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Synthesis and characterization of core–shell polysilsesquioxane-poly(styrene-butyl acrylate-fluorinated acrylate) hybrid latex particles

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ABSTRACT

Core–shell polysilsesquioxane-poly(styrene-butyl acrylate-fluorinated acrylate) [PSQ–P(St-BA-FA)] hybrid latex particles were successfully prepared by seeded emulsion polymerization with polymethacryloxypropylsilsesquioxane (PSQ) synthesized by the hydrolysis and polycondensation of (3-methacryloxypropyl)trimethoxysilane (MAPTS) in the presence of emulsifiers as seeds. The chemical composition and core–shell morphology of the resultant hybrid particles were investigated by Fourier transform infrared (FTIR) spectroscopy and transmission electron microscopy (TEM), respectively. TEM and dynamic light scattering (DLS) analysis indicated that the core–shell hybrid particles were uniform and possessed narrow size distributions. The surface properties of the latex films produced from the core–shell hybrid particles were also investigated by contact angle (CA) analysis and X-ray photoelectron spectroscopy (XPS) analysis. The results proved the enrichment of fluorine on the film surface, and the latex films had high contact angles and low surface free energies. Optical measurements indicated that the incorporation of fluorinated acrylate onto PSQ particles can effectively reduce light reflectivity of the obtained transparent hybrid latex film. Atom force microscopy (AFM) characterization showed that the obtained hybrid latex film had a smooth surface. Additionally, thermogravimetric analysis (TGA) indicated that the PSQ–P(St-BA-FA) hybrid latex film had better thermal stability than the poly(styrene-butyl acrylate) [P(St-BA)] latex film.

1. Introduction

Inorganic–organic hybrid materials have been extensively studied recently due to their unique chemical and physical properties synergistically derived from the two components and their potential applications in areas of coatings, adhesives, electronics, catalysis, and diagnostics [1–6]. Emulsion polymerization is always used to prepare inorganic–organic hybrid materials because of its major advantages, such as use of an environmentally friendly solvent (water), efficient heat transfer, less viscous reaction media, fast polymerization rates, and easy processability [7–11].

Fluorinated polymers have many useful and desirable advantages such as high thermal, chemical, aging and weather resistance; low dielectric constants, friction coefficient and refractive index; and unique surface properties due to the low polarizability and the strong electronegativity of fluorine atom [12–17]. Among inorganic nanoparticles, nano-scale silica has been extensively used as inorganic phase in inorganic–organic hybrid systems [18–20]. There have been some reports about organic–inorganic hybird materials based on fluorinated polymers and silica [21–23]. However, in order to strengthen the interaction and promote the compatibility between silica and fluorinated polymers, some silane coupling agent, such as methacryloxypropyl trimethoxysilane (MAPTS) [22], vinyltriethoxysilicone (VTES) [21] and vinyl trimethoxysilane (VTMS) [23], are used to modify the surface of the silica before the polymerization of vinyl monomers.

In order to avoid the additional modification steps in the synthesis of inorganic–organic hybrid materials based on silica and fluorinated polymers, we are interested in the synthesis of functional polysilsesquioxane (PSQ) nanoparticles with reactive groups, which are supposed to be used as the seed directly without any pretreatment for further emulsion polymerization of monomers instead of silica. Nowadays, many polysilsesquioxanes materials are being developed. They are a class of three-dimensional oligomeric organosiliceous compounds with the general structural formula $(RSiO_{1.5})_n$, where n is an even number and R can be any of a large number of groups (typically methyl, ethyl, vinyl, or phenyl)

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[24]. They have attracted much attention for their extraordinary heat and fire resistance, superior mechanical and electrical properties, and biocompatibility [24–26] and they have been applied in many fields, ranging from protective layers [27], low dielectric material [28], and aerospace materials [29] to optical materials [30], precursors in making ceramics [31], and flame-retardant agent [32]. However, by far very little work has been done to prepare and characterize the inorganic–organic core–shell hybrid particles with PSQ nanoparticles as cores surrounded by fluorinated polymers.

In the present study, core–shell polysilsesquioxane-poly(styrene-butyl acrylate-fluorinated acrylate) hybrid latex particles were successfully prepared by seeded emulsion polymerization of styrene, butyl acrylate and fluorinated acrylate, using polymethacryloxypropylsilsesquioxane synthesized by hydrolysis and polycondensation of (3-methacryloxypropyl)trimethoxysilane (MAPTS) in the presence of emulsifiers as seeds. Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), dynamic light scattering (DLS) analysis, contact angle (CA) analysis X-ray photoelectron spectroscopy (XPS), optical measurements, atom force microscopy (AFM) and thermogravimetric analysis (TGA) were used to characterized the obtained core–shell polysilsesquioxane-poly(styrene-acrylate-fluorinated acrylate) hybrid latex particles and the corresponding latex films.

2. Materials and methods

2.1. Materials

Butyl acrylate (BA) and styrene (St) were obtained from Tianjin Fuchen Chemical Reagent Factory (China) and were purified by distillation under reduced pressure. Dodecafluoroheptyl methacrylate $CH_2=C(CH_3)COOCH_2CF(CF_3)CFHCF(CF_3)_2$ (FA) and 3-(methacryloxypropyl)trimethoxysilane (MAPTS) were, respectively, obtained from Harbin XEOGIA Fluorine-Silicon Chemical Co. Ltd. (China), and Momentive Performance Materials Inc., and used as received. Sodium dodecyl sulfate (SDS), polyoxyethylene (10) octylphenyl ether (OP-10), sodium hydroxide (NaOH) and ammonium persulfate (APS) were all purchased in their reagent-grade form from Fuchen Chemical Reagent Factory (China) and used without further purification. The water used in the experiment was deionized and prepared in our lab.

