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The role of functional monomers on producing nanostructured lattices obtained by surfactant-free emulsion polymerization – A novel approach

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ABSTRACT

Nanostructured lattices were prepared in a single step emulsion polymerization reaction in the absence of surfactants by exploring the so called "pickering" stabilization mechanism. The synthesis protocol and the properties of the obtained particles were evaluated and discussed simultaneously considering processing and formulation aspects with special emphasis to the chemical properties of the functional monomers selected on the present study. Colloidal silica was used to ensure the physical stability required to produce nanoparticles as a result of the emulsion polymerization route. Three different monomers including methyl metacrylate (MMA), styrene (Sty) and vinyl acetate (VAC) were used to structure the particles of interest. Four different functional polymers including acrylic acid (AA), styrene sulfonate ($StySO_3$), hydroxyethyl methacrylate (HEMA) and dymethylamino ethyl methacrylate (DMAEMA) were evaluated.

The obtained lattices were comparatively characterized regarding to surface tension, particle size distribution, morphological aspects, viscosity, zeta potential and colloidal stability.

The one-step pickering emulsion polymerization proved to be an effective approach to prepare lattices of industrial interest without the use of surfactants. The obtained particles presented average mean diameters ranging from 155 to 345 nm with relatively low polydispersity indices (0.39–2.02). The most promising behavior was experimentally verified once selecting the styrene sulfonate ($StySO_3$) as the functional monomer. The hydroxyethyl methacrylate (HEMA) also proved to be an interesting alternative although its limitation related to high surface tension applications. The high resolution images registered with the HRSEM-FEG technique explicit morphological aspects that effectively contribute to elucidate the "pickering" stabilization mechanism and the resultant core–shell structure derived thereof.

1. Introduction

In recent years, considerable efforts have been devoted to the design and controlled fabrication of functional nanomaterials with complex structures and compositions [1]. Waterborne polymer colloids, often referred to as 'latex dispersions', are

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well-established for diverse applications in many commercial products from different industrial segments including cosmetics, pharmaceuticals, adhesives, coatings and paints [2]. A key advantage of the colloidal approach is that it enables direct control of internal structure organization of the particles at nanoscale. The meso and even macroscale organization of the system can also be controlled by the creation of ordered assemblies of particles. Nanostructured lattices have been commonly prepared by emulsion polymerization processes in the presence of emulsifying agents to ensure the physical stability and the nanometric size of the resultant particles. Examples of miniemulsion, suspension or dispersion polymerization processes can be found in the literature but emulsion polymerization is by far the most frequently used technique [3].

Two different strategies to produce latex dispersions are frequently described in related literature. The first one considers a conventional emulsion polymerization preceded by adding at least one surfactant to stabilize the colloidal particles [4]. The second approach deals with the blend of colloidal polymer particles and a second type of particle (inorganic or polymeric) [5]. It is important to note that, despite the significant contribution related to the physical stability of the colloidal system during the whole process; the surfactants may pose adverse effects on the resultant latex properties and may compromise the final desired application.

For some applications the presence of surfactants imposes limitations, especially if the product is designed for film formation and water resistance, high surface energy and weathering resistance (e.g. oxidation) are desired properties. An alternative to replace the emulsifiers is the use of solid particles such as protective colloids, also known as "Pickering Emulsions". This name came about because of the name of the researcher Pickering, S., who was among the first to suggest the feasibility of stabilizing an emulsion using solid particles. According to him, the colloidal solid particles self-aggregate at the interface of the two immiscible phases of the emulsion, thus preventing the droplets and resultant particles to coalesce [6]. According to Pieranski theory [7], this phenomenon is related to the fact that colloidal particles spontaneously adsorb at the interface of the droplets (internal phase) by decreasing the total free energy of the system. The stability of a "Pickering Emulsion" depends on the particle size of the protective colloid (specific surface area) and also on the affinity and interactions established simultaneously with the internal and external phases that compose the emulsion. The "Pickering" stabilization technique is used in various areas such as food, paper industry, paints and cosmetics.

Some authors had first demonstrated the possibility of using the "Pickering Emulsion" concept in emulsion polymerization processes [4]. The related works that stand out demonstrate the potential to synthesize hybrid organic/inorganic materials based on polymers and silica, producing well-defined structures such as "raspberry", "currant bun" and "core–shell". According to the authors, these structures can be confirmed through advanced analytical techniques such as X-ray photoelectron spectroscopy (XPS) analysis and elemental mapping distribution. Moreover, they noted that the choice of initiator is very important for the formation of a stable colloidal suspension. The exact mechanism of how the formation of a structure such as "core–shell" evolves still remains undefined, but there is strong evidence that the silica particles constitute the shell of the formed structure. This follows from the fact that the colloidal silica promotes the stabilization of monomer droplets, which are in the order of a few microns at the start of the process and after the completion of the polymerization the resultant hybrid polymeric particles present a few hundred nanometers [4,6].

Bourgeat-Lami et al. [8] described the use of modified clays for the synthesis of hybrid materials exploring the emulsion polymerization process. A prior modification of the clay, improving its compatibility with the polymer formed during polymerization, is reported to be crucial for success. Another detail of the work of Bourgeat-Lami is the use of emulsifiers to help stabilizing the system during polymerization [8].

Song et al. [6] used the polymerase "Pickering Emulsion" for synthesizing photocatalytic materials based on titanium dioxide. The authors synthesized polystyrene stabilized with colloidal titanium dioxide and also used some hydrophilic monomers (acrylic acid and ethylene glycol dimethacrylate) to modify the final properties of the particles. Liu et al. [1] also demonstrated the synthesis of different polymers in the presence of colloidal TiO_2. Schmid et al. [9] developed the synthesis of polystyrene by emulsion polymerization stabilized with colloidal silica in alcoholic medium. The authors used methanol and isopropanol as reaction media for the polymerization process and obtained hybrid particles of polystyrene/silica with size ranging from 331 to 464 nm and with silica content ranging from 13 to 26% by weight [9].

Preparation of polystyrene/nano-SiO_2 composite microspheres with core–shell structure was cited by Zhang et al. [10], synthesis of ZnO/polystyrene composites particles [4], armored soft polymer latexes using laponite clay as stabilizer [11] polystyrene/Fe_2O_3 composite particles that present magnetoresponsive properties [12] polystyrene/laponite composite nanoparticles exhibiting electrorheological characteristics [13] organic–inorganic hybrid hollow spheres prepared from TiO_2-stabilized [14] were reported in literature, all using pickering emulsion polymerization.

Chen et al. [4] carried out the synthesis of polystyrene employing the emulsion polymerization process using zinc oxide to stabilize the system. The authors demonstrated that depending on the initiator (hydrophilic or hydrophobic) that is used in the polymerization, different morphological structures for the hybrid materials can be obtained. Once a hydrophobic initiator was selected, a resultant "core–shell" structure was formed because the colloidal silica particles preferably concentrate and remain on the polymeric particle surface that represents the inner core.

In this work we report a manufacturing protocol to prepare nanostructured lattices using the single step emulsion polymerization reaction in the absence of surfactants. The role of different functional monomers and the effect over resultant properties of the hybrid particles were evaluated and the results are presented herein. A relevant contribution of this work is to present an alternative method to produce nanostructured lattices which dispenses the use of special high energy equipment to emulsify the monomer (oil) and water phases, such as ultrasound, turrax or high pressure homogenization (HPH) and yields nanoparticles with a very low polydispersity index and regular morphology. The production of surfactant-free