Epoxy-Acrylic Core-Shell Particles by Seeded Emulsion Polymerization

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Abstract

We developed a novel method for synthesizing epoxy-acrylic hybrid latexes. We first prepared an aqueous dispersion of high molecular weight solid epoxy prepolymers using a mechanical dispersion process at elevated temperatures, and we subsequently used the epoxy dispersion as a seed in the emulsion polymerization of acrylic monomers comprising methyl methacrylate (MMA) and methacrylic acid (MAA). Advanced analytical techniques, such as scanning transmission X-ray microscopy (STXM) and peak force tapping atomic force microscopy (PFT-AFM), have elucidated a unique core-shell morphology of the epoxy-acrylic hybrid particles. Moreover, the formation of the core-shell morphology in the seeded emulsion polymerization process is primarily attributed to kinetic trapping of the acrylic phase at the exterior of the epoxy particles. By this new method, we are able to design the epoxy and acrylic polymers in two separate steps, and we can potentially synthesize epoxy-acrylic hybrid latexes with a broad range of compositions.

Keywords:

Mechanical dispersion, Seeded emulsion polymerization, Epoxy-acrylic core-shell particles, Scanning transmission X-ray microscopy, Peak force tapping atomic force microscopy

1. Introduction

Hybrid polymer latexes with complex morphologies have been widely used in coating, construction, and adhesive applications [1,2]. Synergy between two distinct chemistries can be achieved to offer tremendous advantages in performance over an individual polymer latex or a blend of two different latexes. Hybrid polymer latexes are commonly synthesized by either a mini-emulsion polymerization [3] or seeded emulsion polymerization process [4]. There have been tremendous research efforts on the preparation of hybrid polymer latexes, such as silicone-acrylate [5], acrylate-urethane [6], styrene-acrylate [7], and PVDF-acrylic [8]. Among these examples, various particle morphologies, including the core-shell morphology, were often specifically designed [9].

We are interested in epoxy-acrylic hybrid latexes where the unique performance attributes of both chemistries can be combined. Acrylic latexes have been used in various applications owing to their tunable mechanical, aesthetic, and chemical properties, while waterborne epoxy dispersions have been applied in protective and maintenance coatings due to their benefits such as hardness and chemical resistance [10]. The mini-emulsion approach has been widely taken to synthesize the epoxy-acrylic hybrid latexes. The epoxy prepolymers are first dissolved into the acrylic monomers. The mixture is emulsified in water to form well-defined submicron droplets, and finally, the monomers are polymerized by free radical polymerization [11-13]. By this approach, the epoxy groups from the original epoxy prepolymers remain intact throughout the polymerization process. Liu and coworkers demonstrated the epoxy-acrylic hybrid latexes by a two-stage emulsion polymerization process [14], but the morphology of the resulting latexes was still ill-defined. In addition, a new method was recently developed to synthesize epoxy-acrylic hybrid latexes [15], where a liquid epoxy prepolymer was post-mixed with the acrylic latexes

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4 and absorbed into the acrylic particles. In all of the previous examples, only liquid epoxy
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6 prepolymers were successfully used in the synthesis of epoxy-acrylic hybrid latexes, and the
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8 epoxy prepolymers were typically limited to less than 50 wt% in the hybrid particles. For some
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10 applications where performance attributes from epoxy resins are strongly desired, new methods
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12 are required to broadly tune the composition of the epoxy-acrylic hybrid latexes.
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16 In this paper, we developed a novel method for synthesizing epoxy-acrylic hybrid latexes as
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18 illustrated in Figure 1. We first prepared an aqueous dispersion of high molecular weight solid
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20 epoxy prepolymers by a continuous solvent-free mechanical dispersion process. This process
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22 was developed to create stable aqueous dispersions of polymers that cannot be produced by
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24 conventional emulsification techniques. By this process, high internal phase ratio emulsions [16]
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26 were first formed and then diluted to polymer dispersions at the desired solid content [17]. For
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28 example, high viscosity silicone polymers were processed to form very small droplet sizes with
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30 narrow particle size distributions [18]. Herein, we have successfully prepared solid epoxy
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32 particles of less than 400 nm with a narrow particle size distribution by using polyvinyl alcohol
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34 as a dispersant. Next, we used the epoxy dispersion as a seed in the emulsion polymerization of
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36 acrylic monomers comprising methyl methacrylate (MMA) and methacrylic acid (MAA). We
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38 characterized the morphology of the epoxy-acrylic hybrid latex particles by using both scanning
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40 transmission X-ray microscopy (STXM) and peak force tapping atomic force microscopy (PFT-
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42 AFM) techniques and proved a well-defined core-shell morphology. This new approach allows
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44 us to tune the composition of the hybrid polymer latexes in two independent steps, and it can
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46 produce new epoxy-acrylic hybrid latexes potentially useful for various applications.
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58 **2. Materials and methods**

