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Nano-structured polymeric microparticles produced via cationic aerosol photopolymerization

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ABSTRACT

Microparticles with non-full structures are interesting in many applications. In their production, however, issues related to purification are common. To overcome these issues, in this study a continuous polymerization process was developed in order to obtain powdered, nano-structured microparticles using neither surfactants nor a liquid medium.

More specifically, a photo-induced cationic polymerization in aerosol was applied. A monomer solution was sprayed and irradiated with UV-light. During the reactor passage, both polymerization and phase separation occurred inside the single droplet. By adjusting the solvents amounts and ratios, different structures could be realized. Nano-structured particles with tunable pore shapes and dimensions were obtained. Capsule-like structures were obtained with the addition of a co-solvent able to get involved in the polymerization.

An active ingredient was encapsulated within the particles. Results showed that the addition of the active ingredient did not affect the synthesis; furthermore, the particles structure had an impact on the release kinetics.

1. Introduction

Interest in nano- and micro-scale particles has been increasingly growing in the last few decades since they can be used in various fields, ranging from textile industry to environmental treatments and in medicine [1–4]. Applications include antimicrobial particles for textile materials and drug releasing devices or body imaging [5]. Polymeric particles are among the most versatile type of nano and micro particles. Their characteristics can easily be designed by choosing an appropriate polymeric material and the proper production technique [6].

There are many techniques that can be used to obtain a suspension or a powder of polymeric carriers. Among them there are: emulsion techniques, microfluidics, photolithography and spray drying [7–10]. These techniques can be divided based on whether they imply or not a reaction step. Usually, microfluidics and photolithography include a polymerization step which is confined within a dispersed phase or simply a small volume [11]. These two techniques have the advantage to be continuous or semi-continuous but their drawback are low amount of production and the need of purification in a downstream process. Spray drying is commonly used with polymeric solutions. No chemical reaction is needed and only a solvent evaporation occurs, followed by the precipitation of polymeric material. In this way the production of full particle is simple, while the particles structuring can be tricky and must be carefully designed [12]. Emulsion represents a wide class of techniques that can be subdivided based on the presence/absence of reaction, the mechanism used to produce the emulsion and the types of reactions involved. This class of techniques is usually quite versatile, but it implies a burdensome work of purification to achieve a pure product [13–15].

In this work a new strategy to obtain nano-structured microparticles is presented, employing an aerosol technique combined with photoinitiated polymerization. In aerosol photopolymerization, a monomer solution is sprayed using a nozzle and nitrogen as gas carrier. The droplet aerosol thus achieved is directed in a quartz tube reactor where UV lamps are used to trigger the polymerization to obtain a polymeric particle aerosol. Aerosol photopolymerization has been used in the last 20 years in various fields [16]. This technique has been applied by Vorderbruggen et al. [17]

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to produce microbeads for molecular recognition. The droplet aerosol can be achieved using different devices, such as pneumatic or ultrasonic atomizers [18]. Previous works also showed the feasibility of a double step aerosol photo-polymerization in order to coat particles with a polymeric layer and, thus, to obtain a core-shell structure with a solid core [19].

The reaction mechanism chosen in this study is the cationic one. Cationic aerosol photopolymerization technique has previously been applied to obtain spherical polymer particles [20]. As a step forward of this previous investigations, employing the same experimental set-up, a continuous process strategy was developed to design nano-porous microparticles and capsule-like structures, containing a liquid core. The choosen monomer was a fast propagating and biocompatible molecule possessing a polyethylenglycol-like backbone and able to crosslink due to the presence of two functional groups. Specific solvents were added to the monomer solution in order to achieve a structured polymeric material. The first one that we introduced was a "phase separator", namely a bad solvent, to promote the particles structuring [21]. The second one served as a good solvent of both the monomer and the phase separator and was employed to obtain a homogeneous spray solution. Some spray solutions included a third solvent, able to get involved in the polymerization process in order to control the reaction and gelation rates. By varying the monomer to solvent ratio and the ratio between the specific solvents, respectively, we were able to create different structures within the microparticles. Once we successfully studied the formation of different structures, curcumin was loaded as an active ingredient in the polymeric carrier. Structures in the presence of this drug were reproduced and studies on the release kinetics of the active ingredient, from particles with different structures, were carried out.

