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Toughened polystyrene nanoparticles through high-solids miniemulsion polymerization

Ludmila I. Ronco [a], Roque J. Minari [a], Mario C.G. Passeggi Jr. [b], Gregorio R. Meira [a], Luis M. Gugliotta [a,*]

[a] *INTEC (Universidad Nacional del Litoral-CONICET), Güemes 3450, 3000 Santa Fe, Argentina*
[b] *IFIS (Universidad Nacional del Litoral-CONICET), Güemes 3450, 3000 Santa Fe, Argentina*

HIGHLIGHTS

- Synthesis of toughened nanoparticles through high solid miniemulsion polymerization.
- Toughened polystyrene with controlled microstructure and nanomorphology.
- The nanostructured toughened polystyrene exhibits improved mechanical properties.

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ABSTRACT

Polystyrene nanoparticles toughened with polybutadiene were synthesized by miniemulsion polymerization of 50% solids content. The effects of recipes and reaction conditions on the polymerization kinetics, polymer microstructure, particle morphology, and mechanical properties of the produced thermoplastic materials, are discussed. The final material characteristics are strongly dependant on the chemical nature of the employed initiator, and an interpretation for the observed effects is presented. The obtained nanostructured polystyrenes exhibit mechanical properties similar to those of the commercial HIPS, but with the typical advantages of polymerizations in disperse medium such as low environmental impact, high monomer conversion, and fast heat transfer.

1. Introduction

Mechanical properties of fragile polymers such as impact fracture are improved by incorporation of dispersed rubber particles into the main vitreous matrix. Such particles act as stress concentrators and facilitate a more uniform dispersion of the applied mechanical energy [1,2]. High-impact polystyrene (HIPS) is commonly produced in continuous bulk (or quasi-bulk) processes, where, styrene (St) is polymerized at 90–250 °C in the presence of 5–10 wt% of a dissolved rubber such as polybutadiene (PB) or a St-butadiene block copolymer. The initial prepolymerization stage ends at styrene conversions of around 30%. It is carried out under stirring, and in the presence of a chemical initiator to promote rubber grafting. The second (finishing) stage is unstirred (to preserve the particle morphology generated at the end of the prepolymerization), and is carried out at higher temperatures to promote initiation by thermal monomer decomposition. In continuous bulk processes, the final St conversion is approximately 75%; and the unreacted St must be removed in a final devolatilization stage [3,4]. The final product typically exhibits "salami" morphologies, with a vitreous PS matrix containing dispersed rubber particles of around 1 μm in size, that in turn contain multiple PS occlusions.

Several articles have investigated the development particle morphology in PS/PB blends (with PS as the major component), and with addition of minor fractions of styrene-butadiene copolymers. Jiang et al. [5] employed simple PB-g-PS copolymers with around 1 PS branch per molecule in average. When simultaneously varying the molecular weights of the free PS and grafted PS chains, the following was observed by transmission electron microscopy (TEM) [5]: (i) the 2 phases were totally immiscible when the molecular weight of free PS was much larger than the molecular weight of the grafted PS branches; (ii) the degree of mixing improved when the molecular weight of the grafted PS chains became closer to those of the free PS; and (iii) the morphology exhibited PB microdomains dispersed in the PS matrix when the molecular weight of the free PS was lower than that of the PS grafted branches. These observations are in agreement with Inoue et al. [6] and Jiang and Xie [7] for homopolymer/diblock copolymer

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* Corresponding author. Tel.: +54 342 4511546; fax: +54 342 4511079.
E-mail address: lgug@intec.unl.edu.ar (L.M. Gugliotta).

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blends. In addition, when comparing IZOD impact resistances, it was observed that short diblock copolymers are ineffective as interface agents in PS/PB blends, while the best performance was obtained with asymmetric diblock copolymers of sufficiently high molecular weights for generating entanglements in the main interfaces [8].

Toughened PS has also been produced by blending sub-micrometer core–shell PB/PS particles into PS homopolymer [9–11]. In these experiments, the particles were obtained by emulsion polymerizations of St in the presence of a PB seed with different initiators (an oil-soluble [9], a water-soluble [11], and redox pairs [9,10]); and then such particles were blended with commercial PS, yielding blends of 20 wt% rubber content. With redox initiators, Gao et al. [9] observed that the particles contained small PS microphases inside the rubber cores, and that the obtained materials exhibited a low toughness and low impact strength. These mechanical properties were improved when employing an oil-soluble initiator (1,2-azobisisobutyronitrile), and this improvement was attributed to the larger PS occlusions generated in the rubber core [9]. Gao et al. [10] and Cai et al. [11] synthesized core–shell particles of different PB/PS ratios; observing that the degree of grafting affected both the dispersion of the rubber particles, and the mechanical properties of the final materials.