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2.1. Materials.

Bisphenol-A epoxy resin prepolymers [19] (D.E.R.TM 331, D.E.R.TM 669E) were obtained from The Dow Chemical Company. Polyvinyl alcohol (MowiolTM 4-88) was purchased from Kuraray. Sodium formaldehyde sulfoxylate (SFS), tert-butyl peroxide (70% solution in water) (t-BuOOH), sodium dodecylbenzene sulfonate (SDBS), methylmethacrylate (>99% purity), and methacrylic acid (>99% purity) were obtained from Aldrich and were used without further purification.

2.2. Synthesis of epoxy-acrylic hybrid latex

2.2.1. Batch Dispersion Process. The experimental protocol was described in the literature [20].

A blend of D.E.R.TM 331 and D.E.R.TM 669E in a weight ratio of 45:55 (50.0 g) and a polyvinyl alcohol (PVOH) solution (28.0 wt% solid) (18.0 g) were first charged into a 300-mL stainless steel Parr reactor equipped with a Cowles blade. The reactor was pre-heated to 100 °C, and the mixture was stirred for 10 min to allow sufficient mixing of the epoxy phase and the PVOH solution at a speed of 1800 rpm. To this mixture, deionized (DI) water was added using an HPLC pump at the rate of 1.0 mL/min over 20 min. After that, the addition rate of DI water was increased to 10 mL/min for an additional 4 min. The reactor was then cooled down to 50 °C in a water bath at a mixing speed of approximately 500 rpm. The resultant dispersion was collected by filtration through a 190 micron filter.

2.2.2. Seeded Emulsion Polymerization. The experimental procedure was modified based on the protocol described in the literature [21]. A diluted epoxy dispersion (94.1 g, 40 wt% solids) was charged into a 250 mL three-neck flask fitted with a condenser and a mechanical stirrer. The flask was soaked in a water bath set at 65 °C. The stir rod was inserted through the Teflon adaptor and glass sleeve and connected to the center of the flask. The stirrer rate was set at 200 rpm. Nitrogen was slowly purged through the reactor, and cooling water was turned on to flow

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4 through the condenser. MMA (8.21 g) and MAA (2.05 g) were mixed with DI water (2.56 g) and
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6 SDBS (0.020 g) in a glass jar to form an emulsion, and the mixture was fed into the flask by a
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8 syringe pump at a steady rate over 40 min. SFS (0.062 grams) and t-BuOOH (70% active) (0.088
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10 grams) were dissolved in 5 g of DI water, respectively, and then fed by two separate syringe
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12 pumps into the reactor at the same rate over 60 min. After feeding the initiators, the reaction was
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14 held at 65 °C for one hour. Finally, the epoxy-acrylic hybrid latex was collected by filtration
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16 through a 190 micron filter. Some of the dispersion sample was dried at ambient temperature to
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18 form a powder for further analyses.
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23 **2.3. Transmission electron microscopy (TEM)**

