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Transposition from a batch to a continuous process for microencapsulation by interfacial polycondensation

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ABSTRACT

A novel continuous process is proposed and investigated to produce microcapsules by interfacial polycondensation. Polymeric microcapsules are obtained via a two-step process including an initial emulsification of two immiscible fluids in static mixers and a subsequent interfacial polycondensation reaction performed in two different continuous reactors, the Deanhex heat exchanger/reactor or a classical coiled-tube. This study is carried out through a step by step approach. A model system involving polyurea as the polymeric membrane and cyclohexane as the encapsulated species is chosen. A semi-batch reaction kinetic study is first performed in order to obtain kinetics data of the polycondensation reaction and to highlight hydrodynamic issues that can happen when running the encapsulation reaction in classical stirred tank. Parameters influencing droplets size obtained when carrying out emulsification in static mixers are then investigated. The hydrodynamic of the Deanhex reactor used is also characterized in terms of mixing time and residence time distribution. To validate the innovative continuous process, the emulsion droplets obtained at the static mixer outlet are encapsulated firstly in the Deanhex reactor and secondly in the coiled-tube. The apparent reaction kinetics and microcapsules characteristics corresponding to different operating conditions are discussed.

1. Introduction

Microencapsulation is a widely used method to produce microparticles enclosing an active ingredient. These microparticles may be either solid networks forming matrices in which is dispersed the solid or liquid active substance called microspheres, or core–shell systems made of a solid wall enclosing and protecting a liquid or solid core called microcapsules [1–3]. The present study concerns the synthesis of the last form of microparticles. In general, the size of microcapsules ranges from 5 to 200 μm [4]. Interest for microencapsulation is related to the development of various applications such as carbonless copying paper with capsules diameters from several micrometers to 30 μm, medicines, flavor in the food industry [5,6], and cosmetics. Since several years, microencapsulation is also used by the textile industry [7] to propose fragranced or active clothes to customers like perfumed tissue papers or slimming tights.

Microcapsules are high added value products with many different properties which are not easily controllable. These properties may be adjusted and optimized during the formulation step. A homogeneous production without any discrepancy towards the expected properties must be guaranteed by the manufacturing process.

The present work aims at demonstrating the design and the feasibility of a continuous process of microencapsulation by interfacial polycondensation. This chemical encapsulation technique consists in a reaction between two reactive monomers at the interface of droplets. An emulsion involving the active ingredient and a first monomer inside droplets is firstly prepared, then a second monomer is added in the continuous phase. The interfacial reaction at droplets interface starts as soon as both monomers are in contact. Polymer walls prepared by interfacial polycondensation may be for example polyester, polyamide, polyurethane, or polyurea [4]. Continuous processes are well adapted to interfacial polycondensation that present relatively fast reaction kinetics.

Nowadays batch processes involve high volume reactors. They are reliable and flexible, their operating modes are well-known and residence times in such processes are as long as required. Moreover both steps involved in the process require different hydrodynamic conditions that are hardly compatible in the same apparatus. The final microcapsules size distribution is fixed during the

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emulsification step that requires high shear conditions. Then it is important to insure that no coalescence occurs before adding the second monomer and that no agglomeration phenomenon happens during the polycondensation reaction. Concerning this reactive step the key parameters are the hydrodynamic conditions and the second monomer addition rate [8–10]. The continuous phase monomer must be quickly homogenized in this phase in order to guarantee that the reaction takes place simultaneously at the interface of all droplets so as to insure a good homogeneity of microcapsules properties, what requires a fast mixing time. Moreover the flow conditions in the reactor must tend to a plug flow in order to avoid the agglomeration phenomenon and to insure good membrane thickness homogeneity.

That is the reason why the present paper proposes to use continuous technologies well adapted to the hydrodynamic issues of both successive steps involved in interfacial polycondensation. This approach allows to remove hydrodynamic barriers previously cited, while keeping the emulsion droplets size distribution during the polycondensation reaction. In order to increase the process yield we wish to increase as much as possible the microcapsules concentration during the reaction without any agglomeration phenomenon.

In this study the emulsification step is performed in a Sulzer SMX^{TM} static mixer and the reactive step in a wavy channel (Deanhex reactor) or in a classical coiled-tube reactor. Static mixers are fixed structures inserted into cylindrical pipes. The Sulzer SMX mixer consists in an array of crossed bars arranged at an angle of 45° against the tube axis. Static mixers offer the advantages to represent low investments and energy costs compared to a classical stirred tank [11]. Liquid–liquid dispersion or emulsification is achieved by flowing the two immiscible liquids co-currently through the mixer. The energy cost of the operation is related to the pumps required to transport the liquids through the mixer. The energy consumption can be estimated through pressure drop measurements and enables to predict the droplets size [11–15]. Static mixers are particularly interesting for liquid–liquid dispersion as shear stress is more uniform than in stirred tanks, what results in lower times needed to reach the equilibrium between break up and coalescence [16,17].

