Synthesis by interfacial polycondensation of polyamide capsules with various sizes. Characteristics and properties.

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Abstract

Polyamide capsules are synthetized by interfacial polycondensation in an inverse dispersion (water in oil). Four processes are developped to obtain capsules of various sizes (plane films: Ø=∞ ; millicapsules: Ø=1-5mm ; minicapsules: Ø=100-300µm ; microcapsules: Ø=1-10µm). Capsules have been characterized by various techniques: their size by granulometry, their weight composition by gravimetry and their structure and the thickness of the membrane by microscopy investigations (SEM). The dry polyamide represents only 6 to 10% of the total mass of the capsules, the rest is water. All capsules are hollow particules. The membrane presents a disymetric structure, smooth for the aqueous phase, heterogenous for the organic phase and alveolar for the cross section. The membrane thickness depends on the reaction conditions and on the capsule size. The capsules properties are studied on the minicapsules. Capsules are permeable: 80% of the initial encapsulated poly(ethylenimine) (Mw= 70 000g/mol) are released out in 3 months. Capsules are breakable: they are all destroyed after 5mn of ultrasonic irradiation (power 80W).

Introduction

The encapsulation creates growing consideration for a lot of applications in the industrial field (depollution, catalysis, ...) as well as commun use (cosmetology, pharmacology, ...). The capsules, generally obtained by interfacial polycondensation in dispersed media, are hollow particules (diameter between 50nm and 1mm) with a polymeric membrane. They are able to isolate and to protect an active ingredient and to control its release by diffusion or by breaking. The chemical nature and the crosslinking of the polycondensate have an influence on the membrane structure and the capsules properties. For a better understanding of the formation mechanisms of the capsule membrane, we study, in this article, the membrane characteristics (structure and weight composition) and the release properties (permeability and mechanical strength) of polyamide capsules synthetized by interfacial polycondensation in an inverse dispersion. All works on the characteristics and the properties of capsules **[1,2,3]** are essentialy done with capsules having a very small diameter (in order of µm). These caracterization is subject to handling problems due to the small particules dimensions. This encourage us to synthesize model capsules having a bigger size (in order of mm) which allow the study of the permeability properties (release) and the mechanical strength (breaking) with usual methods. To get a model membrane, we synthesize plane films. Some characteristics and properties of them are known **[4,5]**. We study the evolution of the membrane structure in function of the particules diameter.

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Synthesis processes

Capsules membranes are obtained in a two steps synthesis. First the dispersion: an aqueous solution (**Sol.1**) of a diamine (1,6-hexamethylenediamine) and an acid quentcher (sodium hydrogenocarbonate) is dispersed in cyclohexane (**Sol.2**) containing a surfactant (triblock copolymer: lipophilic-hydrophilic-lipophilic, Hypermer B261, from ICI). Then the polycondensation: after the stabilisation of the dispersion (5mn), a solution (**Sol.3**) of diacid chloride (terephtaloyl chloride) and, in some cases, triacid chloride (1,3,5-benzenetricarbonyl trichloride) in cyclohexane, containing the same concentration of surfactant as **Sol.2**, is added. Rapidly, the polymer, obtained by the polycondensation of the monomers, precipitates at the interface and formes the capsule membrane. The reaction goes on by diffusion of one of the monomers through these membrane. When the reaction is finished, the capsules are washed with cyclohexane, with aqueous solutions of a surfactant (Tween 20 ; 5 and 2%) and then with water. They are sifted and stored in an aqueous solution of an antibacterial agent (sodium azide). The capsules size is function of the stirring speed of the dispersion step and the surfactant concentration in the organic phase. The membrane thickness is function of the reaction time.

Model capsules :

Plane films (Ø=∞). The plane films are elaborated in an apparatus developped in our laboratory. In a flat bottom reactor containing **Sol.2**, **Sol.1** or cyclohexane is added slowly. When the interface is stabilized, **Sol.3** is added very carefully to prevent any movement of the interface. With this apparatus, it is possible to obtain plane film without surfactant, with surfactant in the organic phase (similar to the inverse dispersion: water in oil) or with surfactant in the aqueous phase (similar to the direct dispersion: oil in water). The two phases, one phase or none can be stirred (from 1 to 40rpm).

Millicapsules (Ø=1-5mm). The millicapsules are elaborated in an apparatus developped in our laboratory **[6]**. At the top of a long glass column containing **Sol.3,** a drop of **Sol.1,** formed at the end of a needle, is let falling and collected at the bottom of the column in a flask containing **Sol.3**. An interst of this apparatus is that we can get capsules with or without surfactant whereas for the capsules (mini- or micro-) synthesis the surfactant is necessary to stabilize the dispersion. Without surfactant, the capsules size is determined by the diameter of the used needle.

