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Preparation of uniform micrometer-sized polymer particles with closed-cell porous architecture made by limited coalescence of a double emulsion

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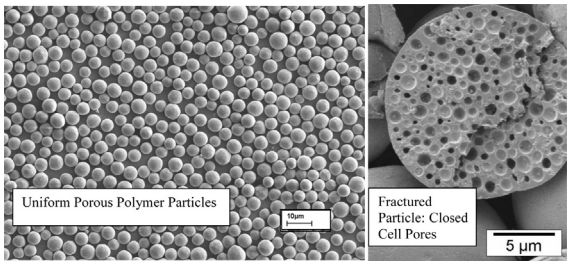
HIGHLIGHTS

- Uniform micrometer-sized porous polymer particles with closed-cell pores.
- Particle size control: limited coalescence of a Pickering ($W_1/O/W_2$) double emulsion.
- Use of ionized hydrocolloid in W_1 for colloidal stability of W_1/O.
- High pressure homogenization of double emulsion without losing W_1 features.
- Control of osmotic pressure in W_1 and W_2 to tailor size of pores and porosity.

GRAPHICAL ABSTRACT



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ABSTRACT

We describe a new and practical process for making narrow size distribution polymer particles in the 4–20 μm size range that contain uniform multiple closed-cell pores with excellent simultaneous predictive regulation of micrometer and sub-micrometer sized features. Our approach involves making a water-in-oil-in-water ($W_1/O/W_2$) double emulsion through a sequence of controlled emulsification and droplet solidification steps with several differentiating aspects from the standard double emulsion method. Firstly, providing colloidal stability to the inner emulsion (W_1/O) through the use of an ionized hydrocolloid in W_1, where the oil phase (O) is a high molecular weight branched polyester in ethyl acetate. Secondly, control of particle size and size distribution using the limited coalescence (LC) process after high pressure homogenization of the water-in-oil-in-water ($W_1/O/W_2$) emulsion through an orifice plate, delivering rapid pressure drop, constant back pressure and large extensional deformation to break up the oil phase droplets of the $W_1/O/W_2$ premix without destroying the integrity of the inner emulsion. While Pickering double emulsions have been made, conventional wisdom regarding the robustness of such emulsions, has precluded high pressure homogenization required in the LC process to make <20 μm, narrow size distribution particles. In this work we present a material system and an emulsification technique that were co-designed to overcome this limitation. Finally, the ionized hydrocolloid enables manipulation of osmotic pressure of the inner and outer water phases across the oil membrane, tuning the size of the internal features from hundreds of nanometers to several microns while maintaining the closed-cell architecture of the final particle. While it is especially challenging to achieve such control in

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structurally complex microparticles, this paper demonstrates a simple, yet truly versatile, adaptable and scalable solution for making functional, closed-cell porous polymer particles. Representative images of whole and fractured porous particles are shown in the Graphical Abstract.

1. Introduction

Porous organic polymer particles have found many applications such as scaffolds for tissue engineering, and carriers for catalysts, drugs and biomolecular assays [1–5]. Closed-cell porous particles are particularly useful for encapsulating active materials that are water soluble or dispersible [6]. Our interest was initially driven by the use of closed-cell porous particles containing colorants as dry toners (marking particles) for electrophotographic printing applications [7]. Such porous particles have been successfully scaled up to make multi kilogram quantities of porous colored toner particles incorporating addenda such as pigments and waxes for use in our electrophotographic printers. Subsequently, these particles have found applications in making porous layers for inkjet receivers, anti-counterfeit tags, and as additives to accelerate laser engraving [8–10].

There are many published methods for making closed-cell porous particles which include porogen templating, foaming, microfluidics, phase separation and a two-step multiple emulsion process [11–17]. In spite of the availability of various techniques, there is no practical, easily scalable process that can control droplet size, pore size and porosity, while producing particles with a narrow particle size distribution. The process described in this paper is based on the double emulsion method in which a first water phase (W_1), is emulsified into an oil phase (O) and then that water-in-oil emulsion (W_1/O) is further emulsified into a 2nd water phase (W_2) without breaking-up the inner (W_1) water droplets, to create a water-in-oil-in-water double emulsion ($W_1/O/W_2$). The resultant water-in-oil-in-water ($W_1/O/W_2$), second emulsion droplets can be solidified through either polymerization or solvent evaporation to form porous polymer particles [18–20]. Typically, the aggressive first emulsification step in a double emulsion process is followed by a gentler second emulsification carried out using SPG (Shirasu porous glass) membranes or in microchannels, but these approaches are quite tedious and not easily scalable.