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25 The polymer latex was diluted in DI water, and then, a ~0.5-μL drop of solution was placed onto
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27 a carbon-coated TEM grid. The dry polymer powder was embedded in BEEM capsules using
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29 D.E.R.TM 330 epoxy resin with D.E.H.TM 24 epoxy curing agent. A Leica UC6 microtome was
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31 used to collect 90-nm-thick sections on 400 mesh copper TEM grids. Sections were vapor
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33 stained over 0.5% ruthenium tetroxide for 3 min. Samples were examined with a JEOL JEM-
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35 1230 TEM operating at 120 kV. Digital images were collected with a Gatan MultiScan CCD
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37 camera.
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43 **2.4. Scanning Transmission X-ray Microscopy (STXM)**

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45 Scanning transmission X-ray microscopy was performed using the X-ray microscope at beamline
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47 5.3.2.2 at the Advanced Light Source at Lawrence Berkeley National Laboratory. The instrument
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49 setup has been described elsewhere [22]. The samples were scanned in the x and y directions
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51 using piezo-ceramic positioning to build up an image on a pixel-by-pixel basis. The spatial
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53 resolution of the measurement was approximately 30 nm. Hyperspectral images were collected
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55 from the sample by acquiring images of the same area at multiple energies providing one
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4 NEXAFS spectrum at each pixel. Transmission images were aligned and transformed into an
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6 optical density image stack using Axis 2000 program [23]. The ratio of the epoxy to acrylic
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8 polymers was determined by performing a non-negative least square fitting (NNLS) on the
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10 NEXAFS spectrum pixel by pixel using a Matlab program developed in-house, assuming the
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12 spectrum at each pixel is a linear combination of the pure component spectra collected from the
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14 pure epoxy and acrylic polymers used in this study (Figure 2) with a non-negative concentration.
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16 The sample was prepared by drying a drop of diluted polymer latex on a thin silicon nitride
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18 window. The polymer latex used for the STXM characterization had a slightly different epoxy
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20 composition (DER669E:DER331=1:1 by weight) than the sample shown in the rest of the paper.
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26 **2.5. Atomic force microscopy (AFM)**

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28 The dried powder was embedded into BEEM capsules using D.E.R.TM 330 epoxy resin with
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30 D.E.H.TM 24 epoxy curing agent. A Leica UC6 microtome was used to collect 150 nm thin
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32 sections on cleaved mica. AFM images were collected using two methods: conventional tapping
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34 mode (TMAFM) and peak force tapping (PFT). Tapping mode AFM is a resonant cantilever
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36 imaging technique that provides both topographic and phase lag imaging, the latter of which is
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38 useful for material contrast. Peak force tapping is a non-resonant mode in which fast load-
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40 displacement curves are measured at each pixel in the image. With the proper calibrations, this
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42 mode provides several channels of information mapping stiffness (modulus), adhesion,
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44 dissipated energy, and deformation in addition to topography [24, 25]. For this work the same
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46 probe was used for both imaging methods and images collected on the same powder particle.
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52 Both imaging methods were carried out on a MultiMode8 AFM using a Nanoscope V controller
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54 running v8.15 Nanoscope software (Bruker-Nano, CA). A silicon cantilever and tip (Arrow
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56 NCR, Nanoworld) was used. The tip radius was 11.2 nm determined by blind reconstruction
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4 using the TipCheck scanning artifact. The optical lever sensitivity of the AFM was determined to
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6 be 44.6 nm/V using indentation on sapphire, and the spring constant of the cantilever was
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8 determined to be 46.7 N/m using thermal tuning. The resonant frequency of the cantilever was
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10 277 kHz. For the tapping mode, the cantilever free deflection was set to 500 mV, and the
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12 imaging set point was 400 mV for a set point ratio of 0.80. For the peak force tapping, the
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14 imaging was obtained with a set point of 100 nN, a peak force amplitude of 50 nm and a
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16 resonance frequency of 2 kHz. The tapping mode images and the peak force tapping were
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18 obtained at 512×512 pixels and 256×256 force curves, respectively. Selected force curves
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20 were analyzed using scanning probe image processor v6.35 (SPIP, Image Metrology, Denmark).
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26 **2.6. Other Characterization**