Capsules :

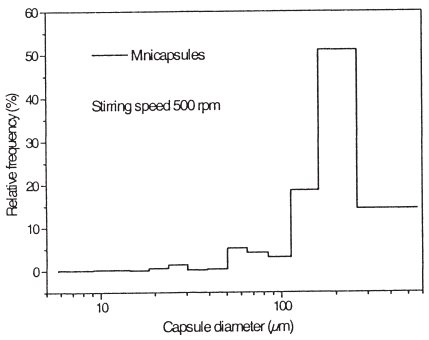
Minicapsules (Ø=100-300μm). In a Sovirel reactor containing **Sol.1** is dispersed **Sol.2** at a stirring speed of 500rpm. After stabilisation of the dispersion, **Sol.3** is added slowly and the polycondensation is done at a stirring speed of 200rpm.

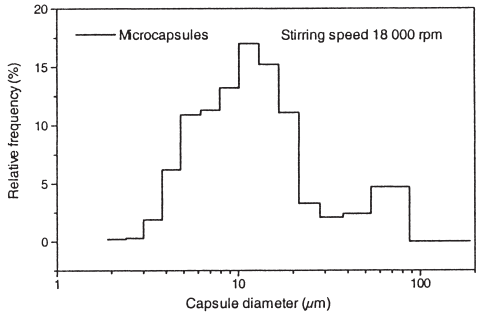
Microcapsules (Ø=1-10μm). In a Waring Blendor containing **Sol.1** is dispersed **Sol.2** at a stirring speed of 18 000rpm. After stabilisation of the dispersion, it is transfered in a Sovirel reactor ; **Sol.3** is added slowly and the polycondensation is done at a stirring speed of 200rpm.

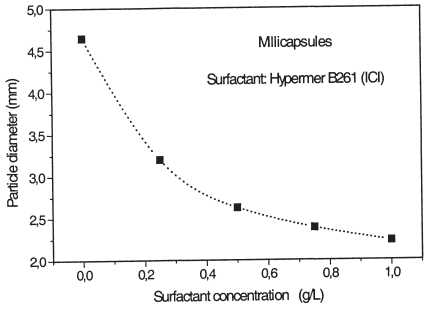
Characteristics

The three capsule types and the plane films are characterised via the observation of the membrane structure, and the mesure of their thickness and their weight composition. The size distribution is also determined for the different capsules.

Size distribution of the capsules:







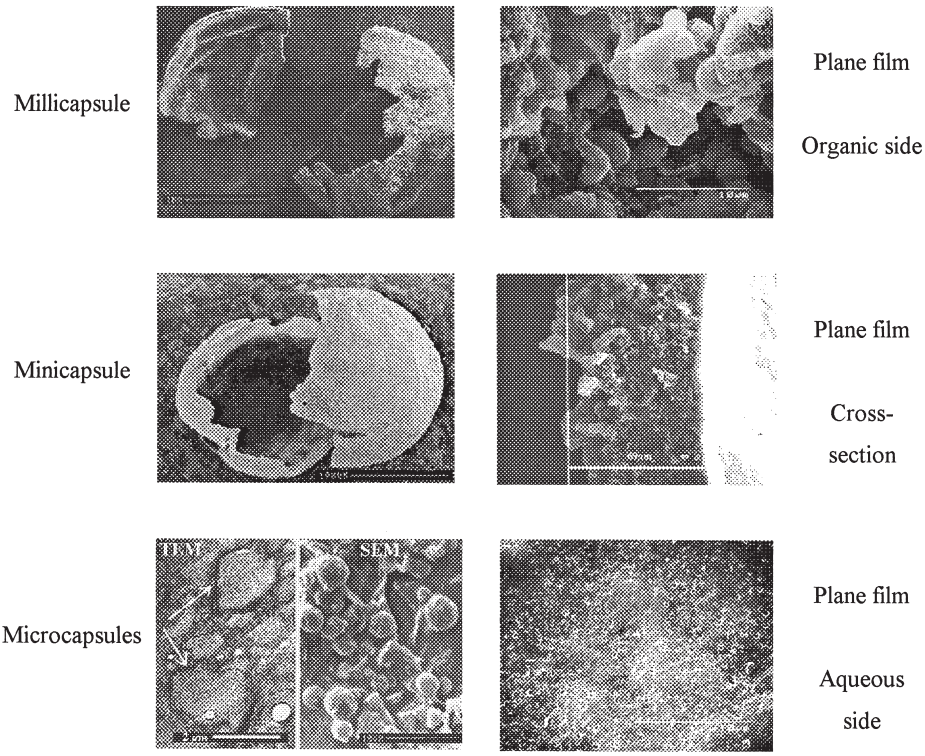
The size distribution of the mini- and the microcapsules depends on the dispersion conditions. It is mesured with a Malvern particule sizer (3600 E Type). In the dispersion conditions described above, the average size distribution of the mini- and the microcapsules is quite narrow. In respect to the millicapsules, their average size is strongly dependent on the needle diameter, the injection flow rate and the concentration of the emulsifier.

