Journal of Fluorine Chemistry 186 (2016) 52–59

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and characterization of poly(fluorinated styrene-acrylate)/silica nanocomposites

Weiming Tang, Ziming Ye, Yichi Chen*, Lin Guo

Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, Beijing Key Laboratory of Bio-inspired Energy Materials and Devices, School of Chemistry and Environment, Beihang University, Beijing 100191,China

ARTICLE INFO

Article history:
Received 3 December 2015
Received in revised form 18 March 2016
Accepted 11 April 2016
Available online 12 April 2016

Keywords:
Poly(fluorinated styrene-acrylate)/silica nanocomposite
Emulsion polymerization
Surface property
Thermal performance

ABSTRACT

Poly(fluorinated styrene-acrylate)/silica (PFSA/SiO_2) nanocomposite latexes with different content of silica were prepared by seeded emulsion polymerization. Chemical composition of the PFSA nanocomposite was evaluated by Fourier transform infrared (FT-IR) spectrometry and energy dispersive spectrometry (EDS) analyses, respectively. Thermal performance of the nanocomposite particles was characterized by differential scanning calorimetry (DSC) and thermogravimetry (TG). Micromorphology of the nanocomposite latex film formed on glass substrate was observed by atomic force microscope (AFM). Furthermore, surface hydrophobicity of the latex film was examined by measurement of water contact angle. The results showed that although only small amount (no more than 1.0 wt% based on the PFSA nanocomposite) of silica contained in the composite, abrasion resistance and thermal properties of the PFSA films were improved significantly. More silica content will cause instability of polymerization. Moreover, dynamic light scattering (DLS) analysis revealed that the presence of silica nanoparticles led to smaller composite particle size as compared with pure PFSA latex particles containing no silica.

1. Introduction

In recent years, the inorganic-organic composite styrene-acrylic emulsions have attracted a great deal of academic and industrial interests in the field of material science, owing to the excellent overall properties thereof including thermal resistance, mechanical performance and even optical, catalytic, magnetic, electric properties, etc. [1–8]. There are many inorganic nanoparticles which are applied to styrene-acrylic emulsions, such as nano-silica, nano-titania, nano-calcium carbonate and nano-alumina [9–12]. Among these inorganic nanoparticles, nano-silica is widely used in styrene-acrylic emulsions because it can improve not only the mechanical and thermal properties, but hydrophobicity [13] and abrasion resistance as well. In addition, Commercially available fluorinated side-chain acrylic and methacrylic polymers are typical low surface energy coating materials. Amongst the numerous molecular structures investigated, a close-packed uniform CF_3 surface was found to possess the lowest surface tension ever measured (15 mN/m) [14]. A polymeric material that can maintain a stable and uniform CF_3 surface can play a key role in producing non-adhesive materials with surface energies much lower than that of poly(tetrafluoroethylene) (20 mN/m) [15]. Therefore, when fluorine-containing entities are incorporated into the structure of polyacrylate, some properties are improved such as oil and water repellency, refraction index, dielectric constant, and thermal resistance [16–18]. So poly (fluorinated acrylate) has attracted a great deal of attention in applying to surface coatings, microelectronics, medicine and optical communication [19–21]. On the other hand, the added silica shields polymeric matrix from ultraviolet rays, so there can be many improvements such as reinforcement, improved thermal stability, better wash-resistance, perdurability and self-cleaning effects etc. [22,23].

Research on organic-inorganic hybrid materials was widely reported in the literature. Nano-silica as an inorganic nanoparticle is the most widely used inorganic material in emulsion for its improvement of emulsion mainly in thermal, mechanical properties [24]. For example, Freris et al. [25] prepared nano-silica by Stöber method and applied it in the emulsion polymerization to obtain polymer encapsulation of nano-silica particles. Generally, sol-gel method was applied to prepare organic inorganic hybrids, such as the organic polymers/silica hybrids in which silica were dispersed in polymeric matrix [26–28]. However, a time-consuming post treatment of solvent is inevitably needed. Emulsion polymerization, as one of the most often used methods, can

* Corresponding author.
E-mail address: chenych@buaa.edu.cn (Y. Chen).

http://dx.doi.org/10.1016/j.jfluchem.2016.04.005
0022-1139/

produce not only organic–inorganic hybrids but also environmental friendly copolymers. Qi et al. [29] used the commercial nano-silica dispersions treated with methacryloylpropyl trimethoxysilane to synthesize acrylate polymer/nano-silica composite particles through miniemulsion polymerization. So far, little research work has been reported in literature about direct introduction of silica into fluorinated polymer via emulsion polymerization to synthesize fluorinated polymer nanocomposite with low surface energy. When silica was introduced directly into a polymer emulsion latex, it was simply embedded and only weak bonds, mainly hydrogen bonds, were present at the interface.