2.2. Preparation of polymethacryloxypropylsilsesquioxane (PSQ) latex nanoparticles

A solution of 0.60 g of NaOH, 0.034 g of OP-10, 0.066 g of SDS and 250 g of water were first stirred for 0.5 h at room temperature. Then a total of 20 g MAPTS was slowly added to the above solution. After addition of MAPTS, the reaction mixture was stirred for another 24 h. The temperature was then increased to 50 °C and the mixture was stirred at that temperature for another 24 h.

2.3. Preparation of core–shell polysilsesquioxane-poly(styrenen-acrylate-fluorinated acrylate) [PSQ–P(St-BA-FA)] hybrid latex particles

A part of polysilsesquioxane emulsion (containing 1.5 g PSQ) and 90 mL water were put into a four-necked flask equipped with reflux condenser, mechanical stirrer, dropping funnels and inlet for nitrogen gas. The mixture was first stirred for 0.5 h in nitrogen atmosphere. When the temperature was raised to 80 °C, the monomers mixture of St, BA and FA in the dropping funnel was fed into the flask under starved-feed addition. Simultaneously APS aqueous solution (0.08 g of APS dissolved in 10 mL water) in the dropping funnel was also fed into the flask with an appropriate dropping rate to initiate the polymerization of monomers at 80 °C. When the monomers mixture and APS solution were completely fed, the temperature was maintained at 80 °C for another 4 h. Then the obtained latex was cooled to room temperature and the pH value of the final latex was adjusted to 7.0–8.0 with ammonia. The conversion of the emulsion polymerization was determined gravimetrically and is reported in Table 1.

Table 1
Recipes and properties of the core–shell PSQ–P(St-BA-FA) hybrid latex particles.

Sample code	CS-1	CS-2	CS-3	CS-4	CS-5
PSQ (g)	1.5	1.5	1.5	1.5	1.5
St (g)	4.8	4.8	4.8	4.8	4.8
BA (g)	3.2	3.2	3.2	3.2	3.2
FA (g)	0	0.51	1.10	1.76	2.53
APS (g)	0.08	0.08	0.08	0.08	0.08
DI water (g)	100	100	100	100	100
Conversion (%)	97.72	94.42	92.18	91.15	90.92
Particle size (nm)	276.3	280.6	283.7	287.3	293.1
Polydispersity	0.014	0.003	0.014	0.012	0.003

Scheme 1 illustrates the preparation process of PSQ and PSQ–P(St-BA-FA).

2.4. Characterization

The particle sizes and particle size distributions of the prepared PSQ and core–shell PSQ–P(St-BA-FA) latex particles were measured using a Zetasizer Nano-ZS (Malvern Instruments, UK). The samples were diluted with distilled water before testing to prevent multiple scattering effects.

The morphology of PSQ and core–shell PSQ–P(St-BA-FA) latex particles was investigated by a Hitachi (Japan) H-800 transmission electron microscope (TEM) with an acceleration voltage of 200 kV.

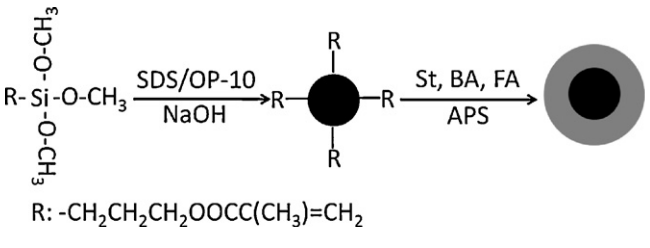
Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 37 FTIR spectrometer in the range from 4000 cm^{-1} to 400 cm^{-1} by the KBr pellet method.

Contact angle (CA) measurements with the sessile drop method were recorded and analyzed at room temperature on an OCA-20 contact angle meter (DataPhysics Instruments GmbH, Filderstadt, Germany) with SCA20 software. Reported contact angles are the average of at least 10 measurements. Wetting liquids used here for CA measurements were distilled water and n-hexadecane, as suggested by Owens and Wendt [33]. Total surface-free energies and their polar and dispersion components of different samples could be calculated by the following equations [34].

$$\gamma_l(1+\cos\,\theta)=2\left[(\gamma_l^d\gamma_s^d)^{1/2}+(\gamma_l^p\gamma_s^p)^{1/2}\right] \qquad (1)$$

$$\gamma_s=\gamma_s^p+\gamma_s^d \qquad (2)$$

where θ is the static contact angle of the liquid on the film surface; γ_l and γ_s are the surface tension of the wetting liquid and the surface free energy of solid, respectively; p and d, are respectively the polar and dispersion components of each surface free energy. By measurement of the contact angles on a solid surface with the two liquids, the total surface free energy of a solid and its components can be calculated. Here, surface tension, dispersion component and



Scheme 1. Preparation process of PSQ and PSQ–P(St-BA-FA).