



Well-defined inorganic/organic nanocomposite by nano silica core-poly(methyl methacrylate/butylacrylate/trifluoroethyl methacrylate) shell

Gang Chang, Ling He^{*}, Wei Zheng, Aizhao Pan, Jing Liu, Yingjun Li, Ruijun Cao

Xi'an Jiaotong University, School of Science, Xi'an 710049, China

ARTICLE INFO

Article history:

Received 11 November 2012

Accepted 10 January 2013

Available online 24 January 2013

Keywords:

Core-shell nanocomposite
Fluoroacrylate terpolymer
Nano-SiO₂
Silane coupling grafting
Morphology controlling
Film properties

ABSTRACT

The novel inorganic/organic core-shell SiO₂/P(MMA/BA/3FMA) nanocomposite for coating application is synthesized in this paper by seed emulsion polymerization, in which the inorganic phase is composed of nano-SiO₂ modified by vinyl-trimethoxysilane (VMS) or γ -methacryloxy propyl trimethoxysilane (MPMS), and the organic phase is made of terpolymer by 2,2,2-trifluoroethyl methacrylate (3FMA), methyl methacrylate (MMA), and n-butyl acrylate (BA). The chemical structure of SiO₂/P(MMA/BA/3FMA) is characterized by FTIR. The effect of surfactant polyvinylpyrrolidone (PVP), sodium dodecyl sulfate (SDS)/octyl phenyl polyoxyethylene ether (TX-10), sodium dodecyl benzene sulfonate (SDBS)/TX-10 and sodium hexametaphosphate (SHMP) on the grafting ratio (GR) of VMS and MPMS, the dispersion of nano-SiO₂ particles and the film properties of SiO₂/P(MMA/BA/3FMA) are investigated by TGA, DLS, TEM, SEM, and XPS. The morphology variation and the particle size distributions of SiO₂/P(MMA/BA/3FMA) with the content of surfactant and P(MMA/BA/3FMA) are characterized. It is found that MPMS is more effective than VMS in improving GR and the dispersion of nano-SiO₂ particles. The surfactants are favor of gaining the higher GR in the multilayer grafted nano-SiO₂, especially SDS/TX-10 for 17.6% GR. The morphology of SiO₂/P(MMA/BA/3FMA) is controlled by the amount of SDS/TX-10 and P(MMA/BA/3FMA) as the core-shell particles, the stacked pomegranate seed with multicore and the multicore-single shell structure when $w(\text{MMA})/w(\text{BA})/w(\text{3FMA}) = 1.3/1/1$. Among the different surfactants, SDBS/TX-10 and PVP could give the monodispersing nano-SiO₂ in the terpolymer matrix of the films, but SDS/TX-10 and SDBS/TX-10 could perform the fluorine-rich surface.

Crown Copyright © 2013 Published by Elsevier Inc. All rights reserved.

1. Introduction

The inorganic/organic nanocomposites are generally made of organic polymer matrix with inorganic nanoparticles in order to improve the properties of nanostructured polymeric materials [1]. The nanocomposites composed of nano-SiO₂ and the fluorinated acrylate copolymers have attracted much attention in coating applications because of their hydrophobic properties, thermostability, and anti-chemicals [2–6]. It is reported that the quantity and the dispersion of nano-SiO₂ in the polymer matrix have a real effect on the properties of the final materials [7–9]. Actually, the homogeneous dispersion of nano-SiO₂ in the fluorinated acrylate copolymer matrix could be obtained when nano-SiO₂ is premodified by a coupling agent in order to overcome the high active surface of silica nanoparticles [10,11]. It is well known that grafting polymer chains to nano-SiO₂ are an effective method to bring about tunable interfacial interactions in nanocomposites

[12–14]. Generally, there are two main approaches to chemically attaching polymer chains to silica surface: covalent attachment of end-functionalized polymers to the nano-SiO₂ surface (“grafting to” method) and in situ monomer polymerization with monomer growth of polymer chains from immobilized initiators (“grafting from” method) [15–20]. The silane coupling agents with hydrolyzable and organofunctional groups grafting to nano-SiO₂ surface have been proved as the reliable approach for achieving satisfactory surface coverage of desired functional groups, and for gaining the strong chemical bonding force between nano-SiO₂ and fluorinated copolymer [21–23], because the organofunctional groups could offer a variety of functionalities chosen to meet the requirements of the polymer, and the hydrolyzable groups could react with hydroxyl groups on SiO₂ surface [24,25].