2. Experimental section

2.1. Materials

All chemicals used were reagent grade and purchased from Sigma Aldrich. The monomer was tri(ethylene glycol) divinyl ether (DVE3), the photoinitiator (PI) was triarylsulfonium hexafluoroantimonate (TAS-HFA). The solvents used to prepare the spray solutions were: 2-octanone, 2-ethylhexanol, 1-hexanol and hexadecane. The nitrogen employed to produce the aerosol was withdrawn from a cylinder, purchased from Air Liquide (Paris, France). The purity of the gas was higher than 99,999%. The active ingredient used in the loading and release tests was curcumin (Sigma Aldrich, purity > 65%). Pure curcumin was prepared by dispersing powder in pure ethanol. The dispersion was then mechanically stirred. After settling of the dispersion, supernatant was withdrawn and dehydrated at room temperature. Ethanol was purchased from Sigma Aldrich (purity > 99.8% v/v).

2.2. Equipment and instrumentation

The aerosol experimental setup consists of a gas driven collision-type aerosol generator (ATM 220, Topas GmbH, Dresden, Germany) and an in-house developed photoreactor. The nozzle uses pressurized nitrogen to withdraw a liquid solution from a glass flask by the Venturi effect. The gas and the withdrawn solution pass through the orifice (diameter of 0.3 mm) where the atomization takes place. The nitrogen stream drives then the droplet aerosol inside the photoreactor, which consist of a cylindrical quartz tube (440 mm long, 52 mm inner diameter) and 6 UV fluorescent tubes (each 410 mm long, positioned at ~5 cm distance from the quartz tube outer wall), that emit light with a relatively broad peak at 308 nm (irradiance is approximately 5 mW/cm^2). The mean residence time of the aerosol droplets inside the reactor is dependent upon the nitrogen pressure used. The polymeric product is collected at the outlet of the photoreactor by impact on aluminum plates.

2.3. Synthesis of micro-particles

The synthesis of micro-particles is accomplished by preparing a monomer solution and spraying it under UV-light irradiation. The recipe used for the spray solution is crucial for the type of structure favored to be achieved. First, a homogeneous base solution was prepared by dissolving the photoinitiator (2% w/w) into the pure monomer, DVE3. Specific solvents were then added to the base solution in various amounts. Table 1 presents the compositions of each spray solution for the synthesis of different samples. It must be pointed out that the curcumin was added as a percentage of the monomer amount. The flask (reservoir) of the atomizer was filled with 30 ml of spray solution and the droplet aerosol was produced at a nitrogen pressure of 1 bar. Thus, the mean residence time of the droplets inside the reactor was about 60 s. Each production lasted 2 h, so that the amount of collected product was approximately 1 g. The temperature at which the process was conducted was almost constant at 25 °C, measured inside the reactor with a thermocouple during irradiation and under nitrogen flow.

2.4. Micro-particles characterization

2.4.1. Dimension and morphology analyses

For the evaluation of particles dimension and morphology an high resolution field-emission scanning electron microscope (SEM) was used (Leo Gemini 1530, Carl Zeiss, Oberkochen,

Table 1
Composition (in mass percentage) of the spray solutions.

Formulation	DVE3	hexadecane	2-octanone	1-hexanol	2-ethylhexanol	curcumin[a]
F1	100	–	–	–	–	–
F2	70	–	30	–	–	–
F3	70	30	–	–	–	–
F4	70	17.5	12.5	–	–	–
F5	67	17	16	–	–	–
F6	70	20	–	10	–	–
F7	70	18	–	–	12	–
F8	60	25	10	–	5	–
F9	60	27.5	7.5	–	5	–
F10	100	–	–	–	–	0.75
F11	70	18	12	–	–	0.75
F12	60	27.5	7.5	–	5	0.75

[a] Mass percentage with respect to the monomer amount.