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28 The pH of the dispersion was measured using a Denver Instruments pH meter. The solid content
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30 of the dispersion was analyzed using an Ohaus MB35 series moisture analyzer. The dispersion
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32 particle size was analyzed on a Malvern Zetasizer Nano at 25.0 ± 1 °C, at a detection angle 173°
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34 (backscattering), and the samples were diluted with deionized water and loaded into a disposable
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36 plastic cuvette.
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41 The glass transition temperature (T_g) was measured using a DSC 2920 differential scanning
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43 calorimeter from TA Instruments. Approximately 10 mg of polymer was weighed into a DSC
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45 pan and then loaded into the instrument. The sample was cooled to -40 °C, held for 1 min, and
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47 heated to 140 °C at a scan rate of 10 °C per min while measuring the heat flow. The midpoint of
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49 the heat flow transition was taken as the T_g .
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53 The epoxy content was titrated using an automated titrator (815 Robotic USB Sample Processor
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55 XL). The desired amount of epoxy powder (~ 0.3 g) was weighed out into a flask followed by the
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57 addition of 50 mL of methylene chloride. The solution was stirred with a magnetic stir bar until
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the epoxy powder was completely dissolved. Then, the solution was placed on the auto-sampler. Each sample was titrated at least twice to obtain consistent results.

3. Results and Discussion

This mechanical dispersion process has been applied to prepare aqueous dispersions of solid epoxy prepolymers with a wide range of anionic or non-ionic surfactants that maintain interfacial activity at high temperatures. PVOH is an effective dispersant to disperse epoxy prepolymers in water at elevated temperatures. Aqueous dispersions of solid epoxy prepolymers with well-controlled particle sizes have been successfully prepared [20]. In this work, we used a miscible blend of liquid epoxy prepolymer (D.E.R.TM 331) and solid epoxy prepolymer (D.E.R.TM 669E) to balance the physical properties of the epoxy phase. Liquid and solid epoxy prepolymers at a weight ratio of 45:55 were melt blended to form a homogenous semi-solid with a glass transition temperature of 23.1 °C based on the DSC profile in Figure 3. By using 10 wt% of PVOH based on the total epoxy solids, the resultant epoxy dispersion showed a mean average particle size of 346 nm by DLS. The pH of the epoxy dispersion was approximately 6.0.

In the previous methods for preparing epoxy-acrylic hybrid latexes [11-14] where liquid epoxy prepolymers were miscible with acrylic monomers, it was difficult to control the phase separation between the epoxy prepolymer and the acrylic polymer in the resulting latexes. Besides, liquid epoxy prepolymers are known to form a rigid but brittle thermoset after curing with amine agents. Despite good performance attributes of epoxy resin, it is often preferred to have low epoxy content in the hybrid latex particles to produce mechanically durable coatings. In comparison, high molecular weight epoxy prepolymers are capable of producing more flexible coatings upon crosslinking, and therefore, higher content of solid epoxy prepolymers in the

