



Macromolecular Nanotechnology

Incorporation of polybutadiene into waterborne polystyrene nanoparticles *via* miniemulsion polymerizationLudmila I. Ronco^a, Roque J. Minari^a, Jorge R. Vega^{a,b}, Gregorio R. Meira^a, Luis M. Gugliotta^{a,*}^aINTEC (Universidad Nacional del Litoral-CONICET), Güemes 3450, 3000 Santa Fe, Argentina^bFacultad Regional Santa Fe (Universidad Tecnológica Nacional), Lavaisse 610, 3000 Santa Fe, Argentina

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ABSTRACT

The incorporation of polybutadiene in waterborne polystyrene nanoparticles by miniemulsion polymerization is expected to positively combine the properties of both materials, improving the impact resistance and toughness. The kinetics of the miniemulsion polymerization used to synthesize these hybrid nanomaterials and the effect of the reaction variables on the polymer microstructure and particle morphology were investigated. Both molecular microstructure and final particle morphology (core-shell, “salami” or three-phase type) depended on the nature of the employed polybutadiene based rubbers and initiators. The mechanisms responsible for these effects were discussed.

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1. Introduction

In the production of engineering plastics, elastomeric particles are incorporated into brittle thermoplastic matrices to improve mechanical properties such as impact resistance and toughness. Thus, high-impact polystyrene (HIPS) is produced by incorporating polybutadiene (PB) into polystyrene (PS). To this effect, styrene (St) is polymerized in the presence of 5–10 wt% of PB in bulk (or quasi-bulk) processes that include a chemical initiator and reaction temperatures between 90 and 230 °C. The initial prepolymerization stage is carried out under stirring, and it ends at around 30% conversion. Then, an unstirred finishing stage is included to preserve the particle morphology generated at the end of the prepolymerization. In the continuous bulk processes, the final St conversion is limited to approximately 75% and the unreacted St is removed in a devolatilization stage [1,2]. The final HIPS may present different morphologies. In the “salami” morphology, the dispersed rubber particles exhibit diameters of 1 μm or larger, and are heterogeneous, with multiple vitreous PS

occlusions. Smaller “core-shell” rubber particles containing single PS occlusions can also be produced. Alternatively, coils, mazes, shell, or capsule morphology could be obtained when partially replacing PB by St-butadiene (B) block copolymers [3,4].

Core/shell latex particles of PS and PB to be employed as impact modifiers have been produced in 2-stage emulsion polymerizations. Thus, Wei et al. [5] synthesized particles of a St/B block copolymer in 2 stages, with a miniemulsion polymerization of St by Reversible Addition-Fragmentation Chain Transfer (RAFT) followed by a PS seeded RAFT emulsion polymerization of B. They observed that particle morphology depends on the composition of the PS-co-PB segment. Gao et al. [6] investigated the mechanical properties of modified PS obtained by mixing PS with core-shell PB-g-PS rubber particles synthesized *via* emulsion polymerization of styrene in the presence of a polybutadiene latex. A redox water-soluble initiator produced small PS microphases inside the rubber core, yielding a low toughness and low impact strength material. However, both mechanical properties were improved when employing the oil-soluble initiator 1,2-azobisisobutyronitrile, due to the larger PS occlusions generated in the rubber core. Also, this type of core-shell particles of PB-g-PS were introduced

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into commercial HIPS to improve the mechanical properties of the resulting composite [7].

Miniemulsion (ME) polymerization represents an alternative for the synthesis of hybrid latexes; and enables the incorporation of a hydrophobic component into the polymer particles in a single step process, without requiring its diffusion through the aqueous phase. Many publications have been focused on the production of waterborne coatings and adhesives by ME polymerization, such as polyurethane-acrylic hybrid nanoparticles [8,9], hybrid latex particles of acrylic and tackifying resins [10], and acrylic/alkyd “solvent-free” coatings [11]. Thus, ME polymerization could enable the production of nanostructured particles with potential applications as reinforced materials, by direct incorporation of B-based rubbers into PS nanoparticles; with the advantage of reducing the mixing and heat transfer problems compared to an equivalent bulk (or quasi-bulk) process.

