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Synthesis and characterization of organic fluorine and nano-SiO_2 modified polyacrylate emulsifier-free latex

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ABSTRACT

In this research, organic fluorine and nano-SiO_2 modified polyacrylate emulsifier-free emulsion was successfully synthesized via emulsifier-free emulsion polymerization with ethyl silicate (TEOS) as precursor for nano-SiO_2 and dodecafluoroheptyl methacrylate (DFMA) as fluorinated monomer. The stability of latex prepared in the presence of alkyl vinyl sulfonate was much higher than that of latex prepared in the presence of sodium dodecyl benzene sulfonate. With increasing DFMA content, the latex particle size and hydrophobicity of hybrid film increased. Furthermore, the hybrid film presented highly solvent-resistant and good mechanical properties. In addition, the FT-IR spectrum indicated that the DFMA and nano-SiO_2 were successfully introduced into the hybrid polymer. AFM and SEM measurements confirmed that the hybrid film had a rough surface. At last, the formation mechanism of the hybrid film was established.

1. Introduction

In recent years, organic–inorganic composite materials have been given much attention and applied to many areas [1–3] such as coatings, adhesives, catalysis and fuels due to their unique chemical and physical properties including excellent optics, electricity property, mechanical property, hydrophobicity, thermal stability and flame retardant [4]. Among the organic components, fluorine-containing polyacrylate polymers have many excellent properties including high thermal, chemical, aging, solvent and weather resistance, low dielectric constant and surface free energy due to low polarizability and strong electronegativity of fluorine atom. Hence, the fluorine-containing polyacrylate polymers have been widely studied in recent years as useful materials [5–7] in the field of biomaterials and coatings for leather, textile, paper and walls of buildings. Meanwhile, many kinds of nano-particles such as nano-SiO_2, TiO_2, Al_2O_3, ZrO_2 and $CaCO_3$ [8–10] are used to fabricate nanocomposites. Among them, nano-SiO_2 can improve the mechanical property and thermal stability of organic polymers, and has been extensively used as inorganic phase in inorganic–organic hybrid system [11–13].

Up to now, many approaches have been applied to prepare organic–inorganic composite materials. And an effective way is to synthesize the organic–inorganic composite materials by emulsion polymerization. Emulsion polymerization has many advantages, including the use of an environmentally friendly solvent, high heat transfer rate, low viscosity, fast polymerization rate and easy processability [14–16]. However, the residual emulsifier in materials will have negative effects on the properties of product and pollute the environmental [17]. Studies have proved that the emulsifier-free emulsion polymerization can effectively eliminate the disadvantages of emulsifier to the properties of the materials because there is no emulsifier migration during film formation [18,19]. Therefore, in the emulsion polymerization, reactive surfactants have been widely used, especially in the preparation of fluorinated polyacrylate polymer/inorganic composite materials, as they can react with fluorinated monomers and acrylate monomers and become a part of fluorinated polyacrylate polymer, endowing the latex films with the excellent water and oil repellence properties [20,21].

In this work, the organic fluorine and nano-SiO_2 modified polyacrylate emulsifier-free emulsion was synthesized by emulsifier-free emulsion polymerization with ethyl silicate (TEOS) as precursor for nano-SiO_2 and dodecafluoroheptyl methacrylate (DFMA) as fluorinated monomer, as shown in Scheme 1. The influences of the amount of TEOS and DFMA on the properties of the copolymer were discussed. Fourier transform infrared (FT-IR) spectrometry, dynamic light scattering (DLS) analysis, contact angle (CA) analysis, atom force microscopy (AFM) and scanning electron microscopy (SEM) were used to characterize the obtained organic fluorine and nano-SiO_2 modified polyacrylate hybrid latex particles and the corresponding latex films. In addition, the formation

