastics in urban watersheds, Rev Environ Sci Biotechnol. 19 (2020) 275–336. https://doi.org/10.1007/s11157-020-09529-x.

[18] C.M. Rochman, Microplastics research—from sink to source, Science (1979). 360 (2018) 28–29. https://doi.org/10.1126/science.aar7734.

[19] O.H. Fred-Ahmadu, G. Bhagwat, I. Oluyoye, N.U. Benson, O.O. Ayejuyo, T. Palanisami, Interaction of chemical contaminants with microplastics: Principles and perspectives, Science of the Total Environment. 706 (2020) 135978. https://doi.org/10.1016/j.scitotenv.2019.135978.

[20] I.F. Sequeira, J.C. Prata, J.P. da Costa, A.C. Duarte, T. Rocha-Santos, Worldwide contamination of fish with microplastics: A brief global overview, Mar Pollut Bull. 160 (2020) 111681. https://doi.org/10.1016/j.marpolbul.2020.111681.

[21] J.R. Jambeck, R. Geyer, C. Wilcox, T.R. Siegler, M. Perryman, A. Andrady, R. Narayan, K.L. Law, Plastic waste inputs from land into the ocean, Science (1979). 347 (2015) 768–771. https://doi.org/10.1126/science.1260352.

[22] T.S. Galloway, M. Cole, C. Lewis, Interactions of microplastic debris throughout the marine ecosystem, Nat Ecol Evol. 1 (2017) 0116. https://doi.org/10.1038/s41559-017-0116.

[23] S. Piehl, A. Leibner, M.G.J. Löder, R. Dris, C. Bogner, C. Laforsch, Identification and quantification of macro- and microplastics on an agricultural farmland, Sci Rep. 8 (2018) 17950. https://doi.org/10.1038/s41598-018-36172-y.

[24] H. Deng, J. He, D. Feng, Y. Zhao, W. Sun, H. Yu, C. Ge, Microplastics pollution in mangrove ecosystems: A critical review of current knowledge and future directions, Science of The Total Environment. 753 (2021) 142041. https://doi.org/10.1016/j.scitotenv.2020.142041.

[25] J. Gasperi, S.L. Wright, R. Dris, F. Collard, C. Mandin, M. Guerrouache, V. Langlois, F.J. Kelly, B. Tassin, Microplastics in air: Are we breathing it in?, Curr Opin Environ Sci Health. 1 (2018) 1–5. https://doi.org/10.1016/j.coesh.2017.10.002ï.

[26] N. Weithmann, J.N. Möller, M.G.J. Löder, S. Piehl, C. Laforsch, R. Freitag, Organic fertilizer as a vehicle for the entry of microplastic into the environment, Sci Adv. 4 (2018) eaap8060. https://doi.org/10.1126/sciadv.aap8060.

[27] C. Scherer, N. Brennholt, G. Reifferscheid, M. Wagner, Feeding type and development drive the ingestion of microplastics by freshwater invertebrates, Sci Rep. 7 (2017) 1–9. https://doi.org/10.1038/s41598-017-17191-7.

[28] C. Le Guen, G. Suaria, R.B. Sherley, P.G. Ryan, S. Aliani, L. Boehme, A.S. Brierley, Microplastic study reveals the presence of natural and synthetic fibres in the diet of King Penguins (Aptenodytes patagonicus) foraging from South Georgia, Environ Int. 134 (2020) 105303. https://doi.org/10.1016/j.envint.2019.105303.

[29] L.C. Dovidat, B.W. Brinkmann, M.G. Vijver, T. Bosker, Plastic particles adsorb to the roots of freshwater vascular plant Spirodela polyrhiza but do not impair growth , Limnol Oceanogr Lett. 5 (2020) 37–45. https://doi.org/10.1002/lol2.10118.

[30] P. Schwabl, Microplastics in hot water, Nat Food. 1 (2020) 671–672. https://doi.org/10.1038/s43016-020-00174-9.

[31] D. Li, Y. Shi, L. Yang, L. Xiao, D.K. Kehoe, Y.K. Gun'ko, J.J. Boland, J.J. Wang, Microplastic release from the degradation of polypropylene feeding bottles during infant formula preparation, Nat Food. 1 (2020) 746–754. https://doi.org/10.1038/s43016-020-00171-y.

[32] T. Wang, L. Wang, Q. Chen, N. Kalogerakis, R. Ji, Y. Ma, Interactions between microplastics and organic pollutants: Effects on toxicity, bioaccumulation, degradation, and transport, Science of the Total Environment. 748 (2020) 142427. https://doi.org/10.1016/j.scitotenv.2020.142427.

[33] X. Guo, Y. Liu, J. Wang, Equilibrium, kinetics and molecular dynamic modeling of Sr2+ sorption onto microplastics, J Hazard Mater. 400 (2020) 123324. https://doi.org/10.1016/j.jhazmat.2020.123324.

[34] X. Guo, J. Wang, Projecting the sorption capacity of heavy metal ions onto microplastics in global aquatic environments using artificial neural networks, J Hazard Mater. 402 (2021) 123709. https://doi.org/10.1016/j.jhazmat.2020.123709.

[35] A. Menéndez-Pedriza, J. Jaumot, Interaction of Environmental Pollutants with Microplastics: A Critical Review of Sorption Factors, Bioaccumulation and Ecotoxicological Effects, Toxics. 8 (2020) 40. https://doi.org/10.3390/toxics8020040.

[36] B.K. Green, L. Schleicher, United States Patent Office Pressure responseve record materials, 1956.

[37] B. Tylkowski, M. Giamberini, S. Fernandez Prieto, eds., Microencapsulation, De Gruyter, 2020. https://doi.org/10.1515/9783110642070.

[38] V. Marturano, J. Kozlowska, A. Bajek, M. Giamberini, V. Ambrogi, P. Cerruti, R. Garcia-Valls, J.M. Montornes, B. Tylkowski, Photo-triggered capsules based on lanthanide-doped upconverting nanoparticles for medical applications, Coord Chem Rev. 398 (2019) 213013. https://doi.org/10.1016/j.ccr.2019.213013.

[39] S. Bose, L.R. Volpatti, D. Thiono, V. Yesilyurt, C. McGladrigan, Y. Tang, A. Facklam, A. Wang, S. Jhunjhunwala, O. Veiseh, J. Hollister-Lock, C. Bhattacharya, G.C. Weir, D.L. Greiner, R. Langer, D.G. Anderson, A retrievable implant for the long-term encapsulation and survival of therapeutic xenogeneic cells, Nat Biomed Eng. 4 (2020) 814–826. https://doi.org/10.1038/s41551-020-0538-5.

[40] H. Liu, R.P. Singh, Z. Zhang, X. Han, Y. Liu, L. Hu, Microfluidic Assembly: An Innovative Tool for the Encapsulation, Protection, and Controlled Release of Nutraceuticals, J Agric Food Chem. (2021) acs.jafc.0c05395. https://doi.org/10.1021/acs.jafc.0c05395.

[41] S. Çakir, E. Bauters, G. Rivero, T. Parasote, J. Paul, F.E. Du Prez, High-Throughput Platform for Synthesis of Melamine-Formaldehyde Microcapsules, ACS Comb Sci. 19 (2017) 447–454. https://doi.org/10.1021/acscombsci.7b00037.

[42] S.M. Jafari, An overview of nanoencapsulation techniques and their classification, in: Nanoencapsulation Technologies for the Food and Nutraceutical Industries, Elsevier, 2017: pp. 1–34. https://doi.org/10.1016/B978-0-12-809436-5.00001-X.

[43] J.A.B. Valle, R. de C.S.C. Valle, A.C.K. Bierhalz, F.M. Bezerra, A.L. Hernandez, M.J. Lis Arias, Chitosan microcapsules: Methods of the production and use in the textile finishing, J Appl Polym Sci. 138 (2021) 50482. https://doi.org/10.1002/app.50482.

[44] J. Park, J. Kim, S. Jin, Microcapsule, structure having a microcapsule, article having a microcapsule, and method of preparing microcapsules, 8951554, 2015.

[45] J. Smets, S. Fernandez Prieto, R. Rodrigo Gomez, A. Gasull Morales, J.E.K. Quansah, Encapsulates, 10604728, 2020.

[46] J.F. Miravet Celades, B. Escuder Gil, V.J. Nebot-carda, J. Smets, S. Fernandez Prieto, Encapsulates, 9644174, 2017.

[47] G. León, N. Paret, P. Fankhauser, D. Grenno, P. Erni, L. Ouali, D.L. Berthier, Formaldehyde-free melamine microcapsules as core/shell delivery systems for encapsulation of volatile active ingredients, RSC Adv. 7 (2017) 18962–18975. https://doi.org/10.1039/C7RA01413A.

[48] I. Lewis, M. Popplewell, N.J. Us, K. Daniel, N.J. Us, G.L. Pluyter, N.J. Us, J. Brain, B. Nl, Y. Zhen, P.A. Us, United States Patent. Patent Pub. No . US 7,585,824 B2 (2009), 2009.

[49] S. Schreiber, T. Fr, J. Goodall, H.K. Gb, P. Fr, I. Michael, P. Fr, Patent Application Publication Pub . No .: US 2015/0044262 A1. US 2015, 2015.

[50] F. Casanova, L. Santos, Encapsulation of cosmetic active ingredients for topical application – a review, J Microencapsul. 33 (2016) 1–17. https://doi.org/10.3109/02652048.2015.1115900.