Miniemulsion polymerization of St in the presence of a rubber is an alternative for synthesizing hybrid latexes; since it incorporates hydrophobic components into the polymer particles in a single step, without requiring their diffusion through the aqueous phase. Jeong et al. [12] polymerized St in the presence of a styrene–butadiene-styrene triblock copolymer (SBS, Kraton®), added in a 20/80 weight ratio of PB rubber to St. They observed a preferential concentration of SBS in the larger particles with respect to the smaller; due to the faster nucleation of the smaller particles, combined with an additional monomer diffusion stage from the bigger particles into the smaller. Only cellular morphologies were observed, with PB-rich phases surrounded by PS-rich phases. More recently, miniemulsion polymerization was employed to obtain PS nanoparticles with different amounts of medium-cis PB or styrene-butadiene rubber (SBR) of 20% solids content [13]. The grafting efficiency and particle morphology were affected by the chemical nature of the initiator and by the molecular characteristics of the rubber; observing that increased grafting efficiencies induced more complex particle morphologies [13].

The production of high-solids latexes is industrially important; and miniemulsion polymerizations contribute toward this goal through the relatively broad particle size distributions involved, that yield low system viscosities [14–16]. The aims of this work are: (i) to synthesize PB-toughened PS nanoparticles by miniemulsion polymerization of 50 wt%. solids content; and (ii) to investigate the effects of changes in the PB concentration and in the nature of the initiation system on the polymerization kinetics, molecular microstructure, nanoparticle morphology, and mechanical properties of the final thermoplastic.

2. Experimental

2.1. Materials

The following initiators were employed as received: potassium persulfate (KPS) from Mallinckrodt (purity 99%), and benzoyl peroxide (BPO) from Akzo Nobel (Perkadox L-W75 in 25% water). Hexadecane (HD) from Aldrich (purity $\geqslant$ 99%) was the latex costabilizer; Dowfax 2EP from Dow (purity 45%) was the surfactant; tert-dodecyl mercaptan (tDM) from Fluka (purity 95%) was the chain transfer agent (CTA); and hydroquinone from Fluka (purity > 99%) was the polymerization inhibitor. Technical grade styrene was first washed with a KOH aqueous solution to remove polymerization inhibitors, and then with demineralized water until reaching the pH of the washing water. The PB was a Buna CB 55 GPT by Lanxess (medium-*cis* rubber produced by solution anionic polymerization with an organolithium catalyst). Its average molar masses were determined by size-exclusion chromatography (SEC), yielding: $\bar{M}_n$ = 142800 g/mol; and $\bar{M}_w$ = 281,200 g/mol. These values were determined through a universal calibration obtained with PS standards, and the following Mark–Houwink parameters in tetrahydrofuran at 30 °C taken from Kurata and Tsunashima [17]: (a) for PS, $K_{PS} = 1.10 \times 10^{-2}$ mL/g and $a_{PS} = 0.725$; and (b) for PB, $K_{PB} = 2.56 \times 10^{-3}$ mL/g, and $a_{PB} = 0.74$. The tetrahydrofuran SEC carrier was from J.T. Baker (HPLC Solvent). Finally, methyl-ethyl ketone (MEK, from Anedra, 99% purity) was the selective solvent for the determination of the grafted PS mass. Demineralized water was used throughout the work.

2.2. Miniemulsification

The following was common to all miniemulsions: (a) 50 wt%. of solids; (b) 5–10% wbop (weight based on organic phase) of PB; (c) 3% wbop of active surfactant; (d) 4% wbm (weight based on monomer) of HD; and (e) 0.2% wbop of $NaHCO_3$. Prior to the miniemulsifications, the following were dissolved in the monomer phase: (i) the grated PB; and (ii) the BPO initiator, and the tDM CTA (in the reactions where these reagents were employed). To produce the miniemulsion, the organic and aqueous phases were first strongly mixed by magnetic stirring during 15 min., and the resulting pre-emulsion was sonified during 45 min. in a Sonics VC 750 (power 750 watts) at 100% of amplitude, in cycles of 20 s on and 5 s off. Sonication time was determined as that required to obtain a low average droplet diameter ($\bar{d}_d$) and a narrow droplet size distribution (both measured on the miniemulsions by dynamic light scattering: DLS). Due to the high solid content and high organic phase viscosity, longer sonication times than those typically employed for St miniemulsions were needed [18]. Sonication was carried out in a refrigerated jacketed vessel, to maintain the miniemulsion temperature below 35 °C.

2.3. Polymerizations

The polymerizations were carried out in a 0.2 L batch glass reactor equipped with a reflux condenser, a stirrer, a sampling device, and a nitrogen inlet. The reaction temperature (70 or 90 °C) was adjusted by manipulation of the reactor jacket temperature, in turn controlled by a water bath. The miniemulsion was loaded into the reactor, and the system was kept under stirring and nitrogen bubbling until the desired reaction temperature was reached. Polymerizations with KPS were started by injecting its water solution as a shot. Note that while KPS generates hydrophilic radicals in the water phase, BPO generates hydrophobic radicals in the organic phase. Thus, BPO radicals are restricted to a small phase volume that enhances bimolecular termination, lowering the efficiency of those radicals with respect to the water-soluble KPS radicals [19]. For this reason, experiments involving BPO were carried out at higher temperatures, and in most cases at higher initiator concentrations. Furthermore, total polymerization times were 2 h for reactions with KPS, and 3 h for reactions with BPO.

2.4. Measurements

Prior to the reactions, the miniemulsion stability was determined in a Turbiscan TMA2000, where the intensity profile of backscattered light along a vertical tube was measured every 5 min. along 4 h; and the miniemulsion surface tension was measured with a Krüss tensiometer K8.