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Thermoset–thermoplastic hybrid nanoparticles and composite coatings

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ABSTRACT

Structured thermoset–thermoplastic hybrid nanoparticles and composite coatings were successfully synthesized through a novel one-pot approach. Both the polyaddition of epoxy curing and the free radical polymerization of various vinyl monomers were performed in sequence in miniemulsion droplets. Benefiting from the precise control of the compatibility between thermoset phase (epoxy monomer/amine curing agent) and vinyl phase (vinyl monomers/polymers), colloidally stable, core–shell structured thermoset–thermoplastic hybrid nanoparticles between 100 and 200 nm were obtained through chemically induced phase separation. The influence of the compositions on the colloidal stability and morphology of the final hybrid latexes and films was studied in detail. Meanwhile, the mechanical properties of thermoset–thermoplastic coatings and corresponding thermoplastic coatings were investigated. It is found that the thermoset–thermoplastic composite coatings showed significantly improved film properties in terms of hardness compared to the analogous thermoplastic coatings. Furthermore the thermoset–thermoplastic hybrid films were highly transparent even with 33 wt% of epoxy thermoset domains embedded.

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1. Introduction

Over the last decade structured hybrid particles have attracted tremendous academic and industrial interest. A variety of materials, such as noble metal, metal oxide nanoparticles and different polymers, have been incorporated into single particles with different morphologies [1–6]. For example, the strategy to prepare polymer-based core–shell particles with a soft shell and a hard core is widely used in water-borne coating and adhesive industry for the production of composite films. The properties of the composite films, such as flexibility, toughness, hardness, adhesion, *etc.* can be balanced due to the embedment of hard domains in soft matrices [7]. During drying, hard materials in the core can form isolated domains that provide mechanical, thermal and barrier properties, while the soft polymer shell can fuse together and form continuous films. There is no need to use environmentally unfriendly volatile additives and organic solvents to assist the film-formation process

of rigid latex particles through softening. Commonly used rigid materials are various inorganic fillers, i. e. silica [8], and rigid polymers like polystyrene [9,10]. Generally speaking, inorganic fillers are more efficient than rigid polymers, especially for the improvement of mechanical and thermal properties, because they are much harder and more stable. However, substantial time and amount of dispersants are needed to create or disperse inorganic fillers in organic phase without phase separation in most cases [11]. In contrast, it is much easier to create polymer hybrid particles with a rigid polymer as hard domains through continuous heterophase processes. In addition, a large refractive index difference between polymer matrices and inorganic fillers makes it much more difficult to obtain transparent hybrid films, especially with higher filler concentration and fillers with relatively large size. It is because the transparency of multiphase systems is determined by two major factors: the refractive index difference between dispersing phase and matrix, and the size of dispersing phase [12]. When the refractive index difference is large, the dispersing phase has to be sufficiently small (the top limit is usually around 50 nm) to maintain a high transparency of the hybrid materials. In comparison, although there are differences in the refractive index between various polymer species, the difference is much smaller than the

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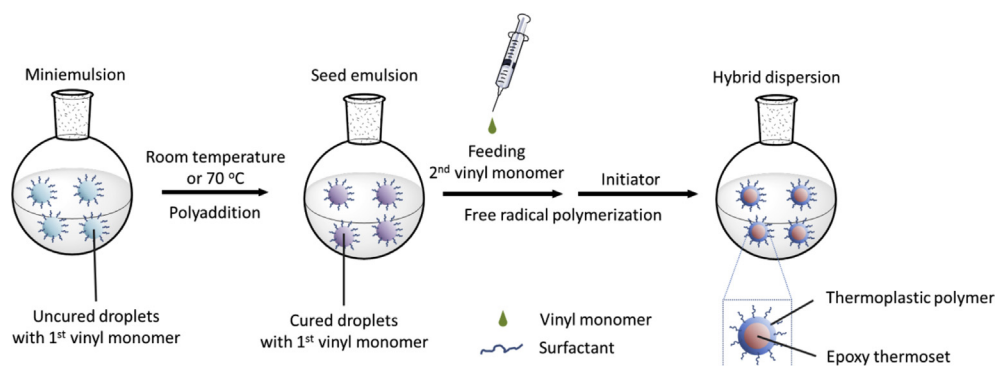


Fig. 1. A schematic diagram for the synthesis of thermoset–thermoplastic hybrid core–shell nanoparticles.

one between inorganic fillers and polymer. Therefore, polymeric “fillers” are much more suitable for hybrid systems requiring high transparency.

To be noticed is that the most commonly used rigid polymers for reinforcement are thermoplastic polymers with high glass transition temperature, T_g . Surprisingly so-called thermosets as another important category of polymer materials are rarely reported as functional domains in hybrid latex systems, especially as core materials. However, thermoset polymers are supposed to be more suitable as rigid domains or cores than thermoplastic polymers because they are highly crosslinked and therefore possess superior mechanical properties like higher stiffness in combination with thermal and chemical stability. The most likely reason for this phenomenon is that it is difficult to obtain stable aqueous dispersions with cured thermoset polymers as dispersing phase through conventional emulsion techniques. In this respect, miniemulsion polymerization, which involves the generation of small droplets by high shear forces, can be utilized as a facile technical solution to overcome this issue [13–15]. In miniemulsions, droplets can be seen as independent nanoreactors, in which various reactions from free radical polymerization to polyaddition can be carried out as in bulk [16]. Furthermore, hybrid particles can be generated through a

one-pot approach even with various reactions involved. For instance, different polymerizations, such as free radical polymerization and polyaddition, have been carried out either simultaneously [17] or subsequently in miniemulsion droplets [18]. An earlier work from our group has reported the successful synthesis of high molecular weight polyurethane (PU)/polystyrene (PS) and PU/poly(butyl acrylate) (PBA) hybrid nanoparticles with the size in the range from 90 nm to 130 nm by subsequent polymerizations [19]. However, most of the reported work on the combination of various polymerization mechanisms is still focused on the incorporation of soft polymers like PU rather than highly crosslinked, rigid thermosets.

In this work, we demonstrate that structured thermoset–thermoplastic hybrid nanoparticles embedded with highly crosslinked thermoset domains can be fabricated easily by seeded emulsion polymerization and utilized for the design of advanced composite coatings. Thermoset-containing seed emulsions are prepared first by miniemulsion polymerization. Bisphenol F based epoxy resin as epoxy monomer and a hydrophobic amine curing agent was selected as thermoset precursors to form an epoxy network as typical thermoset model component. Meanwhile, various vinyl polymers (based on methacrylic, acrylic monomers and styrene)

Table 1

Chemical structure of epoxy monomer and amine curing agent.

	Chemical structure
Bisphenol F based epoxide resin	
Amine curing agent	

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