Double emulsions of the water-in-oil-in-water ($W_1/O/W_2$) kind are usually formed by emulsifying the first water phase (W_1) in the oil phase (O) in the presence of a low HLB surfactant emulsifier followed by dispersing the resulting water-in-oil emulsion (W_1/O) in the second water phase (W_2) using a high HLB surfactant emulsifier [21]. Alternatively, hydrophobic and hydrophilic silica (solid) particles can be used in place of (or along with) conventional surfactant emulsifiers to stabilize the inner (W_1/O) and outer ($W_1/O/W_2$) emulsions respectively to form stable double emulsions [22,23]. These are examples of Pickering emulsions where solid particles adsorb at the oil water interfaces. The type of emulsion, formed, whether water-in-oil (W/O) or oil-in-water (O/W), will depend on the degree of wetting of the solid particles by the fluids at the interface as determined by contact angle measurements. Porous polymer microspheres have also been prepared from Pickering emulsions, for example, by suspension polymerization of a double Pickering emulsion [24–29].

Pickering single emulsions are stable over time, and narrow size distributions are achieved through the limited coalescence (LC) process [30–34]. When small (<10 μm) particles are desired in this process, high pressure homogenization of the Pickering O/W emulsion premix is used to create numerous small oil droplets whose total surface area is larger than the interfacial area that can be stabilized by the available number of solid particles, resulting in the oil droplets rapidly coalescing into larger drops to reduce the oil–water interfacial area. Coalescence continues until the oil–water interface is saturated with solid particles. The method of homogenization is typically not critical provided the initially homogenized droplets before coalescence are sufficiently small compared to the desired final droplet size.

The oil phase in an LC process of a Pickering emulsion is composed of a water-immiscible, low vapor pressure solvent or monomer. In the latter case, polymerization of the monomer droplets, after the LC process, leads to solid polymer particles with a narrow particle size distribution. Evaporative limited coalescence (ELC) is a process we defined in which, a water immiscible high vapor pressure solvent containing a dissolved polymer is subjected to the LC process and evaporation of solvent from the droplets after coalescence results in polymer particles of very uniform size [35,36]. The standard LC process is usually limited to vinyl (styrenic and acrylic) monomers that can be solidified by suspension polymerization. The ELC process, on the other hand, is much more versatile than the LC process in that a variety of organic solvent soluble polymers, such as styrene-acrylic polymers, polyesters and polyurethanes, can be readily converted to solid particles of uniform size in the micron range.

Solid polymer particles prepared from a single emulsion LC or ELC process have a narrow size distribution with a coefficient of variation (CV) ranging from 10% to 18%. In our study, the goal was to explore use of the scalable ELC process to control the droplet size of the second emulsion ($W_1/O/W_2$) where the oil droplets are complex and contain water droplets of the inner emulsion. Although Pickering double emulsions have been made as precursors to porous particles, their lack of robustness and large inner emulsion droplets, have precluded their premixes being subjected to the high pressure homogenization required for preparing small particles by the LC process. In subjecting a multiple emulsion ($W_1/O/W_2$) to the LC process for uniform particle size control, the fine structure of the inner W_1/O emulsion must be preserved during the second high pressure homogenization step. The reduced outer droplet size prior to coalescence needs to be much larger than the size of the inner water droplets in the first water-in-oil emulsion (W_1/O). This is especially challenging when the desired final particle size of the polymer particles is less than 10 μm. In order to achieve the aim size an orifice plate was used in this study to perform the second homogenization, and an ionized hydrocolloid was included in the first water phase to increase its robustness. These modifications define a practical and scalable method for making a narrow sized water-in-oil-in-water ($W_1/O/W_2$) double emulsion using the ELC process that after the removal of solvents creates solidified organic polymer particles with closed-cell pores. The osmotic balance between the internal water phase (W_1) and the external water phase (W_2) across the oil phase membrane, is critical to the stability of the inner water droplets during homogenization and the ELC process. After the homogenization process is complete, dilution of the exterior water phase (W_2) leads to an osmotic shock that swells the inner water droplets (W_1). The resultant osmotic pressure imbalance is used advantageously to increase the porosity of the particles.

This paper describes a process with predictive design features, developed to create narrow size distribution porous polymer particles (coefficient of variation <20%) in the size range of 4–20 μm possessing discrete uniform closed-cell porous compartments with porosities ranging from 20 vol% to greater than 60 vol%, using a solvent evaporation double emulsion process that can be easily scaled