[51] Microencapsulation Market to Reach $17.31 billion by 2027- Exclusive Report Covering Pre and Post COVID-19 Market Analysis by - Bloomberg, (n.d.). https://www.bloomberg.com/press-releases/2021-03-01/microencapsulation-market-to-reach-17-31-billion-by-2027-exclusive-report-covering-pre-and-post-covid-19-market-analysis-by (accessed March 16, 2021).

[52] M. Saifullah, M.R.I. Shishir, R. Ferdowsi, M.R. Tanver Rahman, Q. Van Vuong, Micro and nano encapsulation, retention and controlled release of flavor and aroma compounds: A critical review, Trends Food Sci Technol. 86 (2019) 230–251. https://doi.org/10.1016/j.tifs.2019.02.030.

[53] S.K. Jain, N.K. Jain, Multiparticulate carriers for sun-screening agents, Int J Cosmet Sci. 32 (2010) 89–98. https://doi.org/10.1111/j.1468-2494.2010.00547.x.

[54] K.J. Ha, J.H. Kwon, S.R. Nam, Y.S. Lee, C.M. Lee, S.J. Choi, Composition for encapsulation and encapsulated apparatus including the same, 9957335, 2018.

[55] D.R. Perinelli, G.F. Palmieri, M. Cespi, G. Bonacucina, Encapsulation of Flavours and Fragrances into Polymeric Capsules and Cyclodextrins Inclusion Complexes: An Update, Molecules. 25 (2020) 5878. https://doi.org/10.3390/molecules25245878.

[56] Home, (n.d.). https://ifrafragrance.org/ (accessed March 16, 2021).

[57] C. Laroche, C. Gonzalez, Fragrance encapsulations in consumer products, 2018.

[58] E. Burakowska-Meise, V. Bem, J. Mecfel-Marczewski, E. Klimov, K. Kolb, M. Bratz, S.J. Bowe, R. Repage, J. Frihauf, Agrochemical microcapsules with a shell of polyvinylalcohol and polyoxazoline, WO/2017/029302, 2017.

[59] Global Microencapsulated Pesticides Market is Expected to Reach USD 817.45 Million by 2025 : Fior Markets, (n.d.). https://www.globenewswire.com/news-release/2019/07/31/1894943/0/en/Global-Microencapsulated-Pesticides-Market-is-Expected-to-Reach-USD-817-45-Million-by-2025-Fior-Markets.html (accessed March 17, 2021).

[60] M.E. Seitz, Microencapsulation process using melamine-formaldehyde and microcapsules produced thereby, 5204185, 1993.

[61] L. Feng, R.S. Bobnock, Controlled release dual walled microcapsules, 10456766, 2019.

[62] J. Chen, E.S. Garcia, S.C. Zimmerman, Intramolecularly Cross-Linked Polymers: From Structure to Function with Applications as Artificial Antibodies and Artificial Enzymes, Acc Chem Res. 53 (2020) 1244–1256. https://doi.org/10.1021/acs.accounts.0c00178.

[63] C. Li, C. Guo, V. Fitzpatrick, A. Ibrahim, M.J. Zwierstra, P. Hanna, A. Lechtig, A. Nazarian, S.J. Lin, D.L. Kaplan, Design of biodegradable, implantable devices towards clinical translation, Nat Rev Mater. 5 (2020) 61–81. https://doi.org/10.1038/s41578-019-0150-z.

[64] ISO 17088:2012(en), Specifications for compostable plastics, (n.d.). https://www.iso.org/obp/ui/#iso:std:iso:17088:ed-2:v1:en (accessed March 29, 2021).

[65] I. Vroman, L. Tighzert, Biodegradable Polymers, Materials. 2 (2009) 307–344. https://doi.org/10.3390/ma2020307.

[66] G.T. Howard, Biodegradation of polyurethane: A review, in: Int Biodeterior Biodegradation, Elsevier, 2002: pp. 245–252. https://doi.org/10.1016/S0964-8305(02)00051-3.

[67] C.C. Chen, L. Dai, L. Ma, R.T. Guo, Enzymatic degradation of plant biomass and synthetic polymers, Nat Rev Chem. 4 (2020) 114–126. https://doi.org/10.1038/s41570-020-0163-6.

[68] J.D. Gu, Biodegradability of plastics: the issues, recent advances, and future perspectives, Environmental Science and Pollution Research. 28 (2021) 1278–1282. https://doi.org/10.1007/s11356-020-11501-9.

[69] European Chemicals Agency, ANNEX XV Restriction Report-: Formaldehyde and formaldehyde releasers, Helsinki, 2019.

[70] Committee for Risk Assessment (RAC) Committee for Socio-economic Analysis (SEAC) Background Document to the Opinion on the Annex XV report proposing restrictions on intentionally added microplastics, n.d.

[71] S.A. Riyajan, Development of a novel pH-sensitive polymer matrix for drug encapsulation from maleated poly(vinyl alcohol) grafted with polyacrylamide, Polymer Bulletin. 76 (2019) 4585–4611. https://doi.org/10.1007/s00289-018-2615-4.

[72] D. Gogna, S. Jain, A. Yadav, G. Agrawal, Microsphere Based Improved Sunscreen Formulation of Ethylhexyl Methoxycinnamate, Curr Drug Deliv. 4 (2007) 153–159. https://doi.org/10.2174/156720107780362285.

[73] R. Walt David, K. Mandal Tarun, S. Fleming Michael, Polymeric microspheres, WO2002041987A3, 2002.

[74] N. Paret, A. Trachsel, D.L. Berthier, A. Herrmann, Developing Multi Stimuli- Responsive Core/Shell Microcapsules to Control the Release of Volatile Compounds, Macromol Mater Eng. 304 (2019) 1800599. https://doi.org/10.1002/mame.201800599.

[75] US10738267B2 - Liquid laundry detergent composition comprising a core/shell encapsulate - Google Patents, (n.d.).

[76] H. Lee, C.H. Choi, A. Abbaspourrad, C. Wesner, M. Caggioni, T. Zhu, D.A. Weitz, Encapsulation and Enhanced Retention of Fragrance in Polymer Microcapsules, ACS Appl Mater Interfaces. 8 (2016) 4007–4013. https://doi.org/10.1021/acsami.5b11351.

[77] Y. Zhang, J. Song, H. Chen, Preparation of polyacrylate/paraffin microcapsules and its application in prolonged release of fragrance, J Appl Polym Sci. 133 (2016). https://doi.org/10.1002/app.44136.

[78] US20040071746A1 - Encapsulated fragrance chemicals - Google Patents, (n.d.).

[79] US4145184A - Detergent composition containing encapsulated perfume - Google Patents, (n.d.).

[80] US20180325786A1 - Polyurea or polyurethane capsules - Google Patents, (n.d.).

[81] U.S. Elesini, J. Švarc, B. Šumiga, R. Urbas, Melamine formaldehyde microcapsules with fragrance core material: Preparation, properties, and end use, Textile Research Journal. 87 (2017) 2435–2448. https://doi.org/10.1177/0040517516671126.

[82] M.S. Stan, L. Chirila, A. Popescu, D.M. Radulescu, D.E. Radulescu, A. Dinischiotu, Essential Oil Microcapsules Immobilized on Textiles and Certain Induced Effects, Materials. 12 (2019) 2029. https://doi.org/10.3390/ma12122029.

[83] K. Bruyninckx, M. Dusselier, Sustainable Chemistry Considerations for the Encapsulation of Volatile Compounds in Laundry-Type Applications, ACS Sustain Chem Eng. 7 (2019) 8041–8054. https://doi.org/10.1021/acssuschemeng.9b00677.

[84] M.A.B. Jiten Odhavji Dihora, United States Patent No. 10 , 143 , 632 B2, 2018.

[85] Y.Z. Lewis Michael, Popplewell Kaiping, Daniel Lee, Johan Gerwin, Lodewijk Pluyter,Joseph Brain, United States Patent No US7585824B2, 2009.

[86] EP2681267B1 - Polyurethane flame retardant formulation - Google Patents, (n.d.).

[87] WO2013007509A1 - Formulation suitable to provide polyurethane - Google Patents, (n.d.).

[88] Q. Wu, J. Lü, B. Qu, Preparation and characterization of microcapsulated red phosphorus and its flame-retardant mechanism in halogen-free flame retardant polyolefins, Polym Int. 52 (2003) 1326–1331. https://doi.org/10.1002/pi.1115.

[89] US20020188048A1 - Microencapsulated red phosphorus - Google Patents, (n.d.).

[90] J. Ni, L. Song, Y. Hu, P. Zhang, W. Xing, Preparation and characterization of microencapsulated ammonium polyphosphate with polyurethane shell by *in situ* polymerization and its flame retardance in polyurethane, Polym Adv Technol. 20 (2009) 999–1005. https://doi.org/10.1002/pat.1354.

[91] Z. Jiang, G. Liu, Microencapsulation of ammonium polyphosphate with melamine-formaldehyde-tris(2-hydroxyethyl)isocyanurate resin and its flame retardancy in polypropylene, RSC Adv. 5 (2015) 88445–88455. https://doi.org/10.1039/c5ra14586d.

[92] L. Liu, Y. Zhang, L. Li, Z. Wang, Microencapsulated ammonium polyphosphate with epoxy resin shell: preparation, characterization, and application in EP system, Polym Adv Technol. 22 (2011) 2403–2408. https://doi.org/10.1002/pat.1776.

