

Preparation and surface properties of core–shell fluorosilicone polyacrylate latex film



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ABSTRACT

Core–shell fluorosilicone acrylic (FSiA) particles were prepared by two stage emulsion polymerization in the presence of common hydrocarbon acrylic monomers, trifluoroethyl methacrylate (TFEMA) and vinyltriethoxysilane (VTES). Morphology of latex particles was characterized by TEM. Surface properties of the film annealed at 100 °C for 1 h, 3 h, 5 h and 8 h were characterized by ATR–FTIR, AFM and SEM–EDS. Thermal properties of FSiA copolymer were investigated by TG–DSC analysis. TEM analysis indicated that two types of core–shell latex particles (CS-1 and CS-2) occurred in the process of emulsion polymerization, one is that fluorine-containing polymer existed at shell (CS-1), the other is that fluorine-containing polymer existed in the core (CS-2). ATR–FTIR and SEM–EDS data showed that as annealing time was increased, more fluorinated segments were found at the film surface. Fluorine content at the film surface increased from 2.25 wt.% (1.7 atom%) to 4.31 wt.% (3.22 atom%). AFM analysis suggested that the film surface topography was affected significantly by annealing time. The film showed excellent water resistant property due to the crosslinked network of Si–O–Si in the film.

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1. Introduction

Increasing attention has been attracted to the combined incorporation of siloxane and fluorinated components into polymers, which have been widely used as surface modification agents for improving surface properties in the fields of coatings, adhesives, films, fibers and moldings. Surface properties of coatings are usually governed by the structure and chemical composition of the outermost surface layer. Fluorinated segments are usually applied in preparation of organic coatings with excellent properties, such as weather durability, thermal stability and low surface energy. Fluorinated acrylate coatings (FAC) exhibit excellent adhesion, strength and hydrophobic properties, however, water resistance of uncrosslinked FAC is not satisfied, since it is unable to prevent the penetration of water into the bulk of the coating film [1]. It is known that fluorinated segments are inclined to migrate to surface and minimize surface energy [2–6], however, mobility of polymer chains is affected by surrounding conditions, and fluorinated segments may migrate to inside of films and hence lead to a decrease in film surface hydrophobicity [7,8]. There have

been many reports focused on properties of fluorine- or silicon-containing polymer films, however, few reports focused on fluorosilicone copolymer films, and migration behavior of fluorine- and silicon-containing segments during film formation has not been studied. Considering that fluorine- and silicon-containing copolymers are very important due to unique properties endowed by fluorine and silicon, such as anti-biofouling [8,9], oil repellency [10], non-stick and water resistance [11–13], it is necessary to investigate surface properties of fluorosilicone polymer films formed in different conditions. Han et al. [14] have studied effect of fluorine- and silicon-containing monomers on surface property and water repellency of the film, demonstrating that two components endowed the film with satisfied hydrophobicity due to the synergistic effect of fluorine and silicon. Guan et al. [15] synthesized fluorosilicone triblock copolymer by RAFT polymerization, and studied the surface hydrophobicity of the copolymer film. Cui et al. [16] prepared core–shell fluorosilicone polyacrylate latex particles and proved that fluorinated polymer was fixed at the surface of polyacrylate due to the crosslinked network introduced by silicon condensation. It has been demonstrated that silicon crosslinking fixed more fluorine at film surface and a preferable hydrophobic surface could be obtained by combining fluorine and siloxane in the copolymer [17]. Although the synergistic effect of fluorine and silicon has been proved by

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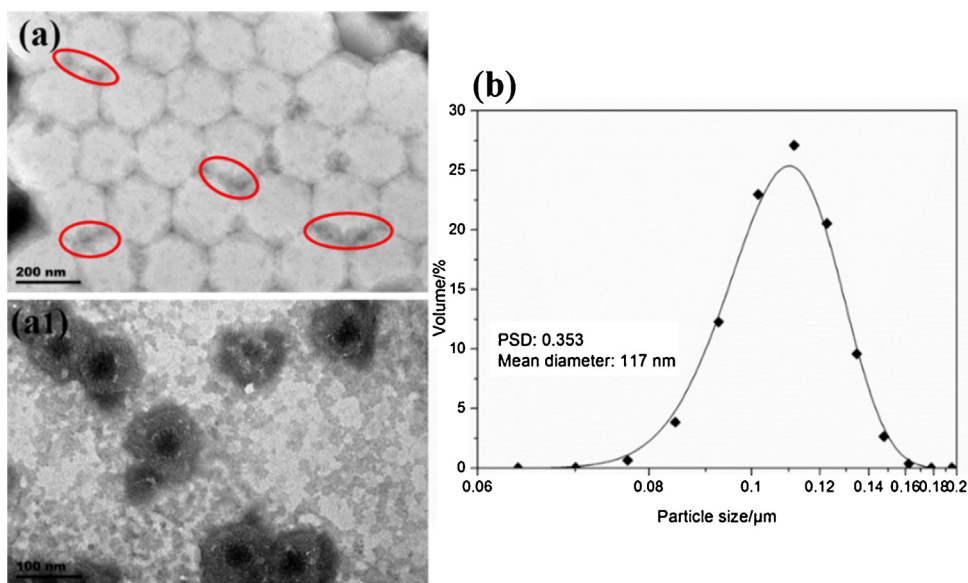