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4 hybrid particles can be beneficial. However, hybrid latex particles containing solid epoxy
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6 prepolymers have not been demonstrated in the literature, because solid epoxy prepolymers are
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8 not readily soluble in acrylic monomers and it is challenging to disperse them in water by using
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10 conventional emulsification techniques.
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14 By our approach, the epoxy seed dispersion is prepared separately from the emulsion
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16 polymerization process, so the selection of epoxy prepolymers is not restricted by the emulsion
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18 polymerization process. We were interested in preparing epoxy-acrylic hybrid particles with a
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20 core-shell morphology. In the seeded polymerization process, we chose a copolymer
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22 composition of MMA and MAA at a 4:1 weight ratio and aimed at a shell to core ratio of 0.3.
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24 This acrylic polymer composition is also known as alkali soluble resin (ASR) [21] and it is
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26 insoluble under acidic conditions. The resultant hybrid dispersion has a pH value of 4.85. The
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28 particle size of the latex samples were characterized by DLS, as shown in Figure 4. The particle
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30 size distribution of the epoxy-acrylic hybrid particles is mono-dispersed and consistently shifted
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32 to higher particle sizes, and more importantly, the particle size data shows that no acrylic
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34 particles formed in the seeded polymerization process. The mean particle diameter of the epoxy-
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36 acrylic hybrid particles increases from 346 to 382 nm, and the averaged shell thickness is
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38 approximately 18 nm. Based on the weight increase of the epoxy-acrylic hybrid particles by
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40 30%, the calculated mean particle diameter is approximately 378 nm assuming both polymers
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42 have the same density, in good agreement with the measured particle size.
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51 From the DSC profiles in Figure 2, two distinct T_g s suggest the epoxy and acrylic phases likely
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53 exhibit a phase-separated structure in the hybrid particles. The T_g of the epoxy phase in the
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55 hybrid particles was 27.6 °C, which slightly increased from the T_g of the original epoxy
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57 prepolymers at 23.1 °C, indicating a small amount of ASR polymer might be mixed into the
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4 epoxy phase. The second T_g transition at 63.8 °C in the hybrid particles is likely associated with
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6 the ASR shell, which is reduced from the T_g of 90.1 °C of the neat ASR polymer. The
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8 suppression of the ASR T_g may be caused by mixing of some low T_g epoxy prepolymers into the
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10 ASR phase, but it would suggest substantial mixing between two polymers. Alternatively, the
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12 suppression of the T_g of ASR can be caused by the confinement effect, when the shell polymer
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14 thickness is less than 50 nm [26]. According to the morphology data shown later, the latter is
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16 more likely the cause, but it will require further research to investigate this.
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21 The TEM images of both the epoxy seed dispersion and the epoxy-acrylic latex are shown in
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23 Figure 5. The epoxy particles coalesced upon drying on the TEM grid, because the T_g of the
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25 epoxy prepolymers is 23.1 °C, close to ambient temperature. In comparison, the hybrid particles
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27 that were dried at ambient temperature maintained the spherical shape. The TEM results indicate
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29 a high T_g polymer shell may have prevented the epoxy particle from coalescence. We attempted
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31 to distinguish the morphology of the hybrid particles by TEM technique, but it was difficult to
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33 selectively stain the polymers using the conventional RuO_4 staining technique.
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38 The scanning transmission X-ray microscopy (STXM) technique has been proven as a powerful
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40 tool to characterize the binary PS and PMMA thin film blend in the literature [27]. Compared to
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42 the conventional TEM method, this technique has a high sensitivity to the chemical structure of
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44 the polymers directly, so it does not need to selectively stain the samples, which could
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46 potentially change the structure of materials. Because the epoxy phase has the C=C π bonds from
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48 its aromatic rings and the ASR polymer has the C=O π bonds from its carbonyl structure, the
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50 reference spectra collected from the two reference samples (Figure 2 in the experimental section)
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52 show strong peaks at 285.4 eV for the epoxy phase and 288.7 eV for the ASR polymer,
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54 corresponding to the C=C and C=O bonds, respectively [28]. By using the NEXAFS spectra of
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the two building polymers, the fitting of the data shows the density map of the individual polymer components in Figure 6. A distinct core-shell morphology was successfully identified in these epoxy-acrylic hybrid particles and the image suggests the hybrid particles have an acrylic shell. Because the STXM image is a 2D view of the 3D core-shell structures, X-ray passes through a big portion of epoxy at the center of the hybrid particles so the concentration of the acrylic is relatively low and difficult to be imaged at the center of the particles even though the epoxy core is three dimensionally covered by ASR. Because of the 3D structure of the hybrid particles and the spatial resolution of the STXM setup is ~ 30 nm, the acrylic shell thicknesses and the defects in the shell is difficult to be fully resolved.

