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Epoxy-acrylic core-shell particles by seeded emulsion polymerization

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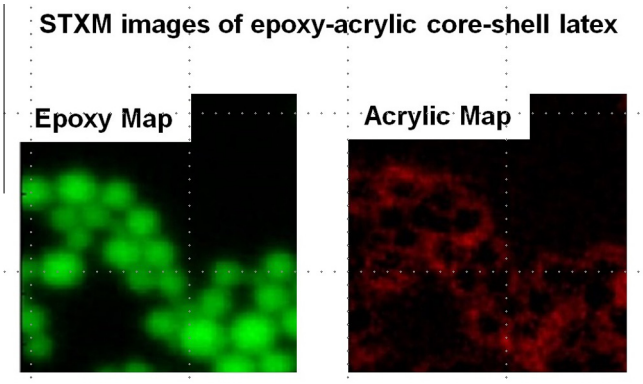
GRAPHICAL ABSTRACT



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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.

1. Introduction

Hybrid polymer latexes with complex morphologies have been widely used in coating, construction, and adhesive applications [1,2]. The 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

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[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 and absorbed into the acrylic particles. In all of the previous examples, only liquid epoxy prepolymers were successfully used in the synthesis of epoxy-acrylic hybrid latexes, and the epoxy prepolymers were typically limited to less than 50 wt% in the hybrid particles. For some applications where performance attributes from epoxy resins are strongly desired, new methods are required to broadly tune the composition of the epoxy-acrylic hybrid latexes.

In this paper, we developed a novel method for synthesizing epoxy-acrylic hybrid latexes as illustrated in Fig. 1. We first prepared an aqueous dispersion of high molecular weight solid epoxy prepolymers by a continuous solvent-free mechanical dispersion process. This process was developed to create stable aqueous dispersions of polymers that cannot be produced by conventional emulsification techniques. By this process, high internal phase ratio emulsions [16] were first formed and then diluted to polymer dispersions at the desired solid content [17]. For example, high viscosity silicone polymers were processed to form very small droplet sizes with narrow particle size distributions [18]. Herein, we have successfully prepared solid epoxy particles of less than 400 nm with a narrow particle size distribution by using polyvinyl alcohol as a dispersant. Next, we used the epoxy dispersion as a seed in the emulsion polymerization of acrylic monomers comprising methyl methacrylate (MMA) and methacrylic acid (MAA). We characterized the morphology of the epoxy-acrylic hybrid latex particles by using both scanning transmission X-ray microscopy (STXM) and peak force tapping atomic force microscopy (PFT-AFM) techniques and proved a well-defined core-shell morphology. This new approach allows us to tune the composition of the hybrid polymer latexes in two independent steps, and it can produce new epoxy-acrylic hybrid latexes potentially useful for various applications.

2. Materials and methods

2.1. Materials

Bisphenol-A epoxy resin prepolymers [19] (D.E.R.™ 331, D.E.R.™ 669E) were obtained from The Dow Chemical Company. Polyvinyl alcohol (Mowiol™ 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.™ 331 and D.E.R.™ 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 μm 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 through the condenser. MMA (8.21 g) and MAA (2.05 g) were mixed with DI water (2.56 g) and SDBS (0.020 g) in a glass jar to form an emulsion, and the mixture was fed into the flask by a syringe pump at a steady rate over 40 min. SFS (0.062 g) and *t*-BuOOH (70% active) (0.088 g) were dissolved in 5 g of DI water, respectively, and then fed by two separate syringe pumps into the reactor at the same rate over 60 min. After feeding the initiators, the reaction was held at 65 °C for one hour. Finally, the epoxy-acrylic hybrid latex was collected by filtration through

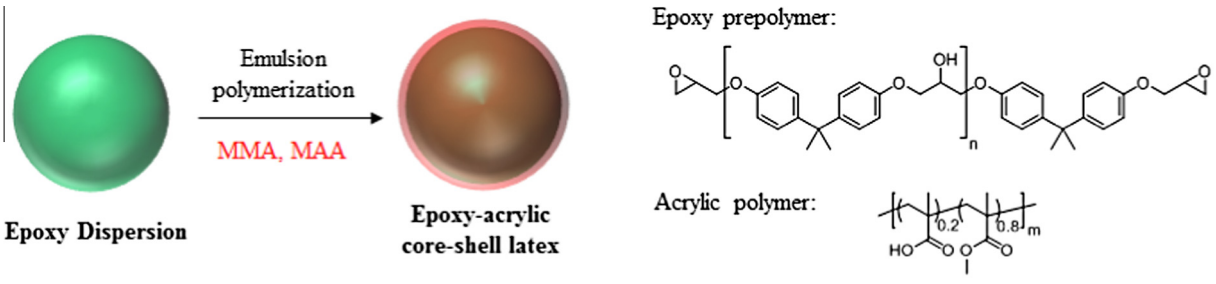

Fig. 1. Preparation of epoxy-acrylic core-shell particles via a seeded emulsion polymerization process.