

CORE-SHELL STRUCTURED NANO-PARTICLES FOR BAROPLASTIC PROCESSING

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Introduction

Recently we proposed a novel class of materials called “baroplastic” block copolymers that can be processed by an applied pressure at low temperature due to a pressure-induced miscibility between two-polymer phases.^{1,2} A series of block copolymers containing a low T_g block such as poly(alkyl acrylate) and a high T_g block such as poly(alkyl methacrylate) or polystyrene exhibited room temperature processability by compression molding under a pressure of 5000 psi for 5 min.^{3,4} Baroplastic materials can provide several advantages over current commodity plastics; for example, lower processing temperatures that save energy in processing, which generally requires heating and cooling cycles. Another advantage is that thermal degradation can be reduced with baroplastic materials, which is typically present in melt processing and is one of the problems with current polymer recycling, where reprocessing leads to a material with poor optical and mechanical properties. Consequently, baroplastic materials can conceivably be processed many times with minimum degradation, resulting in a material with a long recycle life.

To extend the concept of baroplastic materials to blend systems, we applied here core-shell structured nano-particles as a new paradigm for baroplastics. In fact, core-shell nano-particles can be simply synthesized with greater variety of monomers than in a controlled block copolymerization. Emulsification of previously prepared polymers provides further variation in choices of components.

In this work, we synthesize a series of core particles of poly(2-ethyl hexylacrylate), PEHA ($T_g = -50^\circ\text{C}$), poly(*n*-butyl acrylate), PBA ($T_g = -54^\circ\text{C}$), and polyisoprene, PI ($T_g = -63^\circ\text{C}$) covered with a polystyrene, PS ($T_g = 100^\circ\text{C}$), shell by a two-stage micro-emulsion polymerization. The baroplastic properties of these materials were investigated by compression molding under 5000 psi pressure at 25°C with a hydraulic press.

Experimental

Materials. All reagents were purchased from Aldrich Co. The inhibitors were removed, prior to polymerization, by passing through a column packed with basic aluminum oxide. Tetradecyltrimethylammonium bromide, TTAB, 2,2'-azobis(2-methylpropionamide) dihydrochloride, V50, 1-dodecanethiol, DT, and acetone were used as received without further purification. Deionized water was used throughout the experiments.

Polymerization procedure. Core-shell structured particles were synthesized by a two-stage emulsion polymerization technique as reported by Ha et al.⁵ A representative procedure for PEHA/PS core-shell nano-particles is as follows. Under a N_2 atmosphere, 60 g of water, 1.3 g of emulsifier and 11 g of acetone were added to 250 mL glass reactor. After purging with N_2 for 30 min, the solution was heated to 65°C under vigorous stirring. 9 g of EHA were then added slowly and stirred for extra 1 h. The first-stage micro-emulsion polymerization was started by adding 0.1 g of V50 and allowed to proceed for 15 h. 9 g of styrene monomer pre-emulsified solution using 75 g of water, 12 g of acetone and 0.2 g of DT were then added continuously to the reactor for 2 h. After 3 h of reaction time, core-shell particles were precipitated in methanol/water (5/1, v/v, containing trace amounts of NaCl) and washed with water at least 3 times. The obtained product was then dried in a vacuum oven for 3 days at room temperature in the presence of phosphorus pentoxide.

Characterization. The particle size was determined by using a ZetaPALS particle sizer (Brookhaven Instruments Co.) fitted with a 676 nm laser source. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX (300 MHz) in CDCl_3 . Gel permeation chromatography, GPC, was performed at 30°C with a Viscotek GPCmax instrument. THF was used as an eluent at a flow rate of 1.0 mL/min. Atomic force microscopy (AFM) was recorded with a Digital Instruments Dimension 3000 Multimode AFM in

“tapping mode”. A pressure and temperature controlled hydraulic press was used for compression molding with different molds.

Results and Discussion

The core-shell nano-particles were synthesized by a two-stage micro-emulsion polymerization technique and the results are listed in **Table 1**.

Table 1. Characterization of Core-Shell Nano-Particles^a

core	shell	particle size (nm) ^b	composition (w%) ^c
PEHA	PS	53.6 / 67.4	53 / 47
PBA	PS	48.0 / 56.1	45 / 55
PI	PS	18.9 / 29.0	38 / 62

^a Molecular weights of core and shell were around 300K and 100K, respectively from GPC measurement using PS standards.

^b Measured by dynamic light scattering, (core / core-shell).

^c Determined by ^1H NMR analysis in CDCl_3 (core / shell).

