Morphological characteristics of poly(styrene-co-divinylbenzene) microparticles synthesized by suspension polymerization☆

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ABSTRACT

The synthesis of poly(styrene-co-divinylbenzene) microparticles by the suspension polymerization technique requires the use of some protective agents to reduce the coalescence/agglomeration of the microparticles during the polymerization process. Since the effect of each protective agent may vary, depending on the type and proportion of the other reactants in the polymerization mixture, the influence of certain factors affecting the protective properties of tricalcium phosphate on the mean particle size, the particle size distribution, and the agglomeration of microparticles was studied using the design of experiments methodology. The factors investigated were the ammonium hydroxide and surfactant concentrations and impeller off-bottom clearance. The models thus obtained indicate that the absence of NH_4OH in the polymerization mixture, or a low level of the surfactant agent, leads to agglomeration of the microparticles. It was also observed that a low value of the impeller off-bottom clearance factor and a high value of the sodium dodecyl sulfate (SDS) concentration favor the formation of microparticles with a narrower particle size distribution. Additionally, microparticles with the smallest mean size were obtained using the highest value of the impeller off-bottom clearance factor.

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1. Introduction

Many separation processes are based on the selective adsorption of the components of a mixture on polymeric adsorbents. In many cases, spherical polymeric adsorbent microparticles are synthesized by suspension polymerization. Suspension polymerization is a process in which a water-insoluble monomer(s) is(are) dispersed as liquid droplets by stirring, to produce polymeric particles as a dispersed solid phase. In a general suspension polymerization process, the dispersed droplets of the organic phase do not maintain their identity but instead undergo continuous break-up (due to either turbulent pressure fluctuations or viscous shear forces) and coalescence (because of certain effective collisions). Eventually, a dynamic equilibrium in which a spectrum of the sizes of the dispersed droplets is reached, leading to a stable mean droplet size. In a given immiscible liquid-liquid dispersion, the dynamic equilibrium mean droplet size mainly depends on variables related to the stirring regime, such as the reactor geometry, the type of impeller, and the stirring rate, among others [1–3]. However, an increase in monomeric phase viscosity, due to progress in the conversion of monomers to polymers within each droplet, results in variations in the mechanisms of break-up and coalescence and, above a certain level of conversion of the monomeric mixture, droplets tend to undergo a remarkable degree of agglomeration. Thus, an entirely stable dispersion throughout the polymerization process cannot be maintained only by stirring [4,5]. Nevertheless, the coalescence and agglomeration of monomeric droplets during the polymerization processes can be minimized by the use of suspension agents, which are adsorbed on the surface of the droplets to form a protective film [6]. In this case, the enhanced stability of dispersion leads to a controllable monomeric droplet size and solid beads can be produced in the same spherical form in which the liquid monomer was originally dispersed in the aqueous phase. Accordingly, the type and concentration of the suspension agent are also important variables that affect the final particle size distribution (PSD), which is one of the most important characteristics of the resultant microparticles [5]. In addition, the operation conditions under which a suspension agent is used have an important effect on the morphology of the polymeric microparticles, this characteristic being one of most significant with respect to their possible applications [7,8]. The suspension agents employed in suspension polymerization are either macromolecules or water-insoluble inorganic powders. The former are also called protective colloid dispersants, such as poly(vinyl alcohol) [9], while the latter are known as Pickering solids, an example being tricalcium phosphate (TCP) (hydroxyapatite, 3 $Ca_3(PO_4)_2 \cdot Ca(OH)_2$) [10]. Insoluble inorganic powders have some advantages, such as the fact that they are cheaper and the protective layer is easier to remove, thereby preventing

contamination of the product [8]. In this regard, some authors have reported the synthesis of polystyrene gel-type beads using Pickering solids; mainly TCP. In this sense, Deslandes [10] studied the morphology of the layer of TCP that surrounds the polymer beads of poly(styrene-co-butadiene) and observed that it was composed of two distinct parts: a thin layer made of very uniformly distributed TCP primary particles, and a second layer, usually thicker, made of loosely packed aggregates of TCP. That author pointed out that the effect of TCP could depend on the interaction with other operating parameters, such as the concentration of surfactant agent and the energy incorporated during stirring. Other authors [11,12] have studied the effect of several variables that affect particle size and PSD in the suspension polymerization of polystyrene beads, using TCP as a suspension agent. They realized that the TCP should be produced *in situ* to reduce the particle size of the polymeric beads, although the smallest final size attained was around 177 μm. However, since those authors failed to provide accompanying photographs of their microparticles, it is not possible to know either the final morphology of their beads or their size distribution. Shanghaghi and Mahdavian [13] studied the influence of the TCP concentration, of a surfactant agent, and of the ratio of the organic phase to the aqueous phase on the particle size of polystyrene beads. They reported the existence of an interaction between the surfactant agent and TCP on the final particle size. The effect of both factors was explained in terms of the degree of surface covering of the monomeric droplets/polymeric beads by TCP. They also provided photographs of their product in which the microparticles exhibited some degree of agglomeration. The smallest particle size obtained by those authors was 74 μm.