Furthermore, two AFM methods were applied to resolve the morphology of the epoxy-acrylic hybrid particles. The dried powder of the epoxy-acrylic hybrid particles embedded in an epoxy matrix was cross-sectioned for imaging. The center of a dry particle was used for measurement, because it was likely the least affected by the sample preparation process. Selected images from both conventional tapping mode (top) and peak force tapping (bottom) were obtained using the same tip with the same nominal force, 100 nN. Conventional tapping mode AFM was first applied, and the core-shell structure was not clearly illustrated (Figure 7, top images). The boundary between individual particles seemed to be too thin, which was inconsistent with the content of the shell phase. While it is possible that harder tapping conditions might reveal the core-shell structure, the high frequency interaction (277 kHz) of the conventional tapping mode tip may not mechanically distinguish the two materials under the conditions used here. Alternatively, PFT at much lower frequency (2 kHz) illustrates the core-shell morphology of the hybrid particles well within the powder (Figure 7, bottom images). The high T_g ASR shell is stiffer (brighter in the images below) than the epoxy core, and the shell phase appears to

uniformly cover the surface of the epoxy particles based on the PFT image. Few small ASR domains were observed inside the epoxy phase as well. The particle size is in the range of 250–400 nm in diameter, and the shell thickness is approximately 20 nm. In the dried hybrid latex particles, the effect of the PVOH dispersant on the particle size was also evaluated. The water soluble PVOH is more hydrophilic than the ASR phase, so PVOH is expected to adsorb onto the surface of the epoxy-acrylic hybrid particles. Hence, the thickness of the shell phase comprising both ASR and PVOH is approximately 20.5 nm, in good agreement with the shell thickness by AFM, suggesting the mixing of epoxy and acrylic phases was insignificant in the hybrid particles prepared by the seeded emulsion polymerization process.

In addition to imaging, 256×256 force curves were obtained. The force curves were averaged within selected areas in the morphology representing the core (126 curves) and the shell (44 curves) (Figure 8). The averaged curves indicated a greater relative penetration of the tip into the core than into the shell. The unloading slopes can be used to estimate contact stiffness, and the ratio of the shell to core stiffness is ~ 1.2 , which is consistent with the softer epoxy core. The hysteresis between the loading and unloading curves in these force-distance loops indicates the energy dissipated per indentation cycle. The ratio of the energy dissipation of the softer core to the stiffer shell is ~ 1.4 , which is consistent with the lower T_g epoxy core.

Lastly, we would like to investigate the mechanism for the formation of the epoxy-acrylic core shell particles. As shown in the literature [29], acrylic polymers are known to be highly miscible with liquid epoxy prepolymers but become less miscible with crosslinked epoxy resins. It suggests that partial mixing of the epoxy prepolymers and the acrylic polymer is probably favored at thermodynamic equilibrium. Based on the PFT-AFM images, the ASR phase formed a distinguishable shell around the epoxy particles. We hypothesize that the formation of distinct

1 epoxy-acrylic core shell structure was primarily attributed to kinetic trapping under the synthesis
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4 conditions. The monomer emulsion was gradually fed into the epoxy dispersion, where the
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7 monomer droplets were separated from the seed particles, so the epoxy phase was minimally
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10 plasticized by the monomers. During the seeded emulsion polymerization, the ASR oligomers
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13 were initially formed in the aqueous phase and migrated onto the surface of the epoxy particles.
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16 The ASR polymer could further diffuse into the epoxy phase, but it may require a higher energy
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19 due to the higher molecular weight solid epoxy prepolymer. Based on the AFM deformation
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22 images, few small ASR domains inside the epoxy phase prove that migration of the ASR
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25 oligomers into the epoxy phase indeed occurred during the seeded emulsion polymerization, but
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28 only to a relatively small extent.