[93] K. Wu, Y. Zhang, W. Hu, J. Lian, Y. Hu, Influence of ammonium polyphosphate microencapsulation on flame retardancy, thermal degradation and crystal structure of polypropylene composite, Compos Sci Technol. 81 (2013) 17–23. https://doi.org/10.1016/j.compscitech.2013.03.018.

[94] C.-L. Deng, C. Deng, J. Zhao, W.-H. Fang, L. Lin, Y.-Z. Wang, Water resistance, thermal stability, and flame retardation of polypropylene composites containing a novel ammonium polyphosphate microencapsulated by UV-curable epoxy acrylate resin, Polym Adv Technol. 25 (2014) 861–871. https://doi.org/10.1002/pat.3319.

[95] Y. Liu, M.F. Liu, D. Xie, Q. Wang, Thermoplastic polyurethane-encapsulated melamine phosphate flame retardant polyoxymethylene, Polymer - Plastics Technology and Engineering. 47 (2008) 330–334. https://doi.org/10.1080/03602550701870099.

[96] E. Kentin, H. Kaarto, An EU ban on microplastics in cosmetic products and the right to regulate, Rev Eur Comp Int Environ Law. 27 (2018) 254–266. https://doi.org/10.1111/reel.12269.

[97] J. Wang, L. Zheng, J. Li, A critical review on the sources and instruments of marine microplastics and prospects on the relevant management in China, Waste Management & Research: The Journal for a Sustainable Circular Economy. 36 (2018) 898–911. https://doi.org/10.1177/0734242X18793504.

[98] R.A. Gross, B. Kalra, Biodegradable polymers for the environment, Science (1979). 297 (2002) 803–807. https://doi.org/10.1126/science.297.5582.803.

[99] G.E. Luckachan, C.K.S. Pillai, Biodegradable Polymers- A Review on Recent Trends and Emerging Perspectives, J Polym Environ. 19 (2011) 637–676. https://doi.org/10.1007/s10924-011-0317-1.

[100] A. Ammala, Biodegradable polymers as encapsulation materials for cosmetics and personal care markets, Int J Cosmet Sci. 35 (2013) 113–124. https://doi.org/10.1111/ics.12017.

[101] I.T. Carvalho, B.N. Estevinho, L. Santos, Application of microencapsulated essential oils in cosmetic and personal healthcare products - A review, Int J Cosmet Sci. (2016). https://doi.org/10.1111/ics.12232.

[102] A.S. Luyt, S.S. Malik, Can Biodegradable Plastics Solve Plastic Solid Waste Accumulation?, in: Plastics to Energy, Elsevier, 2019: pp. 403–423. https://doi.org/10.1016/B978-0-12-813140-4.00016-9.

[103] T.P. Haider, C. Völker, J. Kramm, K. Landfester, F.R. Wurm, Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society, Angewandte Chemie - International Edition. (2019). https://doi.org/10.1002/anie.201805766.

[104] A. Yunoki, E. Tsuchiya, Y. Fukui, A. Fujii, T. Maruyama, Preparation of Inorganic/Organic Polymer Hybrid Microcapsules with High Encapsulation Efficiency by an Electrospray Technique, ACS Appl Mater Interfaces. 6 (2014) 11973–11979. https://doi.org/10.1021/am503030c.

[105] D. V. Kondratuk, L.M.A. Perdigão, A.M.S. Esmail, J.N. O'Shea, P.H. Beton, H.L. Anderson, Supramolecular nesting of cyclic polymers, Nat Chem. 7 (2015) 317–322. https://doi.org/10.1038/nchem.2182.

[106] Z. Chen, S. Li, F. Xue, G. Sun, C. Luo, J. Chen, Q. Xu, A simple and efficient route to prepare inorganic hollow microspheres using polymer particles as template in supercritical fluids, Colloids Surf A Physicochem Eng Asp. 355 (2010) 45–52. https://doi.org/10.1016/j.colsurfa.2009.11.030.

[107] S. Li, A. Pasc, V. Fierro, A. Celzard, Hollow carbon spheres, synthesis and applications – a review, J Mater Chem A Mater. 4 (2016) 12686–12713. https://doi.org/10.1039/C6TA03802F.

[108] Y. Bao, T. Wang, Q. Kang, C. Shi, J. Ma, Micelle-template synthesis of hollow silica spheres for improving water vapor permeability of waterborne polyurethane membrane, Sci Rep. 7 (2017) 46638. https://doi.org/10.1038/srep46638.

[109] Y. Lu, M. Sturek, K. Park, Microparticles produced by the hydrogel template method for sustained drug delivery, Int J Pharm. (2014). https://doi.org/10.1016/j.ijpharm.2013.11.058.

[110] F. Salaün, Microencapsulation - Processes, Technologies and Industrial Applications, IntechOpen, 2019. https://doi.org/10.5772/intechopen.73747.

[111] T.T. Morgan, H.S. Muddana, E.İ. Altinoğlu, S.M. Rouse, A. Tabaković, T. Tabouillot, T.J. Russin, S.S. Shanmugavelandy, P.J. Butler, P.C. Eklund, J.K. Yun, M. Kester, J.H. Adair, Encapsulation of Organic Molecules in Calcium Phosphate Nanocomposite Particles for Intracellular Imaging and Drug Delivery, Nano Lett. 8 (2008) 4108–4115. https://doi.org/10.1021/nl8019888.

[112] A.I. Petrov, D. V. Volodkin, G.B. Sukhorukov, Protein-Calcium Carbonate Coprecipitation: A Tool for Protein Encapsulation, Biotechnol Prog. 21 (2008) 918–925. https://doi.org/10.1021/bp0495825.

[113] H. Zhang, X. Wang, D. Wu, Silica encapsulation of n-octadecane via sol–gel process: A novel microencapsulated phase-change material with enhanced thermal conductivity and performance, J Colloid Interface Sci. 343 (2010) 246–255. https://doi.org/10.1016/j.jcis.2009.11.036.

[114] S. Liang, Q. Li, Y. Zhu, K. Chen, C. Tian, J. Wang, R. Bai, Nanoencapsulation of n-octadecane phase change material with silica shell through interfacial hydrolysis and polycondensation in miniemulsion, Energy. 93 (2015) 1684–1692. https://doi.org/10.1016/j.energy.2015.10.024.

[115] J. Yuan, W. Xing, G. Gu, L. Wu, The properties of organic pigment encapsulated with nano-silica via layer-by-layer assembly technique, Dyes and Pigments. 76 (2008) 463–469. https://doi.org/10.1016/j.dyepig.2006.10.002.

[116] F.Y. de Boer, A. Imhof, K.P. Velikov, Encapsulation of colorants by natural polymers for food applications, Coloration Technology. (2019). https://doi.org/10.1111/cote.12393.

[117] Encapsulated nanoscale particles of organic pigments, 2009 CA2728758A1, Canada, n.d.

[118] O.F.O. Pgments, Encapsulated nanoscale particles of organic pigments, 2014 US8815394B2, United States, 2014.

[119] J.H. Friedmann, Thomas E.; Lumsdom Simon Owen; Green, Encapsulation of oils by coacervation, WIPO Patent. 1 (2009) 13.

[120] J. Kozlowska, W. Prus, N. Stachowiak, Microparticles based on natural and synthetic polymers for cosmetic applications, Int J Biol Macromol. 129 (2019) 952–956. https://doi.org/10.1016/j.ijbiomac.2019.02.091.

[121] S.Y. Byeon, M.K. Cho, K.H. Shim, H.J. Kim, H.G. Song, H.S. Shin, Development of a Spirulina Extract/Alginate-Imbedded PCL Nanofibrous Cosmetic Patch., J Microbiol Biotechnol. 27 (2017) 1657–1663. https://doi.org/10.4014/jmb.1701.01025.

[122] S.A. Adli, F. Ali, A.S. Azmi, H. Anuar, N.A.M. Nasir, R. Hasham, M.K.H. Idris, Development of biodegradable cosmetic patch using a polylactic acid/phycocyanin-alginate composite, Polymers (Basel). 12 (2020). https://doi.org/10.3390/POLYM12081669.

[123] I.M. Martins, M.F. Barreiro, M. Coelho, A.E. Rodrigues, Microencapsulation of essential oils with biodegradable polymeric carriers for cosmetic applications, Chemical Engineering Journal. 245 (2014) 191–200. https://doi.org/10.1016/j.cej.2014.02.024.

[124] I. Bureau, Nanopartices for cosmetic applications, 2012, WO2012101638A2, 2012.

[125] S. Bin Bae, H.C. Nam, W.H. Park, Electrospraying of environmentally sustainable alginate microbeads for cosmetic additives, Int J Biol Macromol. 133 (2019) 278–283. https://doi.org/10.1016/j.ijbiomac.2019.04.058.

[126] X. Wang, E. Wenk, X. Hu, G.R. Castro, L. Meinel, X. Wang, C. Li, H. Merkle, D.L. Kaplan, Silk coatings on PLGA and alginate microspheres for protein delivery, Biomaterials. 28 (2007) 4161–4169. https://doi.org/10.1016/j.biomaterials.2007.05.036.

[127] J.A. Burdick, C. Chung, X. Jia, M.A. Randolph, R. Langer, Controlled Degradation and Mechanical Behavior of Photopolymerized Hyaluronic Acid Networks, Biomacromolecules. 6 (2005) 386–391. https://doi.org/10.1021/bm049508a.

