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Preparation of ASA (acrylonitrile-styrene-acrylate) structural latexes via seeded emulsion polymerization

Shima Tolue [a], Mohammad Reza Moghbeli [a,*], Seyed Mehdi Ghafelebashi [b]

[a] *School of Chemical Engineering, Iran University of Science and Technology (IUST), Maleklo St., Khavar St. Farjam St. Narmak, P.O. Box 16844-13114, Tehran, Iran*
[b] *Petrochemical Research & Technology Company (NPC-RT), P.O. Box 14358, Tehran, Iran*

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A B S T R A C T

Acrylonitrile-styrene-acrylate (ASA) structural latexes were synthesized in a two-stage seeded emulsion polymerization. In the first-stage, partially cross-linked poly (*n*-butyl acrylate) (P*n*BA) and poly (*n*-butyl acrylate-stat-2-ethyl hexyl acrylate) P (*n*BA-stat-2EHA) (75/25 by wt) rubber cores were synthesized, and then in the second-stage, a hard poly (styrene-stat-acrylonitrile) (SAN) (70/30 by wt) shell was grafted on to the rubber seeds. The effects of surfactant type and second-stage monomer addition mode have been investigated on the final morphology of two-stage emulsion particles. The results indicated that an application of anionic surfactant, that is, sodium dodecyl sulfonate (SDS), along with sodium persulfate (KPS) initiator for both stages, and with first-stage *tert*-butyl hydroperoxide (*t*-BHP) and second-stage KPS initiators led to a hemisphere particle morphology. On the other hand, raspberry and core–shell structures were observed for the structural latexes, which were prepared using a non-ionic surfactant, that is, nonylphenol ethoxylated polyethylene glycol (Igepal CO-850), accompanying KPS initiator for both stages. It is clear, however, that the relative surface hydrophilicity of the core phase, altered by the surfactant type considerably affected the type of morphology formed. For obtained structural latexes, the gradual addition of the second-stage monomers to the core latexes resulted in a fairly real core–shell structure with a higher shell thickness. On the contrary, a raspberry structure in which the rubber phase was enlarged by the second-stage polymer microdomains was observed for the second-stage monomer addition batch. In fact, the shell semi-batch polymerization conditions lower the shell plasticizing effect, and increase the kinetic barrier to prevent from further second-stage monomer diffusion and microdomain formation within the rubbery phase.

1. Introduction

Preparation of structured latex particles with predetermined complex morphologies and a variety of functions has attracted the interest of scientists for many years [1,2]. These polymer materials are widely used in industrial applications, for example, coating, adhesives, paints, and rubber modification of some brittle thermoplastic polymers and thermoset resins to improve their inherent physical and mechanical properties [3–8]. Core–shell impact modifiers as typical structured latex particles have been prepared via a two-stage emulsion polymerization process [9–15]. The rubber cores with low glass-transition temperatures (T_g) are synthesized in the first-stage emulsion polymerization. In the second-stage, that is, seeded emulsion polymerization, a glass thermoplastic polymer is grafted onto the rubber seeds by addition across the residual double bonds or hydrogen abstraction from the rubber chains, to give radicals which add monomer units to form a grafted branch.

In most cases, the resulting particle morphology in the seeded emulation polymerization cannot result in a core–

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[*] Corresponding author. Fax: +91 21 77240495.
E-mail address: mr_moghbeli@iust.ac.ir (M.R. Moghbeli).

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shell structure with completely separated core and shell phases [16,17]. Varying some polymerization parameters, such as emulsifier and initiator types, the amount of cross-linker, core-to-shell phase ratio, monomer composition, and monomer addition mode at different polymerization stages provide various composite particle morphologies [17–25]. In many cases, the observed particle morphology that deviates from the ideal core–shell structure including morphologies are described simply as hemispherical, raspberry, mushroom, and confetti in the literatures [16,17]. In fact, the diversity in composite particle morphologies can be attributed to the phenomenological thermodynamic/kinetic behaviors which control the phase distribution within particles in the seeded emulsion polymerization [17,26].

