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Fabrication of zinc oxide/poly(styrene) grafted nanocomposite latex and its dispersion

Erjun Tang [a,*], Hong Liu [a], Liming Sun [a], Erli Zheng [a], Guoxiang Cheng [b]

[a] College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang Hebei 050018, China
[b] School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

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Abstract

Zinc oxide nanoparticles, with an average size of about 40 nm, were encapsulated by polystyrene using in situ emulsion polymerization in the presence of 3-methacryloxypropyltrimethoxysilane (MPTMS) as a coupling agent and polyoxyethylene nonylphenyl ether (OP-10) as a surfactant. Polymerization mechanism of nanocomposite latex was discussed. Transmission electron microscopy (TEM) proved the presence of ZnO nanoparticle appeared to be monodisperse in nanosize in polymer composite particles. ZnO/PS nanocomposites were characterized by Fourier transform infrared spectra (FT-IR), X-ray photoelectron spectroscopy (XPS), thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results of FT-IR and XPS revealed that the surface of ZnO particle was successfully grafted by PS through the link of the coupling agent between ZnO and polymer. TGA and DSC results indicated an enhancement of thermal stability of composite materials compared with the pure polymer. SEM (scanning electron microscope) images showed a perfect dispersion of the ZnO particles in latex film. In addition, UV–visible absorption measurements demonstrated that the ZnO/PS composite coatings display a perfect performance of absorbing UV light.

Keywords: In situ emulsion polymerization; Surface grafting polymer; Dispersion; Poly(styrene); Zinc oxide nanoparticles; Composite coatings

1. Introduction

Nanoparticles have been the subject of intense scientific and technological activities due to their interesting size dependent physicochemical and optoelectronic properties and consequently exciting application potential [1]. The inorganic–polymer hybrid nanomaterials present the properties of both the inorganic nanoparticles and the polymer by combining thermal stability, mechanical strength, electronical and optical properties with flexibility and the capacity [2]. Therefore these nanocomposite particles offer many potential applications in such diverse areas as photocatalysis [3], lithography [4], optics [5], biotechnology [6] and electronic devices [7]. However, inorganic nanoparticles are very easy to agglomerate in mediums and show poor dispersion in polymers, hence the applications of many

* Corresponding author. Tel./fax: +86 311 8862 4057.
E-mail address: ejtang@eyou.com (E. Tang).

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nanosized particles are largely limited. From the practical point of view, these nanoparticles have to be dispersed in polymer matrix to form nanocomposites for the purpose of gaining stability and processability [8]. To prevent the formation of agglomerated nanoparticles in polymers, the combination of inorganic particles with polymers is usually accomplished by surface modification. The grafting of polymers onto inorganic nanoparticle is one of the most effective and versatile methods for this modification purpose. It can significantly enhance the stability of nanoparticles dispersing in polymer solvents by increasing the affinity of the surface for organic substances [9].

There are two methods of surface grafting: one is that the end-functionalized polymers are grafted to the surface of inorganic particles; the other is that the polymer is grafted onto the surface of inorganic particles [10,11]. As regards with the first method, metal oxide nanoparticles having reactive hydroxyl groups on the surfaces, surface grafting is carried out by the reaction of reactive polymers (having isocyanate, alkoxy silane, etc.) with the hydroxyl groups [12,13]. As to the second method, the polymerization of vinyl monomers can be initiated by introducing the reactive groups such as azo groups [14], peroxyester groups [15] onto the surface of inorganic particles. In addition, the double bonds introduced onto the surface of inorganic particles can also copolymerize with other vinyl monomers [16,17]. The introduction of the initiating groups onto the surface of the inorganic particles usually need multi-step synthesis, while the introduction of the double bonds can be achieved by one-step synthesis using silane coupling agent containing double bonds to modify the surface of the inorganic particles. So this method is employed in the present work.

Nano-ZnO, as one of the multifunctional inorganic nanoparticles, has drawn increasing attention in recent years due to its many significant physical and chemical properties, such as chemical stability, high luminous transmittance, high catalysis activity, effective antibacterial and bactericide function, intensive ultraviolet and infrared adsorption [18–23]. Therefore, nano-ZnO can be potentially applied to UV-shielding material, catalyst antibacterial material and so on [24–26]. The ZnO/polymer nanocomposite materials can enhance the stable dispersion of ZnO nanoparticles in polymer, which is interesting in applying in coatings, plastics, sealants and fibers. Poly(styrene–butyl acrylate) (poly(St–BA)) latex is one of the water-based coating matrix. The aim of this study was to prepare nano-ZnO/poly(styrene)(PS) nanocomposite latex materials by in situ emulsion polymerization. The nanocomposite latex can improve the dispersion stability of nano-ZnO and increase interfacial adhesion between the polymers and nano-ZnO particles. Furthermore, the nanocomposite latex certainly possesses perfect compatibility with the commercial poly(St–BA) latex to help its application in coatings. Prior to polymerization, ZnO nanoparticle was treated with 3-methacryloxypropyltrimethoxysilane (MPTMS) to obtain surface functionality. The surface functionality can fulfill the surface grafting encapsulation between nano-ZnO and polymers.

2. Experimental

2.1. Materials

Styrene (St, CP) was purified by distillation under nitrogen at reduced pressure. Initiator used was potassium persulfate (KPS, analytical grade). Nano-ZnO particle was purchased from Zhejiang Zhoushan Mingri Nanometer Materials Co. Ltd. (China). TEM showed spherical particles of about 20–80 nm. 3-methacryloxypropyltrimethoxysilane (MPTMS) and polyoxyethylene nonylphenyl ether (OP-10, AR) were supplied by Tianjin Research Institute of Synthetic Material (China) without further purification. Ethyl alcohol, methanol, *n*-propanol, toluene were used as received. Bi-distilled water was used throughout the experimental work.

2.2. Preparation of nano-ZnO/PS composite microsphere

2.2.1. Modification of nano-ZnO with MPTMS

ZnO nanoparticles (2 g) were mixed with methanol (50 ml) or a mixture of water and methanol, and then MPTMS (0.5 g) was added to the system. The mixture was first dispersed for 20 min through an ultrasonic instrument (HQ-50,100 W, China) at room temperature and after that the mixture was heated to reflux for at least 4 h. At the end of the reaction, the mixture was cooled down and diluted four or five times with *n*-propanol to improve the solubility of the homocondensates. This sample was centrifuged at 15,000 rpm for 1 h at room temperature. The clear supernatant, containing the homocondensates and unreacted MPTMS, was decanted from the deposit composed of the particles