[128] R. Elia, J. Guo, S. Budijono, V. Normand, D. Benczédi, F. Omenetto, D.L. Kaplan, Encapsulation of volatile compounds in silk microparticles, J Coat Technol Res. (2015). https://doi.org/10.1007/s11998-015-9668-1.

[129] E.M. Pritchard, V. Normand, X. Hu, S. Budijono, D. Benczédi, F. Omenetto, D.L. Kaplan, Encapsulation of oil in silk fibroin biomaterials, J Appl Polym Sci. 131 (2014). https://doi.org/10.1002/app.39990.

[130] P. Sarazin, X. Roy, B.D. Favis, Controlled preparation and properties of porous poly(l-lactide) obtained from a co-continuous blend of two biodegradable polymers, Biomaterials. 25 (2004) 5965–5978. https://doi.org/10.1016/j.biomaterials.2004.01.065.

[131] M.P. Neubauer, M. Poehlmann, A. Fery, Microcapsule mechanics: From stability to function, Adv Colloid Interface Sci. 207 (2014) 65–80. https://doi.org/10.1016/j.cis.2013.11.016.

[132] J. Rydz, W. Sikorska, M. Kyulavska, D. Christova, Polyester-Based (Bio)degradable Polymers as Environmentally Friendly Materials for Sustainable Development, Int J Mol Sci. 16 (2014) 564–596. https://doi.org/10.3390/ijms16010564.

[133] P. L, Microcapsules PCL with Essential Oil Citronella, Advances in Tissue Engineering & Regenerative Medicine: Open Access. (2017). https://doi.org/10.15406/atroa.2017.02.00024.

[134] J.O. Akolade, M. Balogun, A. Swanepoel, R.B. Ibrahim, A.A. Yusuf, P. Labuschagne, Microencapsulation of eucalyptol in polyethylene glycol and polycaprolactone using particles from gas-saturated solutions, RSC Adv. 9 (2019) 34039–34049. https://doi.org/10.1039/C9RA06419B.

[135] H. Majeed, Y.-Y. Bian, B. Ali, A. Jamil, U. Majeed, Q.F. Khan, K.J. Iqbal, C.F. Shoemaker, Z. Fang, Essential oil encapsulations: uses, procedures, and trends, RSC Adv. (2015). https://doi.org/10.1039/c5ra06556a.

[136] B. Solomon, F.F. Sahle, T. Gebre-Mariam, K. Asres, R.H.H. Neubert, Microencapsulation of citronella oil for mosquito-repellent application: Formulation and in vitro permeation

studies, European Journal of Pharmaceutics and Biopharmaceutics. 80 (2012) 61–66. https://doi.org/10.1016/j.ejpb.2011.08.003.

[137] R. Sharma, R. Rao, S. Kumar, S. Mahant, S. Khatkar, Therapeutic Potential of Citronella Essential Oil: A Review, Curr Drug Discov Technol. 16 (2019) 330–339. https://doi.org/10.2174/1570163815666180718095041.

[138] F.M. Bezerra, O.G. Carmona, C.G. Carmona, M.J. Lis, F.F. de Moraes, Controlled release of microencapsulated citronella essential oil on cotton and polyester matrices, Cellulose. 23 (2016) 1459–1470. https://doi.org/10.1007/s10570-016-0882-5.

[139] Z. Zhu, T. Min, X. Zhang, Y. Wen, Microencapsulation of Thymol in Poly(lactide-co-glycolide) (PLGA): Physical and Antibacterial Properties, Materials. 12 (2019) 1133. https://doi.org/10.3390/ma12071133.

[140] E.-H. Kim, H.-K. Kim, Y.-J. Ahn, Acaricidal Activity of Clove Bud Oil Compounds against Dermatophagoides farinae and Dermatophagoides pteronyssinus (Acari: Pyroglyphidae), J Agric Food Chem. 51 (2003) 885–889. https://doi.org/10.1021/jf0208278.

[141] J.R. Kim, S. Sharma, Acaricidal activities of clove bud oil and red thyme oil using microencapsulation against HDMs, J Microencapsul. 28 (2011) 82–91. https://doi.org/10.3109/02652048.2010.529949.

[142] M.G. de Morais, E.G. de Morais, B. da Silva Vaz, C.F. Gonçalves, C. Lisboa, J.A. Vieira Costa, Nanoencapsulation of the Bioactive Compounds of Spirulina with a Microalgal Biopolymer Coating, J Nanosci Nanotechnol. 16 (2016) 81–91. https://doi.org/10.1166/jnn.2016.10899.

[143] H. Jiang, M. Zhang, S. McKnight, B. Adhikari, Microencapsulation of α-Amylase by Carrying Out Complex Coacervation and Drying in a Single Step Using a Novel Three-Fluid Nozzle Spray Drying, Drying Technology. 31 (2013) 1901–1910. https://doi.org/10.1080/07373937.2013.771365.

[144] L.R. Castilho, D.A. Mitchell, D.M.G. Freire, Production of polyhydroxyalkanoates (PHAs) from waste materials and by-products by submerged and solid-state fermentation, Bioresour Technol. (2009). https://doi.org/10.1016/j.biortech.2009.03.088.

[145] F. Masood, Polyhydroxyalkanoates in the Food Packaging Industry, in: Nanotechnology Applications in Food, Elsevier, 2017: pp. 153–177. https://doi.org/10.1016/B978-0-12-811942-6.00008-X.

[146] T. Keshavarz, I. Roy, Polyhydroxyalkanoates: bioplastics with a green agenda, Curr Opin Microbiol. 13 (2010) 321–326. https://doi.org/10.1016/j.mib.2010.02.006.

[147] Y. Konuklu, H.O. Paksoy, The Preparation and Characterization of Chitosan-Gelatin Microcapsules and Microcomposites with Fatty Acids as Thermal Energy Storage Materials, Energy Technology. 3 (2015) 503–508. https://doi.org/10.1002/ente.201402178.

[148] M.G. Eugene N. Chernowsky, Anhydrous cosmetic compositions for thermal skin treatments, 1988, Patent No. 4751075, USA, 1988.

[149] F.N. Rudolf Tuma, Cosmetic composition containing anethoxylated glyceride mixture, 1976, Petent No. 34003 USA, 1976.

[150] D. Klamann, Lubricants and related products. Synthesis, properties, applications, international standards, WO2016/109382Al, 2016, 1984.

[151] F.N. Niyonzima, S.S. More, Detergent-Compatible Bacterial Amylases, Appl Biochem Biotechnol. (2014). https://doi.org/10.1007/s12010-014-1144-3.

[152] T.T. Mong Thu, W. Krasaekoopt, Encapsulation of protease from Aspergillus oryzae and lipase from Thermomyces lanuginoseus using alginate and different copolymer types, Agriculture and Natural Resources. 50 (2016) 155–161. https://doi.org/10.1016/j.anres.2016.06.002.

[153] D.F. Do Nascimento, J.A. Avendaño, A. Mehl, M.J.B. Moura, M.S. Carvalho, W.J. Duncanson, Flow of Tunable Elastic Microcapsules through Constrictions, Sci Rep. 7 (2017) 1–7. https://doi.org/10.1038/s41598-017-11950-2.

[154] M.F. Thorne, F. Simkovic, A.G. Slater, Production of monodisperse polyurea microcapsules using microfluidics, Sci Rep. 9 (2019) 17983. https://doi.org/10.1038/s41598-019-54512-4.

[155] W.J. Duncanson, T.E. Kodger, S. Babaee, G. Gonzalez, D.A. Weitz, K. Bertoldi, Microfluidic fabrication and micromechanics of permeable and impermeable elastomeric microbubbles, Langmuir. 31 (2015) 3489–3493. https://doi.org/10.1021/la504843p.

[156] X.-T. Mu, Y. Li, X.-J. Ju, X.-L. Yang, R. Xie, W. Wang, Z. Liu, L.-Y. Chu, Microfluidic Fabrication of Structure-Controlled Chitosan Microcapsules via Interfacial Cross-Linking of Droplet Templates, ACS Applied Materials & Interfaces. 0 (2020) acsami.0c14656. https://doi.org/10.1021/acsami.0c14656.

[157] G. Sun, Z. Zhang, Mechanical strength of microcapsules made of different wall materials, Int J Pharm. 242 (2002) 307–311. https://doi.org/10.1016/S0378-5173(02)00193-X.

[158] G. Du, J. Hu, J. Zhou, G. Wang, S. Guan, H. Liu, M. Geng, C. Lü, Y. Ming, J. Qu, The study on the mechanical properties of PU/MF double shell self-healing microcapsules, Chin J Chem Eng. 28 (2020) 1459–1473. https://doi.org/10.1016/j.cjche.2020.03.003.

[159] D. Poncelet, R.J. Neufeld, Shear breakage of nylon membrane microcapsules in a turbine reactor, Biotechnol Bioeng. 33 (1989) 95–103. https://doi.org/10.1002/bit.260330113.

[160] A. Aniskevich, V. Kulakov, O. Bulderberga, P. Knotek, J. Tedim, F. Maia, V. Leisis, D. Zeleniakiene, Experimental characterisation and modelling of mechanical behaviour of microcapsules, J Mater Sci. 55 (2020) 13457–13471. https://doi.org/10.1007/s10853-020-04925-8.

[161] B. Thu, P. Bruheim, T. Espevik, O. Smidsrød, P. Soon-Shiong, G. Skjåk-Bræk, Alginate polycation microcapsules: I. Interaction between alginate and polycation, Biomaterials. 17 (1996) 1031–1040. https://doi.org/10.1016/0142-9612(96)84680-1.