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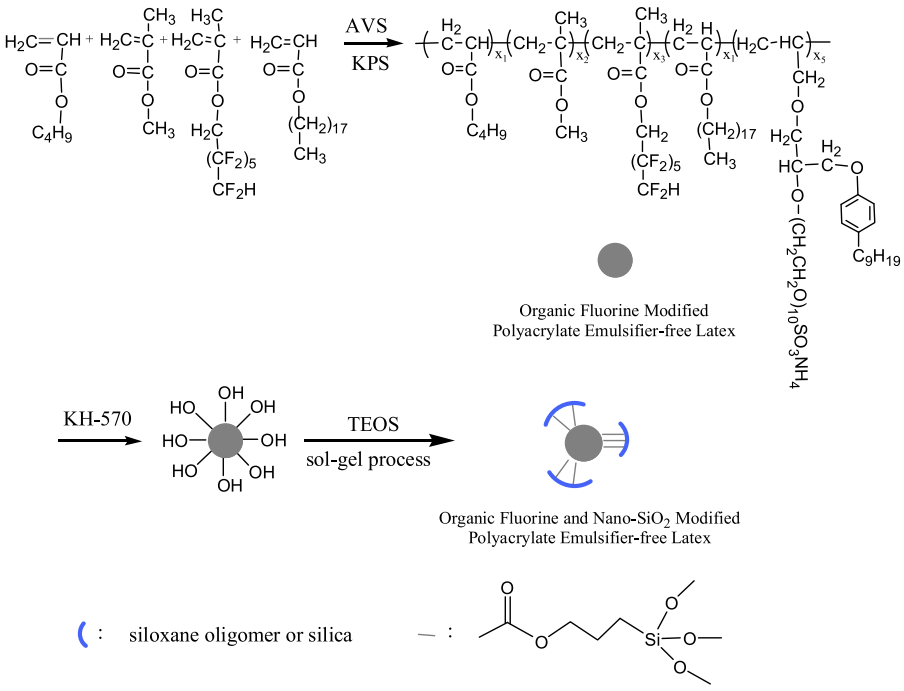

Scheme 1. Synthetic scheme of organic fluorine and nano-SiO_2 modified polyacrylate emulsifier-free latex.

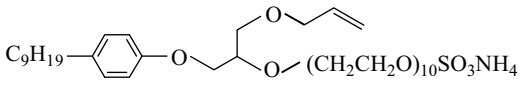

Fig. 1. Structure of AVS.

mechanism of organic fluorine and nano-SiO_2 modified polyacrylate emulsifier-free emulsion was investigated.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), ammonium persulfate (APS), ethyl silicate (TEOS) were purchased from Tianjin Kemiou Chemical Co. Ltd., analytical pure and used as received. γ-methacryloxypropyltrimethoxysilane (KH-570) was purchased from Nanjing Shuguang Chemical Company, and used as received. Alkyl vinyl sulfonate (AVS) (Fig. 1) was produced by Hanerche Chemical Company, industrial purity and used as received. Dodecafluoroheptyl methacrylate (DFMA) was obtained from Harbin Xuejia Fluorin Silicon Chemical Co., Ltd. Stearyl acrylate (SA) was purchased from Tianjin Tianjiao Chemical Co., Ltd. and used as received.

2.2. Synthesis of nano-SiO_2 modified fluorine-containing polyacrylate emulsifier-free emulsion

The recipes for nano-SiO_2 modified fluorine-containing polyacrylate emulsifier-free emulsion were described in Table 1. For a typical experiment, 6.16 g of BA, 4.62 g of MMA, 0.20 g of AVS, and 7.50 g of deionized water were mixed in the beaker and stirred vigorously to form the pre-emulsion I. 2.64 g of BA, 1.83 g of MMA, 2.00 g of DFMA, 0.50 g of SA, 0.30 g of AVS, and 7.50 g of deionized water were mixed in the beaker and then intensively homogenized to form the pre-emulsion II.

A 250-mL three-neck round-bottomed flask equipped with a reflux condenser, a thermometer and a mechanical stirrer was filled with 0.25 g of AVS, 1/3 APS aqueous solution (0.22 g of APS was solved in 15.00 g water), and 1/4 pre-emulsion I and 7.50 mL of deionized water with a stirring rate of 250 rpm at 70 °C and the mixture was kept still for 30 min. Then, both the 1/3 APS aqueous solution and remnant pre-emulsion-were added dropwise into the reacting mixture for 120 min. After that, the reaction was carried out continuously for another 2 h.

Then, the polymerization continued with a slow addition of the pre-emulsion II and remnant APS aqueous solution during 120 min. 1.40 g of KH-570 was added to the flask. The reaction mixture was kept at 80–85 °C for 2 h, then cooled down to 40 °C. Then, 0.80 g of TEOS was added to emulsion, and contents of the flask were stirred at 50 °C for 12 h.

Table 1
Recipes for organic fluorine and nano-SiO_2 modified polyacrylate emulsifier-free emulsion.

Sample	P0	P1	P2	P3	P4	P5	F1	F2	F3	F4
MMA/g	6.45	6.45	6.45	6.45	6.45	6.45	6.45	6.45	6.45	6.45
BA/g	8.80	8.80	8.80	8.80	8.80	8.80	8.80	8.80	8.80	8.80
APS/g	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22
AVS/g	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
KH-570/g	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40
SA/g	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
TEOS/g	0.00	0.00	0.40	0.80	1.20	1.60	0.80	0.80	0.80	0.80
DFMA/g	0.00	2.00	2.00	2.00	2.00	2.00	1.00	3.00	4.00	5.00
DI water/g	37.50	37.50	37.50	37.50	37.50	37.50	37.50	37.50	37.50	37.50