29 In conventional seeded emulsion polymerization, chemical grafting is known as a critical factor
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32 that drives the formation of a core-shell morphology in hybrid polymer latexes [30], and the
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35 formation of new acrylic particles would be greatly suppressed in the seeded polymerization
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38 process. Herein, the grafting reactions between the epoxy and acrylic polymers likely drove the
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41 formation of the epoxy-acrylic core shell particles. There are two possible grafting mechanisms
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44 between the epoxy and acrylic polymers in the literature: the reaction between carboxylic acids
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47 and epoxy groups [31] and radical grafting onto epoxy aliphatic carbon [32]. The epoxy groups
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50 were titrated using a standard method to show an epoxy equivalent weight (EEW) of 386.6
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53 gram/equivalent; meanwhile, the total EEW was calculated to be 388.7 gram/equivalent based on
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56 the epoxy phase. The minor change in the EEW suggests that the reaction of the epoxy groups
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59 and carboxylic acid was insignificant. However, neither of grafting reactions will cause
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62 significant changes in the epoxy EEW because the reactions occur predominantly at the
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4 interface. We will have to further analyze the chemical structure of the epoxy-acrylic hybrid
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6 particles to distinguish the above two mechanisms in future work.
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10 11 **4. Conclusions** 12 13

14 We have demonstrated the synthesis of novel epoxy-acrylic hybrid latexes by a combination of
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16 the mechanical dispersion and traditional emulsion polymerization processes. The resulting
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18 hybrid particles show a unique core-shell morphology by both STXM and PFT-AFM images.
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20 We were able to control the epoxy and acrylic polymers in two independent steps. We can
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22 potentially achieve a broad range of epoxy and acrylic compositions in the hybrid particles, as
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24 compared with the previous literature methods. For the epoxy-acrylic core-shell particles with a
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26 high T_g shell, the well-defined acrylic shell provides the low T_g epoxy core with good protection
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28 against irreversible coalescence upon drying, which can potentially lead to new applications of
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30 the epoxy-acrylic hybrid particles as powder additives [33]. This approach may also be applied
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32 to design epoxy-acrylic hybrid particles with different morphologies. Moreover, this new
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34 approach has shed some light on a new strategy for designing a broad range of novel hybrid
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36 particles beyond using the conventional emulsion polymerization technique.
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45 46 **ACKNOWLEDGMENTS** 47

48 We thank Ben Schaefer for help with the epoxy titration experiment. We also thank Susan
49
50 Fitzwater for valuable discussions and Tom Kalantar for helpful suggestions. The authors thank
51
52 A.L.D. Kilcoyne for beamline support throughout the study and for general discussions of the
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54 beamline and microscope. STXM data acquired at beamline 5.3.2.2 at the Advanced Light
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Source, Berkeley, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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FIGURES

Figure 1. Preparation of epoxy-acrylic core-shell particles via a seeded emulsion polymerization process.

Figure 2. The NEXAFS spectra of the epoxy prepolymers and the acrylic polymer.

Figure 3. The DSC traces of the epoxy prepolymers, the epoxy-acrylic hybrid particles, and the ASR resin. The signals are shifted vertically.

Figure 4. The particle size distribution curves of the epoxy dispersion and the epoxy-acrylic hybrid latex with 30% ASR.

(a)

(b)

Figure 5. The TEM images of the epoxy particles (a) and the epoxy-acrylic hybrid particles (b).

Figure 6. An STXM image of the epoxy-acrylic hybrid particles with 30% ASR (MMA:MAA=4:1).

Conventional
TappingMode

Height

Phase

Peak Force
Tapping

Height

Stiffness

Deformation

Figure 7. The AFM images of the epoxy-acrylic hybrid particles (image $1.5\ \mu\text{m} \times 1.5\ \mu\text{m}$).

Figure 8. Force curve analysis from PFT. Curves from representative core (blue) and shell (red) regions of the morphology were averaged and analyzed; in this case, they are shown in the deformation map (left). Average force vs. distance curves are compared (right). The curves are discontinuous at the peak force because they are averages. The experimental peak force was 100 nN.

STXM images of epoxy-acrylic core-shell latex

Epoxy Map

Acrylic Map