[162] O. Gåserød, A. Sannes, G. Skjåk-Bræk, Microcapsules of alginate-chitosan. II. A study of capsule stability and permeability, Biomaterials. 20 (1999) 773–783. https://doi.org/10.1016/S0142-9612(98)00230-0.

[163] J.M. Van Raamsdonk, P.L. Chang, Osmotic pressure test: A simple, quantitative method to assess the mechanical stability of alginate microcapsules, J Biomed Mater Res. 54 (2001) 264–271. https://doi.org/10.1002/1097-4636(200102)54:2<264::AID-JBM14>3.0.CO;2-7.

[164] W.A. Ducker, T.J. Senden, R.M. Pashley, Direct measurement of colloidal forces using an atomic force microscope, Nature. 353 (1991) 239–241. https://doi.org/10.1038/353239a0.

[165] A. Fery, R. Weinkamer, Mechanical properties of micro- and nanocapsules: Single-capsule measurements, Polymer (Guildf). 48 (2007) 7221–7235. https://doi.org/10.1016/j.polymer.2007.07.050.

[166] A. Rahmat, J. Meng, D.R. Emerson, C.-Y. Wu, M. Barigou, A. Alexiadis, A practical approach for extracting mechanical properties of microcapsules using a hybrid numerical model, Microfluid Nanofluidics. 25 (2021) 1. https://doi.org/10.1007/s10404-020-02401-y.

[167] H. Minato, Y. Nishizawa, T. Uchihashi, D. Suzuki, Thermoresponsive structural changes of single poly(N-isopropyl acrylamide) hydrogel microspheres under densely packed conditions on a solid substrate, Polym J. 52 (2020) 1137–1141. https://doi.org/10.1038/s41428-020-0372-3.

[168] V. V. Lulevich, D. Andrienko, O.I. Vinogradova, Elasticity of polyelectrolyte multilayer microcapsules, Journal of Chemical Physics. 120 (2004) 3822–3826. https://doi.org/10.1063/1.1644104.

[169] F. Dubreuil, N. Elsner, A. Fery, Elastic properties of polyelectrolyte capsules studied by atomic-force microscopy and RICM, European Physical Journal E. 12 (2003) 215–221. https://doi.org/10.1140/epje/i2003-10056-0.

[170] R. Han, X. Wang, G. Zhu, N. Han, F. Xing, Investigation on viscoelastic properties of urea-formaldehyde microcapsules by using nanoindentation, Polym Test. 80 (2019) 106146. https://doi.org/10.1016/j.polymertesting.2019.106146.

[171] Z. Zhang, J.D. Stenson, C.R. Thomas, Chapter 2 Micromanipulation in Mechanical Characterisation of Single Particles, Advances in Chemical Engineering. 37 (2009) 29–85. https://doi.org/10.1016/S0065-2377(09)03702-8.

[172] A.W. Jay, M.A. Edwards, Mechanical properties of semipermeable microcapsules., Can J Physiol Pharmacol. 46 (1968) 731–737. https://doi.org/10.1139/y68-114.

[173] C.T. Lim, E.H. Zhou, A. Li, S.R.K. Vedula, H.X. Fu, Experimental techniques for single cell and single molecule biomechanics, Materials Science and Engineering C. 26 (2006) 1278–1288. https://doi.org/10.1016/j.msec.2005.08.022.

[174] L.K. Fiddes, H.K.C. Chan, K. Wyss, C.A. Simmons, E. Kumacheva, A.R. Wheeler, Augmenting microgel flow viareceptor-ligand binding in the constrained geometries of microchannels, Lab Chip. 9 (2009) 286–290. https://doi.org/10.1039/B807106C.

[175] F. Edwards-Lévy, M.C. Lévy, Serum albumin-alginate coated beads: Mechanical properties and stability, Biomaterials. 20 (1999) 2069–2084. https://doi.org/10.1016/S0142-9612(99)00111-8.

[176] N. Mohammadi, M.R. Ehsani, H. Bakhoda, Design and Evaluation of the Release Characteristics of Caffeine-Loaded Microcapsules in a Medicated Chewing Gum Formulation, Food Biophys. 13 (2018) 240–249. https://doi.org/10.1007/s11483-018-9530-y.

[177] S. Rosiński, G. Grigorescu, D. Lewińska, L.G. Ritzén, H. Viernstein, E. Teunou, D. Poncelet, Z. Zhang, X. Fan, D. Serpy, I. Marison, D. Hunkeler, Characterization of microcapsules: Recommended methods based on round-robin testing, J Microencapsul. 19 (2002) 641–659. https://doi.org/10.1080/02652040210142533.

[178] Z. Zhang, R. Saunders, C.R. Thomas, Mechanical strength of single microcapsules determined by a novel micromanipulation technique, J Microencapsul. 16 (1999) 117–124. https://doi.org/10.1080/026520499289365.

[179] G. Sun, Z. Zhang, Mechanical properties of melamine-formaldehyde microcapsules, J Microencapsul. 18 (2001) 593–602. https://doi.org/10.1080/02652040010019541.

[180] T. Liu, Z. Zhang, Mechanical Properties of Desiccated Ragweed Pollen Grains Determined by Micromanipulation and Theoretical Modelling, Biotechnol Bioeng. 85 (2004) 770–775. https://doi.org/10.1002/bit.10908.

[181] L. Zhao, Z. Zhang, Mechanical Characterization of Biocompatible Microspheres and Microcapsules by Direct Compression, in: Artif Cells Blood Substit Immobil Biotechnol, Artif Cells Blood Substit Immobil Biotechnol, 2004: pp. 25–40. https://doi.org/10.1081/BIO-120028666.

[182] J.T. Chung, K.D.F. Vlugt-Wensink, W.E. Hennink, Z. Zhang, Effect of polymerization conditions on the network properties of dex-HEMA microspheres and macro-hydrogels, Int J Pharm. 288 (2005) 51–61. https://doi.org/10.1016/j.ijpharm.2004.09.011.

[183] S.F. Yap, M.J. Adams, J.P.K. Seville, Z. Zhang, Single and bulk compression of pharmaceutical excipients: Evaluation of mechanical properties, Powder Technol. 185 (2008) 1–10. https://doi.org/10.1016/j.powtec.2007.09.005.

[184] R. Wei, T. Tiso, J. Bertling, K. O'Connor, L.M. Blank, U.T. Bornscheuer, Possibilities and limitations of biotechnological plastic degradation and recycling, Nat Catal. 3 (2020) 867–871. https://doi.org/10.1038/s41929-020-00521-w.

Figure captions

Figure 1. Microplastic definition, main sources.

Figure 2. Microplastic in the ecosystem, direct and indirect delivery routes.

Figure 3. Capsule morphologies, a) continuous shells/core capsules, b) continuous core capsules with more than one layer of the capsule wall material, c) polycore capsules, d) matrix capsules.

Figure 4. Methods of capsule preparation, size ranges.

Figure 5. Polymer materials for capsule shells, a) melamine-formaldehyde polymer; b) phenol-formaldehyde polymer; c) polyurethane; d) polyurea; e) polyacrylate; f) poly(methyl methacrylate); g) poly(vinyl alcohol); h) chitosan; i) calcium alginate; j) polycaprolactone; k) gelatine; l) poly(lactide-co-glycolide) acid; m) polylactic acid; n) poly(glycolic acid); o) poly(propylene fumarate).

Figure 6. Polymerization routes of polyurethane, melamine and phenolic polymers, phenol-formaldehyde polymer; melamine-formaldehyde polymer; poly(ether-urethane-urea).

Figure 7. Biodegradable materials for microcapsule production: PLA: poly(2-hydroxypropionic acid), PLGA: poly(lactide-co-glycolide) acid, PLLA: poly (L-lactic acid), PCL: poly(ε-caprolactone), PGA: poly(glycolic acid), PPF: poly(propylene fumarate).

Figure 8. Examples of reactions involving chitosan-based crosslinked polymers, crosslinked chitosan and crosslinked chitosan-gelatine.

Fig 1

Primary source

MICROPLASTIC

Secondary source

Small polymers additives

⇒ intentional production of personal care products, textiles, medicines, etc.