On the other hand, although these modified silica particles would seem a natural choice for invoking desirable characteristics, there are some issues relating to the chemical modification of these particles that could significantly affect their performance. For instance, the reported densities of silanol groups on silica surfaces are about 4–12 silanols/nm² [6], but the reported alkyl grafting densities have not exceeded 2–3 nm², even when using monofunctional silanes, which enable a possible 1:1 substitution

^{*} Corresponding author. Address: Department of Chemistry, Xi'an Jiaotong University, School of Science, Xianning West Road, 28, Xi'an 710049, China. Fax: +86 29 82668559.

E-mail address: heling@mail.xjtu.edu.cn (L. He).

of surface silanols. As a result, a significant number of hydroxyl groups remain on the surface, which may be occluded by overlaying material or surface rearrangement. Therefore, surface modification based on physical interaction is usually implemented by using of surfactants adsorbed onto the surface of silica particles [26]. The principle of surfactant treatment is the preferential adsorption of a polar group of a surfactant to the surface of silica by electrostatic interaction [27]. Many surfactants are used to reduce the interaction between the silica particles within agglomerates by reducing the physical attraction and could easily be incorporated into a polymer matrix [28–31].

As for the combination of nano-SiO₂ particles and the fluorinated copolymer, the functionalized SiO₂ particles with a fluorinated copolymer shell are attracting attention, based on that it could provided with the improved mechanical and thermal properties of the matrix polymers by the compatibility of the nanoparticles with the fluorinated copolymer [5,32]. For this reason, the emulsion polymerization or seed dispersion polymerization has been proved as the effective method for obtain SiO₂ core-fluorinated copolymer shell nanocomposites [17,33,34]. Furthermore, this core-shell structured nanocomposite could be modified by changing either the constituting materials or the core to shell ratio [35]. During the film formation, it is expected that fluorinated copolymer shell could migrate onto the surface in order to achieve excellent surface properties in a low amount of fluoride, and nano-SiO₂ could disperse into the polymer matrix for improving the thermal property and mechanical property [36].

In this paper, the novel SiO₂/P(MMA/BA/3FMA) core-shell inorganic/organic nanocomposites are obtained by the fumed nano-SiO₂ particles as inorganic phase after modification using vinyl-trimethoxysilane (VMS) or γ -methacryloxy propyl trimethoxyl silane (MPMS), and the terpolymer of 2,2,2-trifluoroethyl methacrylate (3FMA), methyl methacrylate (MMA), and n-butyl acrylate (BA) by seed emulsion polymerization as the organic phase. The effect of surfactant polyvinylpyrrolidone (PVP), sodium dodecyl sulfate (SDS)/octyl phenyl polyoxyethylene ether (TX-10), sodium dodecyl benzene sulfonate (SDBS)/TX-10, and sodium hexametaphosphate (SHMP) on the grafting ratio (GR), the dispersion of nano-SiO₂ particles, the morphology of core-shell nanocomposite, the film-formation behavior of SiO₂/P(MMA/BA/3FMA) and the properties of films are investigated by TGA, DLS, TEM, SEM, and XPS. The control of surfactant and P(MMA/BA/3FMA) amount on the distribution of SiO₂/P(MMA/BA/3FMA) core-shell nanocomposite is discussed.

2. Experimental

2.1. Materials

2,2,2-Trifluoroethyl methacrylate (3FMA, CH₂=CH(CH₃)-COOCH₂CF₃) was supplied by Xuejia Company of China. Vinyl-trimethoxysilane (VMS, CH₂=CHSi(OCH₃)₃), and γ -methacryloxy propyl trimethoxysilane (MPMS, CH₂=C(CH₃)COO(CH₂)₃-Si(OCH₃)₃) was provided by Wu Han University of China. Nano-SiO₂ (VK-SP15) with an average diameter of 10–25 nm and a specific area of 230 m²/g was supplied by Hang Zhou New Material Company of China. Methyl methacrylate (MMA) and n-butyl acrylate (BA) were supplied by Chinese chemical market, which were washed by 10 wt% aqueous solution of sodium hydroxide and water until pH value of the washings became neutral, and then, the purified monomers were dried over anhydrous magnesium sulfate and stored at –5 °C before using. Polyvinylpyrrolidone (PVP), sodium dodecyl benzene sulfonate (SDBS), sodium hexametaphosphate (SHMP), sodium dodecyl sulfate (SDS), octyl phenyl polyoxyethylene ether (TX-10), sodium bicarbonate and ammonium

persulfate (APS), and isopropanol (IPA) were obtained from chemical market.