Weigth composition:

The weight composition of the three capsule types has been determined by thermogravimetric analyses. The results show that, independently of the capsule type, the average weight composition seems to be the same whatever is the synthesis process. The dry polyamide represents only 6 to 10 % of the total mass of the capsule.

Membrane structure:

A SEM-microscope (Cambridge Stereoscan 120) is used to observe the morphology of the membranes. For all the synthesis processes, the disymetric structure of the membrane already observed by L.J.J.M. Janssen **[1]** is confirmed. For an inverse dispersion (water in oil), the aqueous interne face is quite homogeneous, whereas the externe organic side is heterogeneous and composed of big irregular alveoles. In a cross section of the membrane, we could see that the size of these alveoles increases from the aqueous side to the organic side.



Membrane thickness:

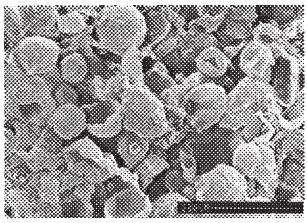
The membrane thickness strongly depends on the reaction conditions: monomers concentration, crosslinking agent fraction, reaction time, etc... The first mesures that were made on the plane films and on the millicapsules gave thickness values between 100 and 300 µm for the films and betweeen 20 and 60 µm for the millicapsules.

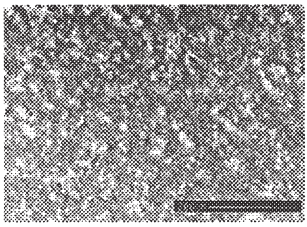
Properties

The active ingredient release is carried out either by diffusion or by breaking. So, the two most interesting properties of the capsules are the permeability and the mechanical strength of the membrane. At the moment, the determination of these properties has been only carried out on the millicapsules (1-5 mm) **[6]** and on the minicapsules (100-300 µm; cf following results).

Mechanical strength:

Minicapsules before sonication



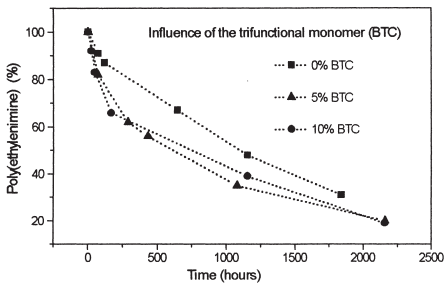


Minicapsules after 5 min sonication

The influence of an ultrasonic sollicitation on the mechanical resistance of the minicapsules was studied. For this purpose, the minicapsules were submitted to an ultrasonic irradiation (power 80 W) for 5 minutes. SEM-observations have permitted to compare the minicapsules before and after the sollicitation. No minicapsules could support such an irradiation. They are all destroyed after 5 minutes sonication. So, it can be concluded that sonication is a good and appropriate process to liberate an active ingredient from minicapsules (100-300 µm) via a mechanical sollicitation.

Permeability:

We have studied the diffusion of a macromolecule, a poly(ethylenimine) (i.e. PEI; Mw = 70 000 g/mol) which is released out of the minicapsules. After encapsulating the PEI, the minicapsules were immersed for a definite time in a large volume of water (1% w/w minicapsules in water). pH-analyses have permitted to detect the decreasing amount of PEI that has remained in the aqueous core solution of the minicapsules. Those analyses were made



at different diffusion times. So we have obtained the kinetics profile of the release of the PEI through the membrane of the minicapsules. As shown on this figure, the trifunctional mononer has no significant influence on the permeability of the minicapsules.

Conclusions

Four synthesis processes have been perfected to produce polyamide capsules with a large scale of sizes. A disymetrical structure of the membrane has been observed, independently of the size of the capsule. The milli-, the mini- and the microcapsules have similar characteristics (hollow particules and same weight composition). We have underlined the permeability of the minicapsules to poly(ethylenimine) and their breakability through sonication.

Perspectives

We are going to perfect a new synthesis process to obtain nanocapsules (50 - 1000 nm). The membrane permeability of the micro- and the nanocapsules will be studied. The mechanical strength of these kind of capsules will be determined in regard with the capsule size, the membrane thickness and its structure. Other chemically different membrane polymers will be also studied.

Aknowledgements

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