Besides the article by Jia et al. [12] which employs small quantities of a low molecular-weight PB (liquid PB) with the aim of co-stabilizing the ME polymerization of St, Jeong et al. [13] is so far the single publication that describes the synthesis of hybrid composite latex by ME polymerization, with incorporation of a B-based rubber into PS particles. The base rubber was a SBS triblock copolymer (Kraton[®]), and it was added in a 20/80 rubber/St weight ratio. The miniemulsions were prepared with a Manton–Gaulin high pressure homogenizer followed by a membrane filtration to eliminate the larger ME droplets. When observing the rubber particles by transmission electron microscopy (TEM) after their fractionation by density gradient centrifugation, different SBS contents were seen between the larger and smaller particles, as a consequence of the faster nucleation of smaller particles with respect to the bigger ones. Only cellular morphologies were observed, and the molecular characteristics of the polymers was not determined [13].

In the present work, the ME polymerization of St in the presence of PB or styrene–butadiene rubber (SBR) is investigated, with the aim of synthesizing waterborne PS-rubber nanocomposites with different molecular microstructures and particle morphologies, able to be applied as a nanostructured engineering plastic. The polymerization kinetics, molecular microstructure, and particle morphology were followed along several reactions, with different combinations of temperature, rubber type and content, and initiation systems.

2. Experimental

2.1. Materials

Demineralized water was used throughout the work. The following reagents were employed as received: potassium persulfate (KPS) from Mallinckrodt (99% purity) was the water soluble initiator; benzoyl peroxide (BPO) from B.D.H. (wet, with 30% water) was the organic soluble initiator; and tert-butyl hydroperoxide/ascorbic acid (TBHP/AA), Aldrich/Cicarelli (molar ratio 2/1) was the water soluble redox initiation system. In addition, hexadecane (HD)

from Merck ($\geq 99\%$ purity) was the costabilizer; sodium lauryl sulphate (SLS) from Cicarelli (95% purity) was the surfactant; and hydroquinone (HQ) from Fluka AG ($>99\%$ purity) was the polymerization inhibitor. Styrene was washed with an aqueous solution of potassium hydroxide (to remove polymerization inhibitors), and then with demineralized water until reaching the pH of the washing water. Three different rubbers were employed (see characteristics in Table 1): a PB (Buna CB 55 GPT) from Lanxess; and two SBR from Petrobras Argentina: a commercial Arpol 1502 sample of a higher molecular weight (SBR_H), and a non-commercial sample of lower molecular weight (SBR_L). A set of 9 (Shodex) narrow PS standards in the range 10^3 – 10^6 g/mol was used to calibrate the size exclusion chromatograph. Tetrahydrofuran (HPLC Solvent, J.T. Baker) was the eluent of the size exclusion chromatography SEC runs. Methyl–ethyl ketone (MEK, Anedra, 99% purity) was employed as a selective solvent for determining the degree of grafting.

2.2. Miniemulsification

All the miniemulsions contained: (a) 20–30% wt of solids; (b) a variable rubber content; (c) 2–2.5% wbop (weight based on organic phase) of surfactant; (d) 4% wbm (weight based on monomer) of HD; and (e) a 0.024 M in aqueous phase of NaHCO₃. The rubber was dissolved in the organic phase for 12 h before the miniemulsification. To produce the ME, the organic and aqueous phases were first strongly mixed by magnetic stirring during 15 min., and the resulting preemulsion was sonified in a Sonics VC 750 (power 750 watts) during 25 min. at 100% of amplitude, and with cycles of 20 s on and 5 s off.

2.3. Polymerizations

Polymerizations were carried out in a 0.3 L batch glass reactor equipped with a reflux condenser, a stirrer, a sampling device, and a nitrogen inlet. The reaction temperature (70–90 °C) was adjusted by manipulating the reactor jacket temperature with a controlled water bath. The ME was loaded into the reactor, and the system was kept under stirring and with nitrogen bubbling until the sought reaction temperature was reached. The BPO initiator was dissolved in the organic phase prior to preparation of the ME. The KPS initiator was dissolved in water and injected into the reactor as a shot. In the experiments with TBHP/AA, 20% of these reactants were loaded at the start of the polymerization, and the remaining 80% were fed during 45 min. in separate streams and at constant flow rates. The total polymerization times were 2 h for the reactions with KPS and TBHP/AA, and 3 h for the reactions with BPO.

Table 1
Base characteristics of the three base rubbers.

| Rubber | B content (weight%) | $M_n \times 10^{-3}$ (g mol ⁻¹) | $M_w \times 10^{-3}$ (g mol ⁻¹) |
|------------------|---------------------|---|---|
| PB | 100 | 275.5 | 445.0 |
| SBR _H | 76.5 | 105.0 | 305.0 |
| SBR _L | 76.5 | 25.3 | 91.3 |

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