Fig. 1. Morphology (a, a1) and particle size distribution (b) of FSiA latex particles.

measuring water contact angle and surface morphology of the film, to our best knowledge, the chemical compositions at film surface and effect of annealing time on surface properties of the fluorosilicone polyacrylate film have not been investigated.

In this work, we prepared core-shell fluorosilicone acrylic (FSiA) latex particles by two stage emulsion polymerization and surface properties of latex film were investigated.

2. Results and discussion

2.1. TEM and DLS analysis

Morphology and particle size of FSiA copolymer latex are shown in Fig. 1. Fig. 1a and a1 presents morphologies of CS-1 and CS-2 particles, respectively. It is shown that two types of core-shell particles are observed in the emulsion. As shown in Fig. 1, the size of CS-2 particle is less than 100 nm, while the diameter of CS-1 particle is about 200 nm, and this result indicates that all the CS-2 particles formed at the second stage. It is seen that fluorine- and silicon-containing polymers exist simultaneously in the shell of particle (CS-1) and in the core of particle (CS-2). In addition, more fluorine-containing polymer is observed in the core of CS-2 particle than that in the shell of CS-1 particle. Fig. 2 presents the formation mechanism of CS-1 and CS-2 latex particles. The formation of CS-2 particles is the result of different hydrophobicity among the monomers. Since TFEMA and VTES are more hydrophobic than acrylic monomers, they are more likely to be wrapped by acrylic polymers in an aqueous phase. Fig. 1b shows that the mean particle

size is 117 nm, and the FSiA latex exhibits a broad particle size distribution (PSD) of 0.353.

2.2. FT-IR and ^{19}F NMR spectra of the FSiA copolymer

Fig. 3 presents the FT-IR spectra of TFEMA, VTES and FSiA copolymer. As shown in Fig. 3b, the peaks at 1260 cm^{-1} and 1150 cm^{-1} are due to stretching vibration C–F. The characteristic absorption at 760 cm^{-1} is ascribed to Si–CH₂–R. Absorptions at 469 cm^{-1} and 1080 cm^{-1} belong to asymmetric stretching vibration of Si–O–C, while the peak at 957 cm^{-1} is ascribed to symmetric vibration of Si–O–C. Fig. 4 shows the ^{19}F NMR spectra of FSiA copolymer, and the signal at -74 ppm is assigned to $-\text{CF}_3$ group.

2.3. Surface properties of FSiA film annealed for different time

AFM height images of FSiA film annealed at $100\text{ }^\circ\text{C}$ are shown in Fig. 5. As annealing time increased from 1 h to 3 h, the film surface

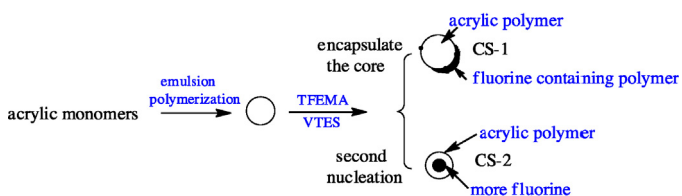


Fig. 2. The formation mechanism of core-shell latex particles.

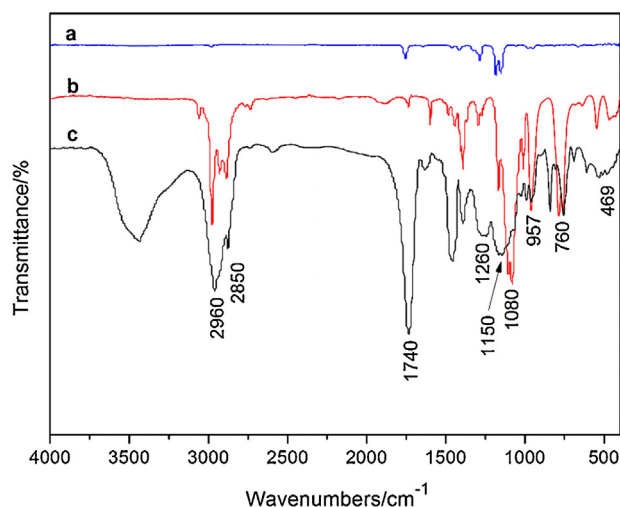


Fig. 3. FT-IR spectra of TFEMA (a), VTES (b) and FSiA copolymer (c).

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