The Deanhex reactor is an example of heat exchanger/reactor which technology is based on the plate heat exchangers [18]. By combining a heat exchanger and a reactor in the same apparatus, an accurate thermal control of the reaction is expected. Moreover the reactors require a sufficient residence time to complete the chemical syntheses. Thus, a way to intensify heat and mass transfers while operating in laminar flow is to structure the chemical path [19–21]. This is the main characteristic of the Deanhex reactor which is made of a reaction plate inserted between two cooling plates. A wavy milli-channel has been machined in the first one. The thermo-hydraulic characterizations of this 2D geometry have been made in homogeneous liquid phase [22]. It shows narrow residence time distributions, high heat and mass transfers and moderate pressure drops in transitional flow regime (Reynolds number around 2000).

The helically coiled tube reactor is well documented in the literature [23–26]. In such reactors the action of centrifugal force on fluid elements moving with different axial velocities in a curved circular pipe induces a secondary flow in the tube cross-section plane. This secondary flow field leads to increased pressure drops, but also to higher heat and mass transfer coefficients, and to narrowed residence times.

The continuous encapsulation process investigated is tested with a model system described in the literature and already studied in batch processes [27–31]. The reaction involves hexamethylene diisocyanate (HMDI) and hexamethylene diamine (HMDA). The emulsification step involves cyclohexane containing HMDI (first monomer) as the dispersed phase, and water as continuous phase. This emulsion is stabilized using a surfactant: Tween 80. Continuous phase (water + Tween 80) containing HMDA as second monomer is then added to the emulsion to initiate the reactive step. The emulsion is thus diluted. The two monomers react through an athermal reaction to form a polyurea membrane at the droplets interface:

$$nH_2N{-}(CH_2)_6{-}NH_2 + nO{=}C{=}N{-}(CH_2)_6{-}N{=}C{=}O \rightarrow -[HN{-}(CH_2)_6{-}NH{-}OCNH{-}(CH_2)_6\,NHCO]n-$$

HMDA + HMDI → Polyurea

The methodology used to transfer the batch encapsulation process to a continuous one involves several experimental steps presented in Fig. 1. The first part of this paper reports the preliminary studies performed in order to acquire the experimental data required to set up the continuous process. The encapsulation reaction is first investigated through a semi-batch process in order to collect kinetics data and to highlight hydrodynamic issues presented by the classical stirred tank. Emulsification in SMX static

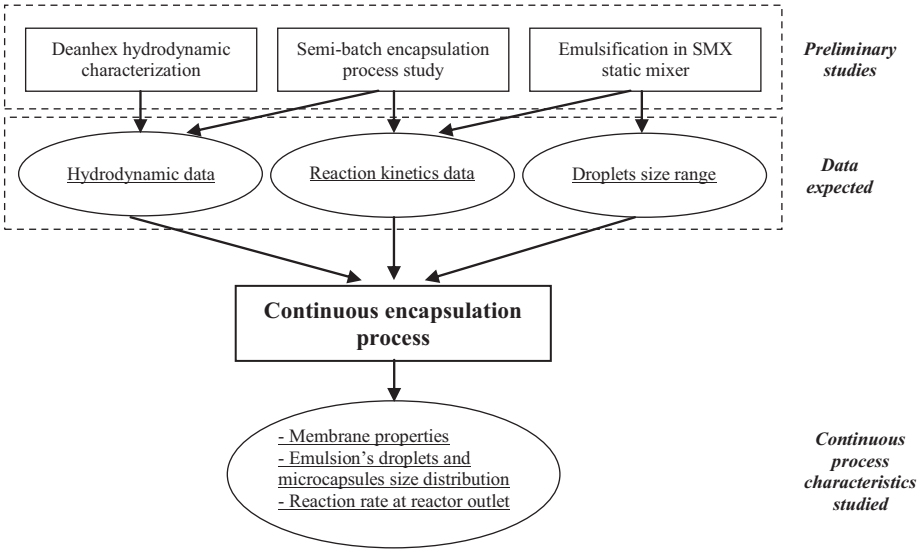

Fig. 1. Schematic diagram of the methodology used to transfer the batch encapsulation process to a continuous one.