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Preparation and investigation of waterborne fluorinated polyacrylate/silica nanocomposite coatings

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ABSTRACT

Fluorinated polyacrylate/silica nanocomposite particles were synthesized by methyl methacrylate (MMA), butyl acrylate (BA) and 1H,1H,2H,2H-heptadecafluorodecyl methacrylate (FA) *via in situ* miniemulison polymerization. Morphology of nanocomposite particles, surface microstructure, chemical composition, hydrophobicity, transparency and thermal performance of the films were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), water contact angle, Fourier transform infrared spectra (FT-IR), ultraviolet–visible spectroscopy (UV–vis), energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and thermogravimetry (TGA) analyses. It is shown that the fluorinated polyacrylate/silica nanocomposite particles present "currunt-bun like" morphology. The hydrophobicity of fluorinated polyacrylate film was increased after incorporation of silica, which was due to the surface enrichment of fluorine and rough surface of the nanocomposite film. Moreover, the fluorinated polyacrylate/silica nanocomposite films exhibited high transparency in visible light range.

1. Introduction

Organic/inorganic nanocomposite particles are of growing interest to researchers in past decades [1–7]. There are numerous applications of these nanocomposite materials, such as outdoor façade coatings [8–10], synthetic mimics for cosmic dust [11] and photonic devices [12]. Among inorganic nanoparticles, silica is the most widely investigated and has many applications in industrial fields. For example, copolymer/silica nanocomposite particles have been manufactured to produce exterior façade coatings [13]. Polymer/silica nanocomposite particles can be simply prepared by heterofluocculation between silica sol and polymer latex [14]. However, this kind of nanoparticles have been proved to exhibit inferior silica adhesion property [14,15] and low transparency after film formation [16]. A lot of research have been focused on *in situ* co-polymerization of vinyl monomers in the presence of silica in alcohol/water mixtures [17,18], aqueous solution [19–21] and alcoholic system [22–24] to produce film-forming polymer/silica nanocomposites. A convenient route to prepare nanocomposite particles includes polymerization of vinyl monomers in the presence of silica sol (*in situ*) *via* aqueous emulsion polymerization. Chen et al. [20,21] synthesized PMMA/SiO_2 hybrid particles with PMMA as core and silica particles as shell by using an auxiliary monomer of 2-(methacryloyl) ethyltrimethylammonium chloride or 1-vinylimidazole to stabilize hybrid microspheres and proposed a formation mechanism of the raspberry-like hybrid microspheres. They pointed out that the strong acid–base interaction between hydroxyl groups of silica surfaces and amino groups was strong enough for promoting the formation of long-stable PMMA/SiO_2 hybrid particles. Zhang et al. [25,26] have synthesized PS/SiO_2 by miniemulsion polymerization in the presence of 3-methacryloxypropyltrimethoxysilane (MPS) modified silica nanoparticles and obtained core–shell morphology nanocomposite particles. The amount of MPS grafted on the silica surface was 8.7 molecules/nm^2 and 10.8 molecules/nm^2 for 45 nm and 108 nm silica, respectively. It has been reported that there are about 7 Si-OH/nm^2 for Stöber silica [27], therefore, the results obtained by Zhang et al. confirmed multiple layers of MPS on silica surface. Qi et al. [28] prepared acrylate polymer/silica nanoparticles *via* miniemulsion polymerization. They found that MPS modified silica particles exhibited a good dispersion ability in the polymer

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Table 1
Formulations for synthesis of PFA/SiO_2 nanocomposite particles (g).

	PFA1	PFA2	PFA3	PFA4	PFA5	PFA6	PFA7	PFA8
MMA	4	4	4	4	4	4	4	4
BA	4	4	4	4	4	4	4	4
FA	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
APS	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
$NaHCO_3$	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
SDS	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
HD	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Silica	0	0.02	0.04	0.06	0.08	0.1	0.12	0.15
Water	40	40	40	40	40	40	40	40

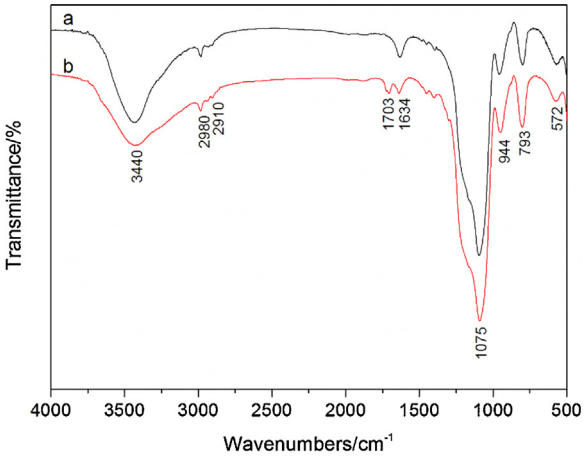


Fig. 1. FT-IR spectra of silica before (a) and after (b) modification.