Smalller than 5 mm in size

Plastic products fragmentation

⇒ time-dependent larger plastic degradation

Fig 2

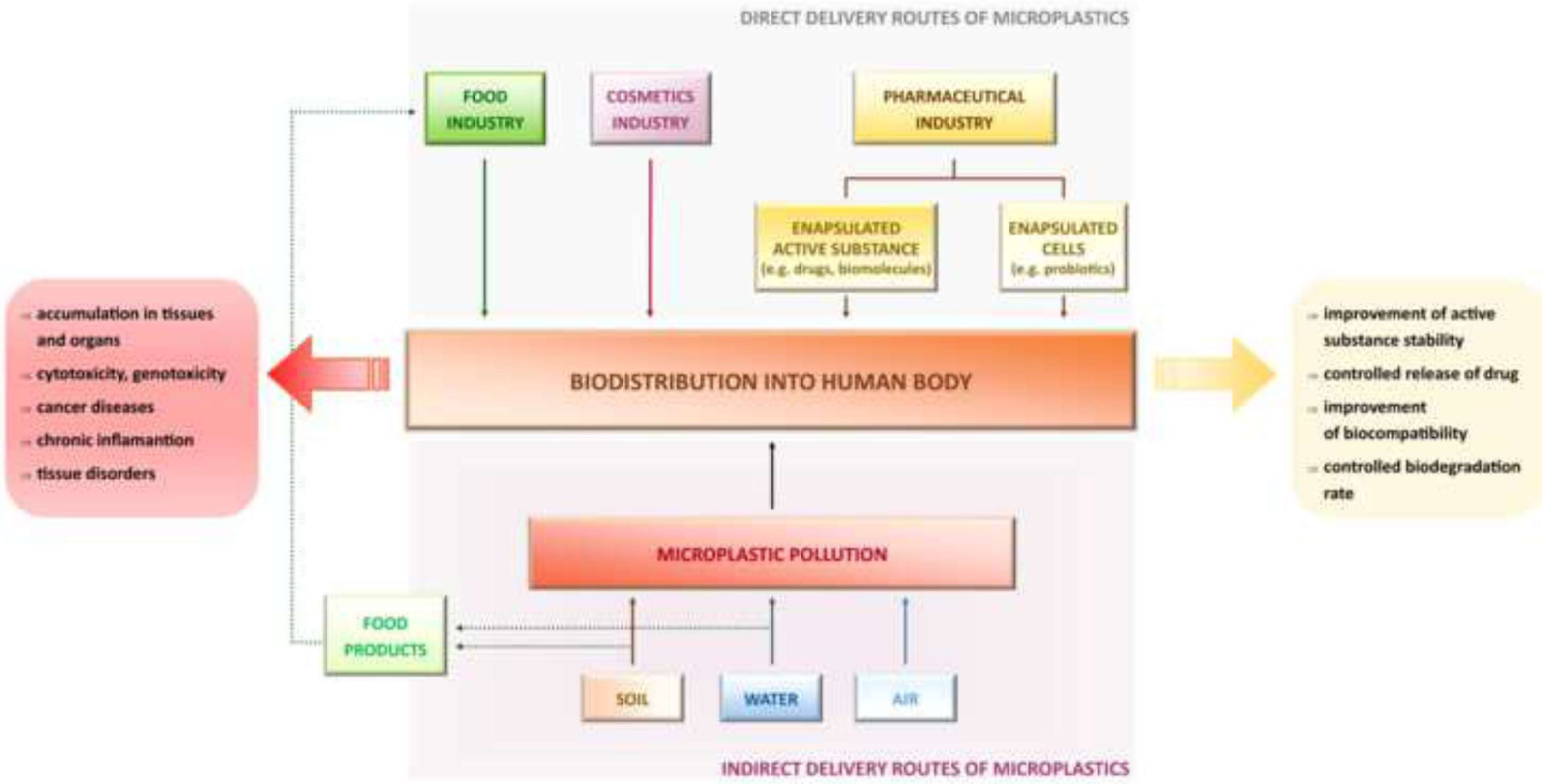

DIRECT DELIVERY ROUTES OF MICROPLASTICS
FOOD INDUSTRY
COSMETICS INDUSTRY
PHARMACEUTICAL INDUSTRY
ENAPSULATED ACTIVE SUBSTANCE (e.g. drugs, biomolecules)
ENAPSULATED CELLS (e.g. probiotics)
accumulation in tissues and organs
cytotoxicity, genotoxicity
cancer diseases
chronic inflamantion
tissue disorders
BIODISTRIBUTION INTO HUMAN BODY
improvement of active substance stability
controlled release of drug
improvement of biocompatibility
controlled biodegradation rate
MICROPLASTIC POLLUTION
FOOD PRODUCTS
SOIL
WATER
AIR
INDIRECT DELIVERY ROUTES OF MICROPLASTICS