The average particle size of core polymers obtained in the first stage were 18.9 - 53.6 nm and increased to 29.0 - 67.4 nm after adding the styrene monomer in the second stage. This increment suggests that the polystyrene grows around the parent particles, forming a core-shell structure. **Figure 1** shows a representative particle size distribution histogram of a PEHA/PS core-shell system. In both histograms, very narrow particle size distributions are clearly observed, which also means the monotonic growth of particles after addition of styrene monomer. The compositions of resulting core-shell particles were calculated by the integral ratio between PS and the core polymer from ^1H NMR measurement. For example, as shown in **Figure 2**, by choosing two characteristic resonances in 6.3 - 7.2 ppm (styrenic aromatic) and 3.8 - 4.1 ppm (OCH_2 - of EHA), the weight ratio of core and shell was estimated as 0.53 and 0.47, respectively, which was quite similar to the feed ratio.

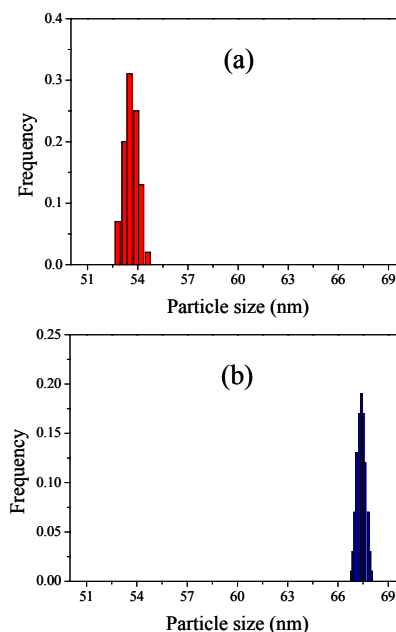


Figure 1. Size distribution curves for (a) core particles and (b) core-shell particles of PEHA/PS measured from DLS.

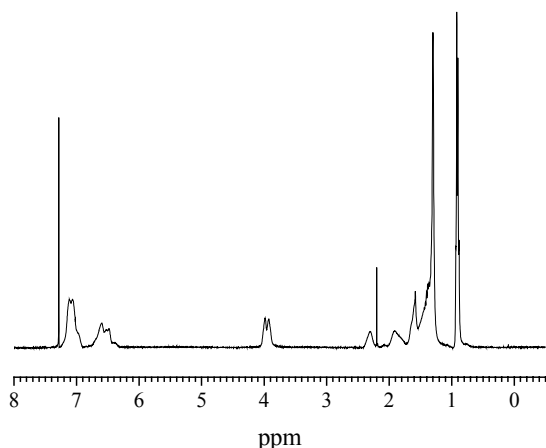


Figure 2. ^1H NMR spectrum of PEHA/PS core-shell particle in CDCl_3 .

Figure 3 shows a typical AFM topographic image of the PBA/PS core-shell nano-particles deposited on glass. The mean diameter was 60 nm, which is somewhat deviated from the result of dynamic light scattering (56.1 nm). In fact, determination of the actual size is difficult because of the convolution with the tip shape in AFM measurement. The baroplastic properties of a PBA/PS core-shell nano-particle are demonstrated in **Figure 4**, which shows a compression molded specimen processed at 5000 psi for 5 min at 25°C from the originally powdered state. Similar baroplastic behavior was demonstrated in PEHA/PS core-shell nano-particles under the same conditions as described above. Furthermore, molded objects reprocessed 10 times seemed to have nearly equivalent optical and mechanical properties as after their first processing, suggesting these core-shell materials can also be readily remolded after processing like PEHA-*b*-PS or PBA-*b*-PS block copolymers. By contrast, PI/PS core-shell particles, which exhibit pressure-induced immiscibility,⁶ seem to process at room temperature but easily craze under applied stresses. Further reprocessing attempts of this material showed rapidly decreasing mechanical and optical properties.

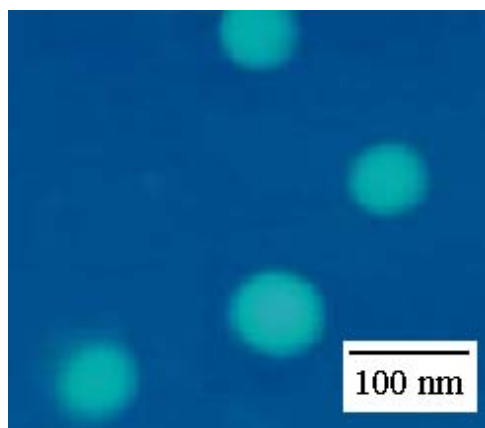


Figure 3. AFM image of PBA/PS core-shell particle on glass surface.



Figure 4. PS/PBA core-shell particles before (right) and after (left) processing at 25°C under 5000 psi for 5 min.

Conclusion

Core-shell nano-particles of PEHA/PS, PBA/PS, and PI/PS were synthesized with narrow particle size distribution by two-stage micro-emulsion polymerization. Among them, PEHA/PS and PBA/PS systems could be processed at 25°C under 5000 psi. Based on a PI/PS core-shell control sample, revealed that pressure-induced miscibility appears to be required for baroplastic processing. The resulting baroplastic core-shell materials could have many advantages due to its simplicity and scalability of synthesis as well as room temperature processability.

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