Commercialized core–shell structured latex particles as impact modifiers are composed of traditional grafted rubber–thermoplastic materials, such as methacrylte-butadiene-styrene (MBS), all-acrylics impact modifier (AIM), and acrylonitrile-butadiene-styrene (ABS). Commercial acrylonitrile-styrene-acrylate (ASA) core–shell latexes, with obvious similarities to ABS latexes, have also been developed for the toughening of rigid SAN copolymers by a few industrial manufacturers [27]. Although the graft shell in both ABS and ASA modifiers is similar, the hydrophobic poly (butadiene) (PB) rubber core within the ABS particles is substituted by the less hydrophobic P*n*BA rubber core in the ASA particles. Thus, the difference in the interfacial tension of various rubber cores against water, and in their compatibilities to the shell polymer units may lead to some significant complexities in their manufacturing process.

Although more research investigations have been carried out in the preparation of ABS latexes, less attention has been paid to the preparation of ASA latexes [27]. In the present research work, the effects of surfactant type and second-stage monomer addition mode on the final morphology of the ASA emulsion particles have been investigated.

2. Experiments

2.1. Materials

All reagents were prepared from Merck Co., unless otherwise stated. Styrene (St), *n*-Butyl acrylate (*n*BA), and acrylonitrile (AN) were distillated under vacuum to remove their inhibitors. Allyl methacrylate (ALMA) from Aldrich and tertiary dodecyl mercaptan (TDM) from Fluka were purchased as cross-linking agent and chain-transfer agent, respectively. Sodium dodecyl sulfonate (SDS) as anionic surfactant and nonylphenol ethoxylated polyethylene glycol (Igepal CO-850) as non-ionic surfactant from Rhodia, potassium persulfate (KPS) and water soluble *tert*-butyl hydroperoxide (*t*-BHP) both as initiators were used directly without any further purification. Tetrahydrofuran (THF) and toluene, both analytical grades, were purchased for solvent extraction experiments. Distillated deionized water (DDI) was prepared in the laboratory of the author.

2.2. Core and core–shell synthesis

The ASA core–shell latexes were synthesized via a two-stage seeded emulsion polymerization. Acrylate rubber core and core–shell polymers were prepared in a 150-ml three-neck glass reactor equipped with a reflux, inlet nitrogen, and a magnetic stirrer. The reactor was held in a bath with thermostatic control. Firstly, P*n*BA and P(*n*BA-stat-2EHA) core latexes were synthesized at 80 °C and 250 rpm for 3.5 h according to the emulsion recipes listed in Table 1. Various types of aforementioned initiators and emulsifiers were utilized to make the rubber cores with different surface polarities. In the second-stage polymerization, the St/AN (70/30) monomer mixture was added to form the shell layer over the rubber cores at 80 °C and 250 rpm for 3.5 h in batch and semi-batch seeded emulsion polymerization processes (Table 2). Synthesized ASA emulsion particles were designated with a common name CS, a recipe number corresponding to a core recipe listed in Table 1, and an abbreviation B or SB which is a representative of the shell batch (B) or semi-batch (SB) emulsion polymerization process.

2.3. Characterization

2.3.1. Gel content of the seed latex

The gel content of rubber seed particles was measured via solvent extraction method. Three samples of dried P*n*BA and P(*n*BA-stat-2EHA) film, 0.25 g each were added to 25 ml THF, and stirred at 300 rpm and room temperature for 48 h. Then samples were centrifuged at 5000 rpm for 1 h. The sediment gel phase was separated from the sol phase and dried in a vacuum oven at 50 °C. The gel fraction was determined gravimetrically, based on the total weight of the sample.

2.3.2. Grafting degree

In order to determine the grafting degree, the composite latexes were freeze-dried to a fine powder, and placed in a vacuum oven at 40 °C for 3 h to remove the trace amount of water. Then, three samples of powder, 1 g each, were dispersed in 25 ml toluene and were stirred at room temperature and 300 rpm for 8 h. The dispersions were centrifuged at 5000 rpm for 2 h at 4 °C. The gel phase at the bottom of the cell was separated from supernatant phase, and both fractions were dried to remove solvents under vacuum at 40 °C for 24 h. The grafting degree, the weight ratio of grafted SAN to rubber seed particles, G_d, was measured gravimetrically.

Table 1
Recipes for the preparation of acrylate seed latexes.

Ingredients[a]	C1	C2	C3	C4
BA	24	24	24	18
2EHA	0	0	0	6
DDI	72	72	72	72
KPS	0.06	–	0.06	0.06
t-BHP	–	0.06	–	–
ALMA	0.09	0.09	0.09	0.09
SDS	0.12	0.12	–	–
Igepal CO-850	–	–	0.33	0.33

[a] Quantities are in weight parts.