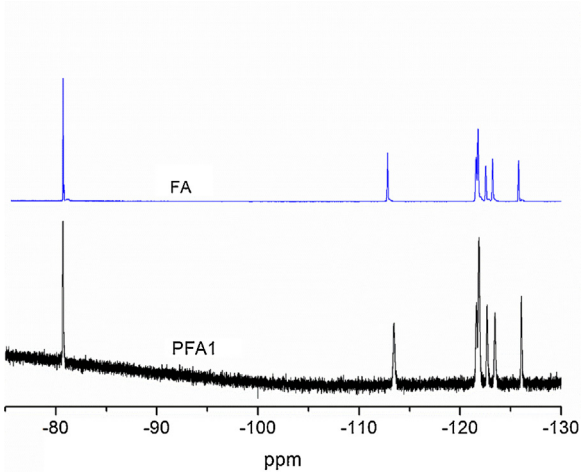
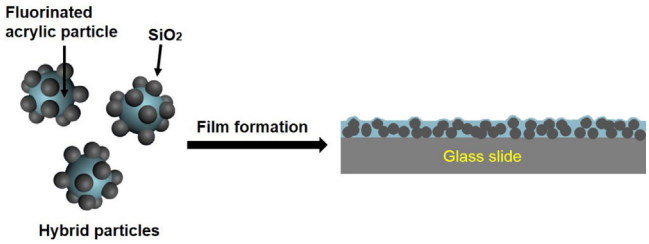


Fig. 2. ^{19}F NMR spectra of the PFA1 copolymer.



Scheme 1. Film formation mechanism of PFA/SiO_2 nanocomposite particles.

matrix, and this kind of nanocomposite latex particles are suitable for coatings or impact modifier for plastics.

Previous literatures are mainly focused on morphology of polymer/silica nanocomposite particles, however, only a few works were concentrated on fabrication of film forming properties and investigation of surface compositions of the nanocomposite films [5,16,29], which will have significant meaning for commercial applications. Fluorinated polyacrylate has good film-forming behavior, low surface energy and thermal stability, therefore, by combining advantages of fluorinated component with silica nanoparticles, it is assumed to obtain novel and special properties of such kind of nanocomposites.

In this work, the synthesis of fluorinated polyacrylate/silica nanocomposite particles and film properties is reported. Thus, a series of fluorinated polyacrylate/silica particles were prepared by *in situ* miniemulsion polymerization in the presence of varying proportions of silica. Correlations of surface microstructure, chemical composition and silica content with the nanocomposite film properties were investigated.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA) and tetraethoxysilane (TEOS) were obtained from Xilong Chemical Co., Ltd (Guangzhou, China). Inhibitor in MMA and BA was eliminated by passing neutral alumina. 1H,1H,2H,2H-heptadecafluorodecyl methacrylate (FA) monomer was prepared in our lab. 3-methacryloxypropyltrimethoxysilane (MPS) was bought from Nanjing Xiangqian Chemical Co., Ltd. The initiator of ammonium persulfate (APS) was obtained from Tianjin Bodi Chemical Co., Ltd and recrystalized before use. The buffering agent of sodium bicarbonate (NaHCO3), sodium dodecyl sulfate (SDS), hexdecane (HD) and ammonia (25 wt.%) were all analytical grade. Deionized water was used throughout the experiment.

2.2. Methods

Fourier transform infrared spectra (FT-IR) were obtained from NEXUS-470 spectrometer (Nicolet, USA) in the range from 500 cm^{-1} to 4000 cm^{-1} with a resolution of 6 cm^{-1} and 32 scans. The ^{19}F NMR spectra were obtained using a Bruker Avance III 400 NMR with deuterated chloroform (CDCl3) as the solvent. Specific surface area of silica was determined by nitrogen absorption method (BET) on Quantachrome Instruments Quantachrome Autosorb Automated Gas Sorption System (USA). Transmission electron microscopy (TEM) was performed on JEOL-2100 instrument operating at 200 kV. A drop of dilute dispersion was dropped on a carbon-coated copper grid and dyed with 2 wt. % phosphotungstic acid before characterization. Ultraviolet–visible spectroscopy (UV–vis) of the nanocomposite film was recorded by a UV-3600 UV–VIS-NIR spectrophotometer (Shimadzu, Japan)