In order to obtain a homogeneous dispersion of inorganic-organic nanocomposite latex in which nano-SiO_2 particles are dispersed uniformly within the emulsion, there need a coupling agent to strengthen the interaction of the nano-silica particles and the (co)polymer. The coupling agent is usually a silane such as γ-methacryloxypropyl trimethoxysilane (MPS), vinyl triethoxysilane (VTES), vinyl trimethoxysilane (VTMS), etc. Yao et al. [30] prepared silica/PFA nanocomposites with core-shell structure via emulsion polymerization, wherein, MPS was utilized to strengthen interaction between the fluorinated polymer of poly(fluorinated acrylate) and silica. Cui et al. [31] prepared a nano-scale core–shell SiO_2-fluorinated polyacrylate nanocomposite latex containing fluorine in the shell using nano-SiO_2 as seeds which was encapsulated by fluorinated polyacrylates. The nano-SiO_2 particles had been pretreated by VTES. The latex particles showed core–shell morphology with very uniform particle size. Although there have been a variety of reports on synthesis of the inorganic-organic nanoparticles based on nano-silica encapsulated copolymers [32–39], there still exists some questions to be solved. As for fluorinated acrylic copolymer grafted nano-silica, there is few work focused on investigation of surface composition, morphology and mechanical properties of this kind of nanocomposite film, therefore, a research on this type of organic-inorganic coating film property is crucial.

In this work, poly(fluorinated styrene-acrylate) (PFSA)/SiO_2 hybrid nanocomposite emulsion latexes containing different amount of silica were synthesized using silica as seeds which was encapsulated by PFSA. Before polymerization, the nano-silica which was prepared by the well-known sol-gel method was modified by MPS. Chemical structure and properties of the PFSA composite were investigated by Fourier transform infrared (FT-IR) spectroscopy, dynamic light scattering (DLS) analyses, scanning electron microscope (SEM), atomic force microscope (AFM), water contact angle measurement, abrasion test, differential scanning calorimetry (DSC) and thermogravimetry (TG) separately.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), styrene(St) were purchased from Shanghai Chemical Reagent Co. (China) which were purified upon distillation under reduced pressure and kept refrigerated until use. Hydroxyethyl methacrylate (HEMA), tetraethoxy silicane (TEOS), γ-methacryloxypropyl trimethoxy silane (MPS), ammonium persulfate(APS), ammonia, sodium carbonate, and anhydrous ethanol were analytical reagents which were all used without further purification. Dodecafluoro heptyl methacrylate (DFMA) was obtained from XEOGIA Fluorine-Silicon Chemical Co., Ltd. of China, alkylphenol ethoxylates (OP-10) and ethoxylated alkyl phenol ammonium sulfate (CO-436) were both supplied by Rhodia France Inc. and used as received. The water used throughout this experiment was deionized.

2.2. Method

2.2.1. FT–IR spectroscopy

FT-IR spectra were recorded on a Fourier transform infrared spectrum analyzer (FT-IR, Nicolet Nexus-470, USA) by KBr pelleting method. It was measured in the wavenumber range from 4000 cm^{-1} to 399 cm^{-1} at a resolution of 8 cm^{-1}.

2.2.2. Dynamic light scattering (DLS) analysis

Particle size distribution and average particle size of the latex particles were determined by a LS 13 320 Laser Diffraction Particle Size Analyzer (BECKMAN COULTER, USA) at 25 °C. All measurements were carried out at a fixed angle of 90° on highly diluted aqueous solution to prevent multiple scattering.

2.2.3. Energy dispersive spectrometer (EDS) analysis

Surface elemental content was analyzed by using a FESEM-7500F instrument equipped with an energy-dispersive X-ray spectrometer (EDS).

2.2.4. AFM measurement

Latex was cast onto glass slides and dried at 100 °C for 1 h before observation. The film surface morphology was measured by atomic force microscope in tapping mode (AFM, Veeco DI, USA) at room temperature. Root-mean-square roughness (R_q) of the films was calculated by the software.

2.2.5. Water contact angle

Water contact angles were measured by DSA20 instrument (KRÜSS, Germany)at room temperature, in which, at least five water contact angles (5 μl/drop) for each sample were measured to report the average value.

2.2.6. Thermogravimetric analysis

Thermogravimetry analysis was carried out with an STA 449 F3 Jupiter instrument (Germany). The samples were heated from 50 to 500 °C at a heating rate of 10 °C/min under N_2 atmosphere.

2.2.7. Abrasion test

Abrasion test was performed by TABER ABRASER (Dongguan lichuan limited company of instrument) and the metallographic abrasive paper (400 mesh, Shanghai grinding wheel company, China) was used. Latex films coated on tin plate were abraded under a load of 500 g for 100 times. The weight loss was recorded per 10 circles to evaluate the abrasion resistance of the films.

2.2.8. Differential scanning calorimetry(DSC) analysis

Differential scanning calorimetry analysis was performed on a DSC 4000 instrument (America). The testing temperature ranged from −20 °C to 200 °C at a rate of 10 °C/min with N_2 protection.

2.2.9. SEM measurement

Latex was cast onto glass slides and dried at 100 °C for 1 h. After cooling down, the specimens was sprayed with gold before observation. Scanning electron micrographs were carried out by a JEOL-JXA 840ASEM.

2.3. Experimental procedure

2.3.1. Preparation of modified silica particles

In this study, the modified nano-silica particles with average particle size of ca.40 nm were prepared by the method of Stöber [40]. Firstly, 2.5 ml ammonia and 50 ml anhydrous ethanol were filled into the flask under continuous stirring. When the temperature was stabled at 50 °C, 1.9 g TEOS was added into the