Fig 3

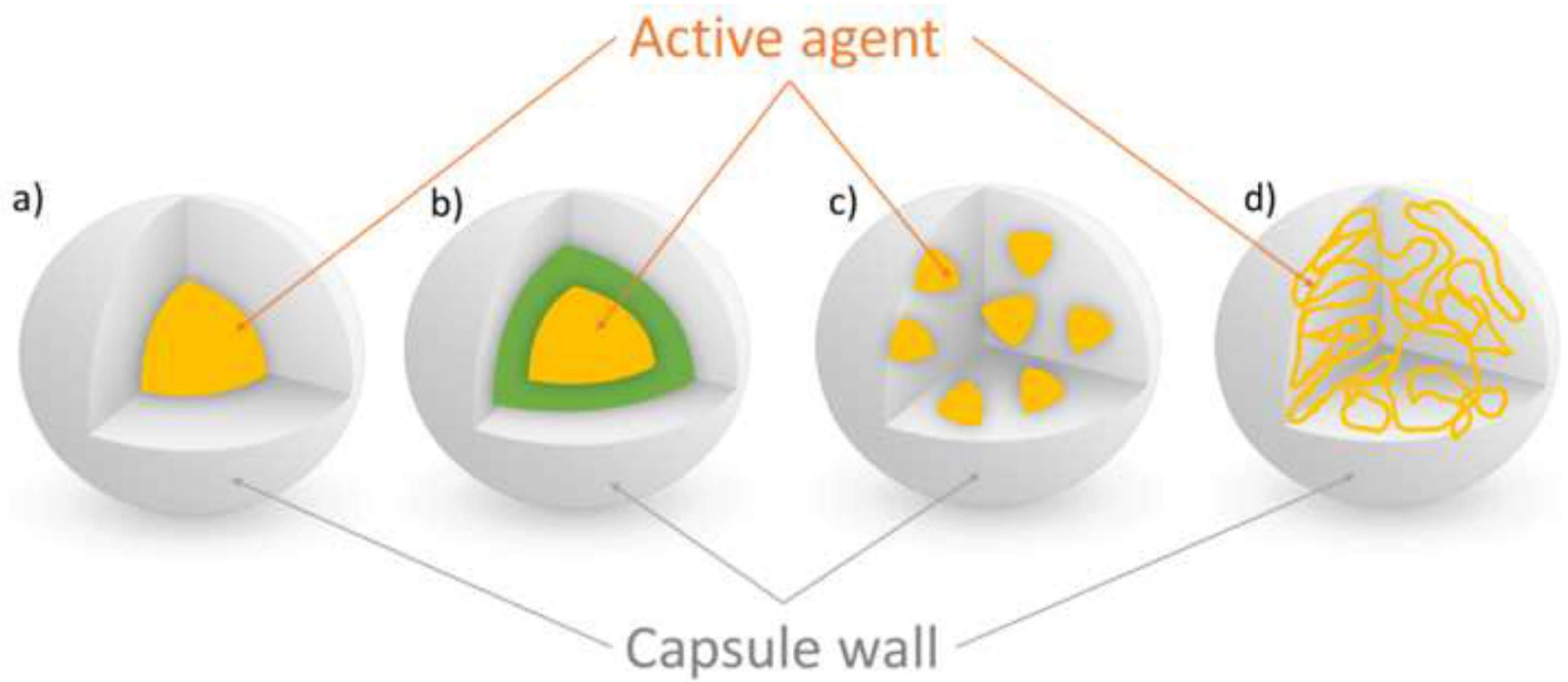


Fig 4

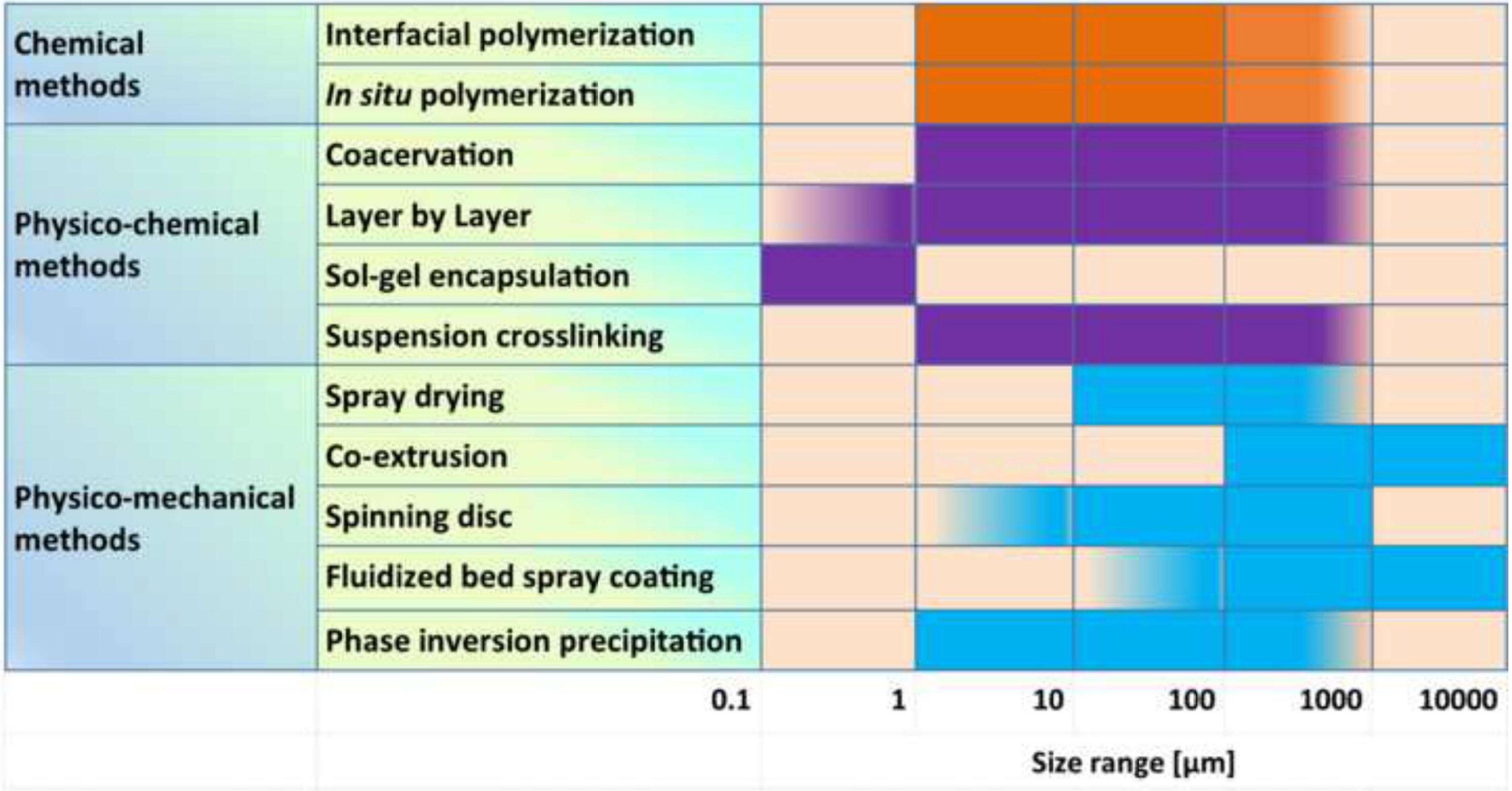

Chemical methods
Interfacial polymerization
In situ polymerization
Physico-chemical methods
Coacervation
Layer by Layer
Sol-gel encapsulation
Suspension crosslinking
Physico-mechanical methods
Spray drying
Co-extrusion
Spinning disc
Fluidized bed spray coating
Phase inversion precipitation
0.1
1
10
100
1000
10000
Size range [µm]

Fig 5

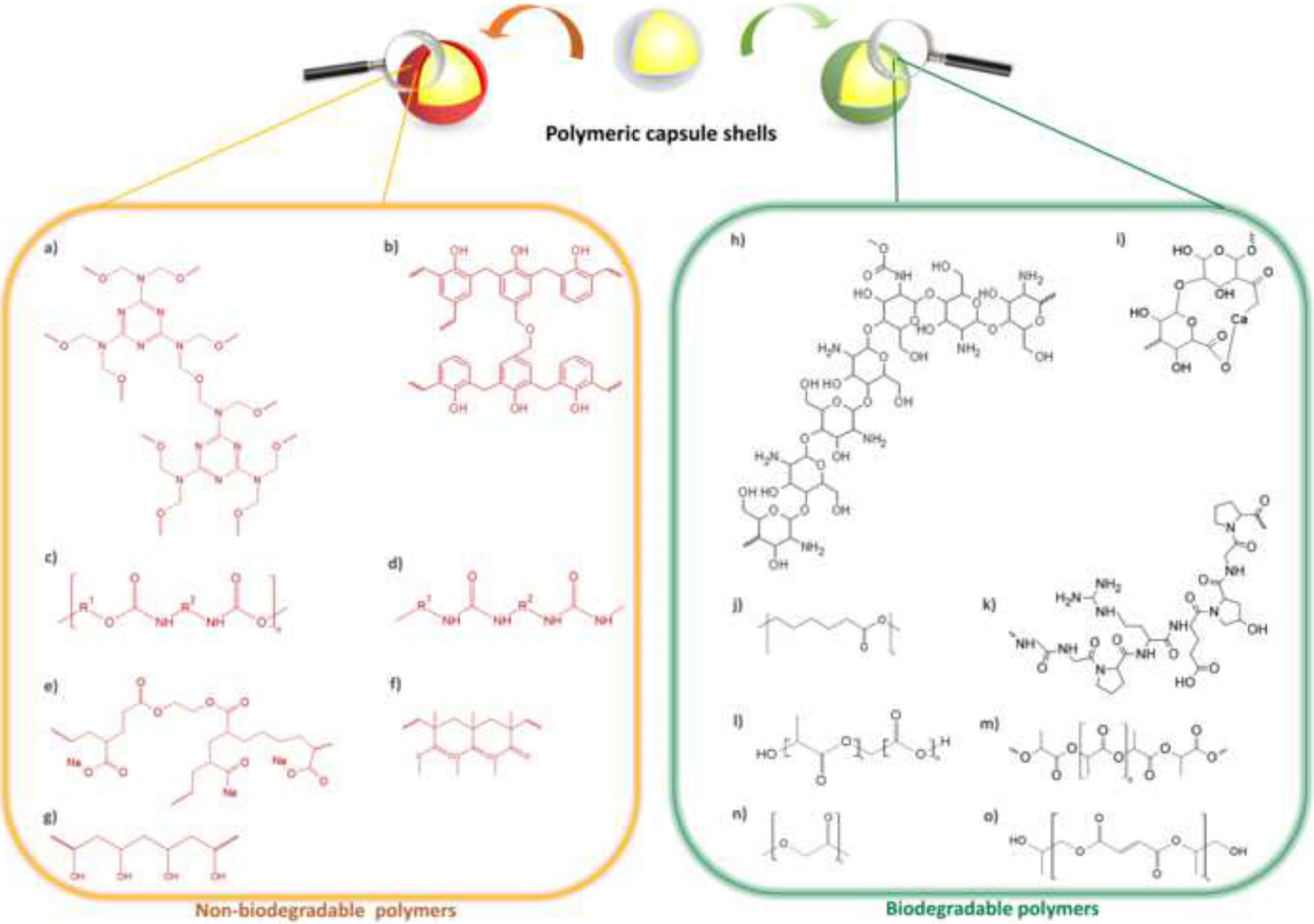

Polymeric capsule shells
a)
b)
c)
d)
e)
f)
g)
Non-biodegradable polymers
h)
i)
j)
k)
l)
m)
n)
o)
Biodegradable polymers