2.2. Surface modification of nano-silica

2.2.1. The monolayer grafted nano-SiO₂

The monolayer grafted nano-SiO₂ was obtained by grafting the fumed nano-SiO₂ surface with VMS or MPMS. When the suspended nano-SiO₂ (4.0 g fumed nano-SiO₂ in 220 ml H₂O/IPA solution ($v/v = 5/6$) with the aid of ultrasound bath for 40 min) was introduced into a four-mouth flask equipped with reflux condenser, mechanical stirrer, thermometer, and inlet of nitrogen gas, 1.75 g VMS (0.012 mol) or 2.92 g MPMS (0.012 mol) was added and was vigorously stirred at pH = 4. Then, the mixture was kept at 82 °C in reflux for 2 h in the protection of N₂ gas for reaction. After being cooled to room temperature and centrifuged for 5 min at a speed of 5000 r/min, the monolayer modified-SiO₂ was obtained and was named as M1 grafted by VMS and M2 grafted by MPMS, as shown in Table 1.

2.2.2. The multilayer grafted nano-SiO₂

The multilayer grafted nano-SiO₂ was obtained by grafting the suspended nano-SiO₂ by MPMS in the help of surfactant PVP, SDS/TX-10, SDBS/TX-10, and SHMP, respectively. When the suspended nano-SiO₂ and 0.24 g surfactant was mixed under ultrasonic agitation for 30 min, the prehydrolyzed MPMS (at pH = 4 for 2 h) was added. The mixture was kept at 82 °C in reflux for 2 h at pH = 9 in the protection of N₂ gas for reaction. After a great amount of white floccules being formed overnight, the multilayer grafted nano-SiO₂ was filtrated by vacuum and named as P1–P4 according to the sequence of PVP, SDS/TX-10, SDBS/TX-10, and SHMP, as shown in Table 1. The sample of multilayer grafted nano-SiO₂ without any surfactant was named as Sample P in Table 1.

2.3. Preparation of SiO₂/P(MMA/BA/3FMA) core-shell nanocomposite

The synthesis of SiO₂/P(MMA/BA/3FMA) core-shell nanocomposite was prepared by seed emulsion polymerization. After the modified nano-SiO₂ powder and the surfactant (SDS:TX-10 = 1:2) were ultrasonically dispersed in deionized water for 5 min and were introduced into a four-mouth flask, Na₂CO₃ and APS solutions were added successively until the temperature reached 75 °C in the water bath. Then, the mixture of MMA, BA and 3FMA was slowly dripped within 4 h. When the polymerization was kept for 2 h at 80 °C, SiO₂/P(MMA/BA/3FMA) core-shell nanocomposite was obtained. The recipes and the suggested diagram for SiO₂/P(MMA/BA/3FMA) were given in Table 2 and Scheme 1. The other surfactants of PVP, SDBS/TX-10, and SHMP were used in the same way for obtaining SiO₂/P(MMA/BA/3FMA) core-shell nanocomposites.

2.4. Measurements

2.4.1. Fourier transforms infrared (FT-IR) spectroscopy

FT-IR spectra were recorded on an AVATER-360 Fourier Transform Infrared Spectrometer (Nicolet, USA) in the range of 400–4000 cm⁻¹ for nano-SiO₂ pellets, modified-SiO₂ and the film formed by SiO₂/P(MMA/BA/3FMA) core-shell nanocomposite, respectively.

2.4.2. Thermogravimetric analysis (TGA)

The grafting ratio of silica particles was determined by the residual weight percentage after removing organic polymer at 600 °C using TGA analyzer (STA449C Jupiter from NETZSCH) under N₂ atmosphere with the temperature rise of 10 °C/min. SiO₂/

Download English Version:

<https://daneshyari.com/en/article/7000138>

Download Persian Version:

<https://daneshyari.com/article/7000138>

[Daneshyari.com](https://daneshyari.com)