Regarding the size of microparticles, it should be recalled that the adsorption phenomenon occurs at active sites located on their internal and external surfaces. Adsorption on the internal surface (walls of the pores) of the adsorbents is generally a slow process, due to mass transfer by diffusion processes. Therefore, in many applications very small particles are desirable because of their higher external specific surface area and because of the lesser importance of mass transfer by diffusion.

In the present work we studied the production of very small (<50 μm) poly(styrene-co-divinylbenzene) gel-type beads by suspension polymerization, the main objective of the research being the determination of the quantitative influence on mean particle size and size distribution of certain operation conditions that can affect the protective properties of the suspension agent used; namely, TCP.

In the experiments carried out, the concentration of the suspension agent was maintained constant, while other experimental conditions were varied to obtain very small microparticles with a narrow size distribution. Moreover, since in most applications microparticle morphology is very important [7,8] the experiments were also oriented to preventing—as far as possible—the agglomeration of the microparticles during the polymerization process and to maintaining the spherical shape of the monomeric droplets. By means of microscopy, the morphology of the microparticles was checked to determine whether the microparticles obtained indeed were spherical and appeared as individual particles.

2. Experimental section

2.1. Materials

2.1.1. Organic phase

The monomers to be polymerized were styrene (99%) and divinylbenzene (DVB, containing 55% DVB isomers, the remainder mainly being 3- and 4-ethylvinylbenzene), supplied by Aldrich (Madrid, Spain). Prior to polymerization, both monomers were first washed with a 10% aqueous NaOH solution to remove the inhibitor, p-tert-butylcatechol, and then with deionized water until neutralization. The initiator, benzoyl

peroxide (BPO, 70%, remainder water), was supplied by Aldrich (Madrid, Spain) and was used as received.

2.1.2. Aqueous phase

Anhydrous calcium chloride (95%), 1-hydrated sodium triphosphate (98%) and ammonium hydroxide solution (32%) were supplied by Scharlau (Barcelona, Spain). Sodium dodecyl sulfate (SDS, 85%) was obtained from Panreac (Barcelona, Spain). All substances were used without further purification. Deonized water was employed to prepare the aqueous solutions.

2.2. Synthesis of gel-type poly(styrene-co-divinylbenzene) microparticles

The suspension agent used was tricalcium phosphate (TCP), prepared *in situ* by means of a mixture of solutions of anhydrous calcium chloride and 1-hydrated sodium phosphate. The concentration of TCP used was 1.4% w/v of the aqueous phase. In a typical suspension polymerization experiment, a three-necked jacketed reactor fitted with a mechanical stirrer, a reflux condenser and a thermocouple was loaded with a solution of TCP. Then, sodium dodecyl sulphate (SDS) at different concentrations, depending on the experiment, was added. Following this, the organic phase was poured into the reactor. This organic phase was composed of a mixture of the monomers (at the proportions given in Table 1) and the initiator, previously well mixed. The organic and aqueous phases were prepared at room temperature. Once both liquids were inside the reactor, the organic phase was dispersed into the aqueous phase at room temperature for 3 h under a stirring rate of 900 rpm. This time was considered sufficient for steady state to be reached, when the break-up and coalescence rates were balanced and the mean size of the organic liquid drops was no longer reduced. This was checked by collecting samples from the reactor at different times and scrutinizing them by light microscopy. Following this, ammonium hydroxide was added and the temperature inside the reactors was increased to 80 °C and kept at this value for 7 h. After approximately 1.3 h after the operation temperature had been reached, the stirring rate was reduced to 550 rpm. At this time of the reaction, after an accelerated increase in viscosity, the droplets became sticky, and it was difficult for the particles to split up and they readily formed agglomerates [6]. The time at which the stirring rate was reduced was determined by taking a sample out of the polymerization system and observing it under light microscopy. We observed that a decrease in the stirring rate at this stage of polymerization diminished the proportion of agglomerated microparticles to a noteworthy extent. When the reaction had been completed, the resulting copolymer microbeads were washed with 2N hydrochloric acid and ethanol, and were finally dried under vacuum in an oven at 40 °C. Table 1 shows the values of the held-constant synthesis conditions for all the experiments. Fig. 1 shows the geometric characteristics of the experimental device used in all the experiments.

Table 1
Held-constant synthesis conditions.

Substances	Proportions
Organic phase, OP (% regarding organic phase volume)	
Styrene	90%
DVB	5.5%
Ethylvinylbenzene	~ 4.5%
BPO	4% (w/v)
Aqueous phase, AP (% regarding aqueous phase volume)	
Deionized water	100%
TCP	1.4% (w/v)
Volume, ml	150
OP/AP	1/6