Fig 6

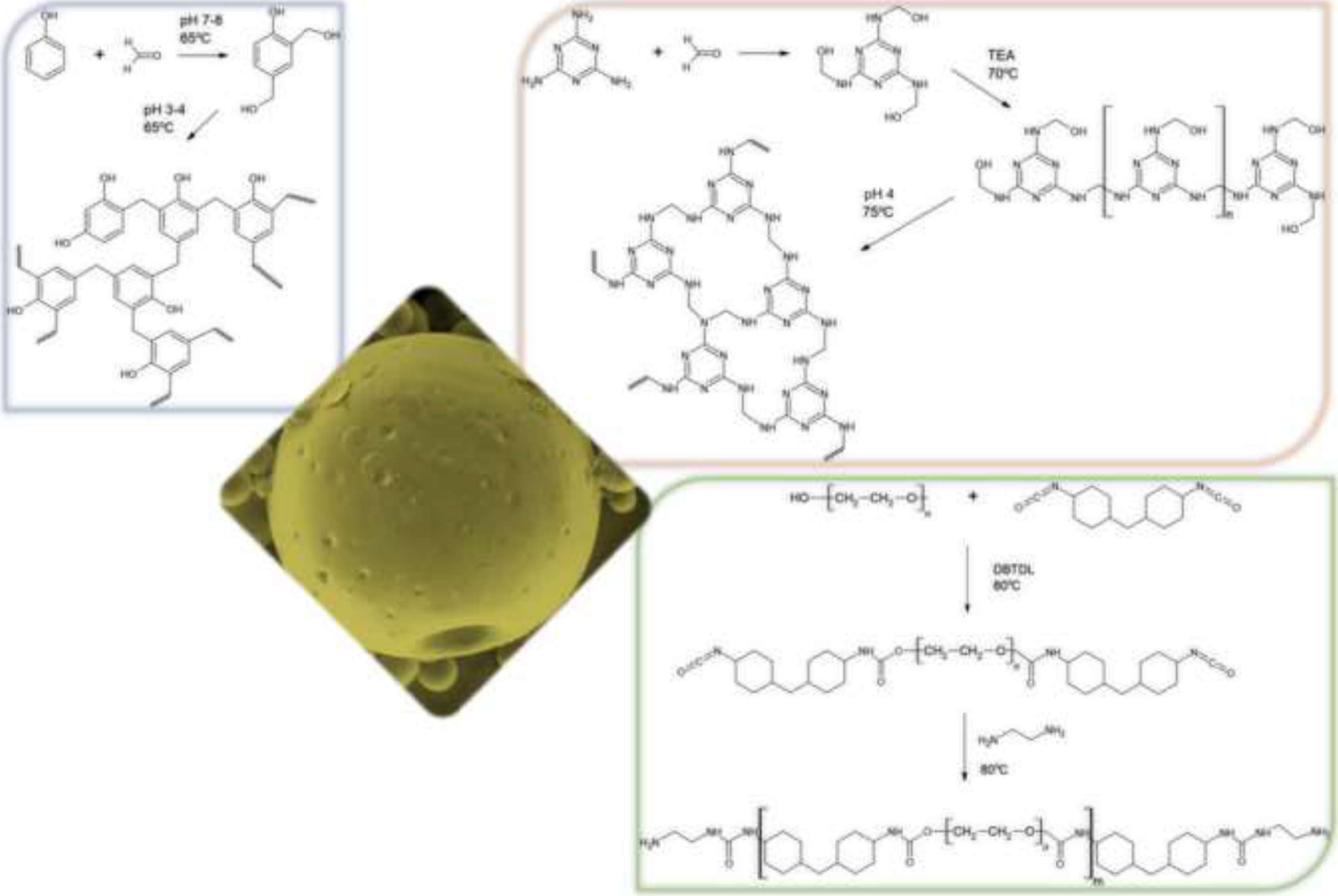


Fig 7

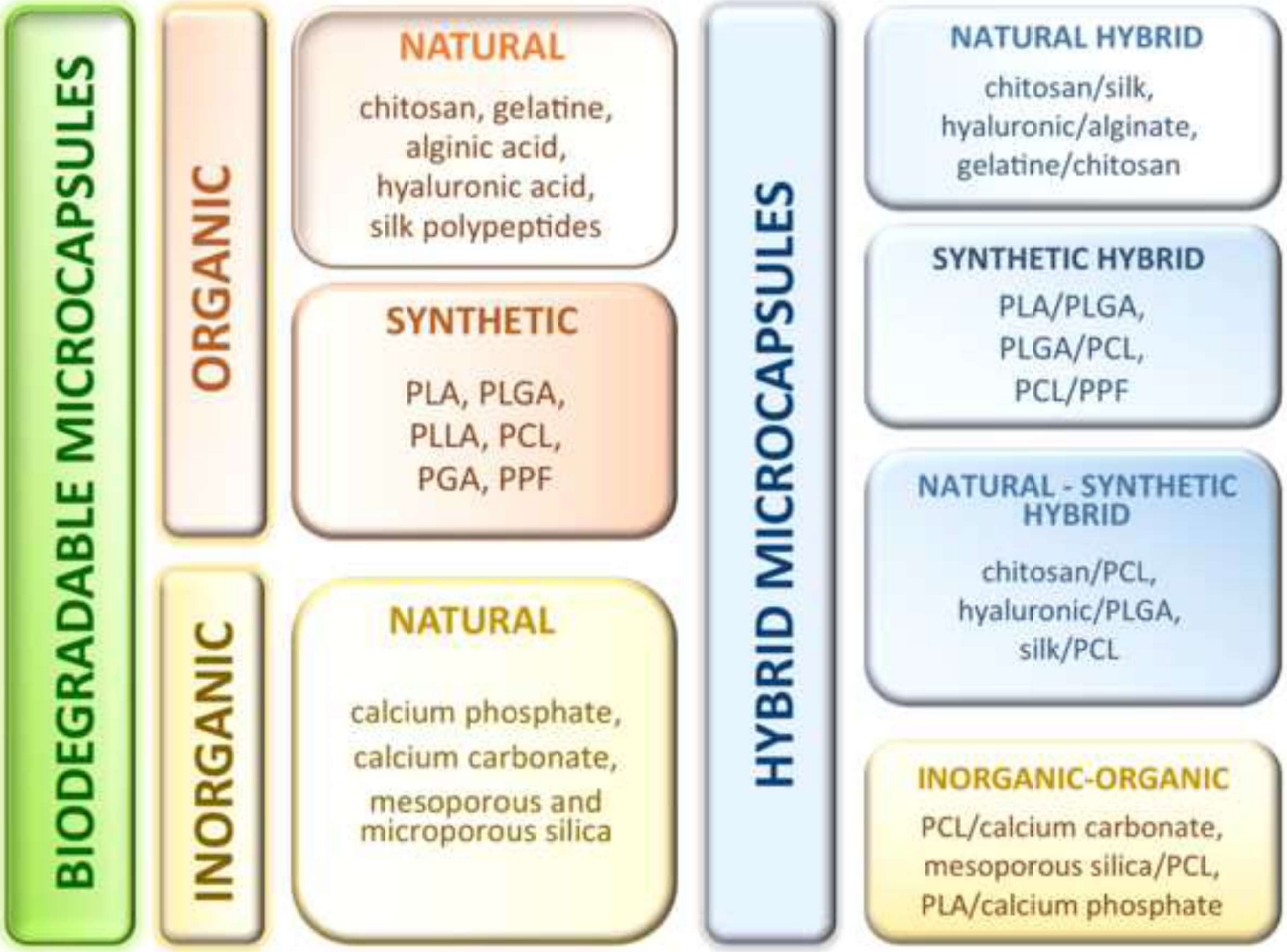
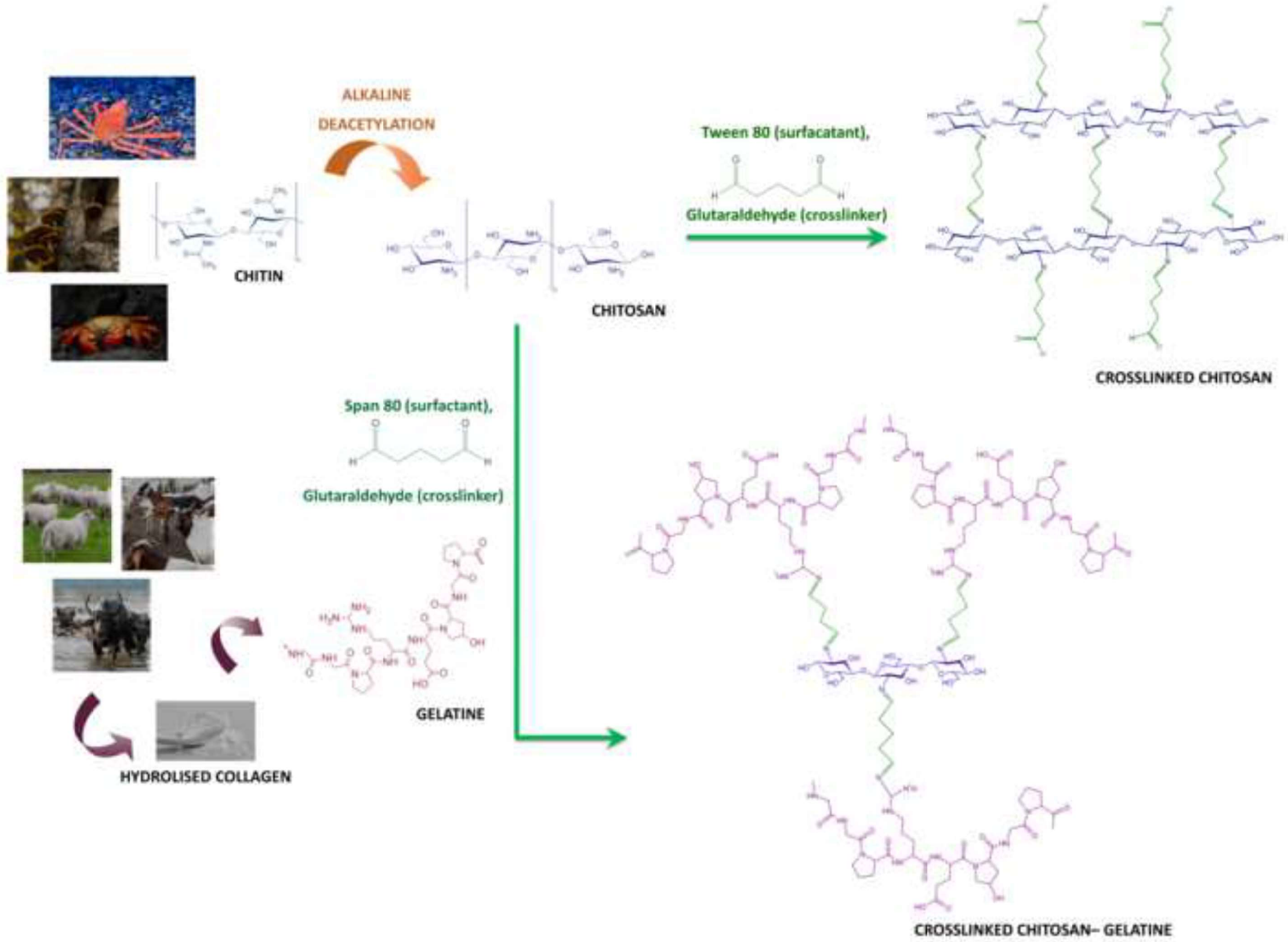

BIODEGRADABLE MICROCAPSULES
ORGANIC
INORGANIC
NATURAL
chitosan, gelatine, alginic acid, hyaluronic acid, silk polypeptides
SYNTHETIC
PLA, PLGA, PLLA, PCL, PGA, PPF
NATURAL
calcium phosphate, calcium carbonate, mesoporous and microporous silica
HYBRID MICROCAPSULES
NATURAL HYBRID
chitosan/silk, hyaluronic/alginate, gelatine/chitosan
SYNTHETIC HYBRID
PLA/PLGA, PLGA/PCL, PCL/PPF
NATURAL - SYNTHETIC HYBRID
chitosan/PCL, hyaluronic/PLGA, silk/PCL
INORGANIC-ORGANIC
PCL/calcium carbonate, mesoporous silica/PCL, PLA/calcium phosphate

Fig 8


ALKALINE
DEACETYLATION
CHITIN
CHITOSAN
Tween 80 (surfacatant),
Glutaraldehyde (crosslinker)
CROSSLINKED CHITOSAN
Span 80 (surfactant),
Glutaraldehyde (crosslinker)
GELATINE
HYDROLISED COLLAGEN
CROSSLINKED CHITOSAN– GELATINE

Declaration of Interest Statement

Declaration of interests

☐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 paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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