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Facile surface modification of silica nanoparticles with a combination of noncovalent and covalent methods for composites application

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ABSTRACT

A simple, efficient and cost-effective approach for preparing surface modified silica nanoparticles (SiO_2) was developed by combining noncovalent and covalent modification process. Tetraoctylammonium bromide (TOAB), which is usually used in aqueous systems as surfactant, was introduced into organic solvent prior to covalent modification in order to assist the dispersion of pristine SiO_2 nanoparticles noncovalently. Then covalent modification was accomplished by radical grafting polymerization. The successful modification of SiO_2 was confirmed and as-prepared modified SiO_2 possessed smaller particle size and larger grafting rate than SiO_2 prepared by conventional method. More interestingly, the amount of TOAB used in the noncovalent process had a direct impact on the particle size and grafting rate. Meanwhile, poly (methyl methacrylate) (PMMA) was selected as the matrix to investigate the effect of as-prepared modified SiO_2 on the property of polymer-based nanocomposites. Owing to the improved modification effect, the prepared PMMA/SiO_2 nanocomposites showed far more excellent mechanical properties compared to those with SiO_2 prepared by conventional modification method. The tensile strength and flexural strength could be enhanced by as much as 80.6% and 127.3% compared to those of pure PMMA, respectively. The highlight of this work lies in the fact that remarkable improvement had been achieved with the facile combination of noncovalent and covalent process, which is relatively easy to realize and manipulate compared to other sophisticated methods.

1. Introduction

Since the introduction of nanotechnology, nanoparticles have been extensively used in polymer matrix composites as reinforcements due to their several favorable properties compared to corresponding micro-fillers [1–3]. One of the most attractive nanoparticles is SiO_2 with several favorable advantages such as relatively inexpensive, nontoxic, biocompatible, high thermal resistant and especially its ability to reinforce polymer matrix's mechanical properties. Therefore, SiO_2 nanoparticles have been extensively used to fabricate polymer-based nanocomposites [4–8]. For example, Motaung et al. prepared polycarbonate/silica nanocomposites and investigated the morphology, mechanical properties as well as the thermal degradation kinetics of the obtained nanocomposites [7]. In another instance, Ma et al. synthesized PMMA/SiO_2 nanocomposites via RAFT-mediated miniemulsion polymerization. The results showed that the thermal stability of polymers increased with increasing content of SiO_2 [8].

As a matter of fact, however, the preparation of polymer/SiO_2 nanocomposites is not that easy because it is very difficult to disperse SiO_2 particles uniformly in polymer matrices. Hydrophilic nanoparticles and hydrophobic polymers are not compatible in nature, which will result in bad dispersion of nanoparticles and poor interfacial interaction between the two components. Therefore, it is necessary to modify the surface of silica nanoparticles [9–11]. For instance, in Zheng's work, compared with the pure epoxy resin, epoxy resin/unpretreated SiO_2 nanocomposite exhibits little improvement in its mechanical properties, while the mechanical properties of epoxy resin/pretreated SiO_2 nanocomposite are greatly improved [10].

So far, conventional modification methods such as physical coating using surfactant [12], chemical coating using coupling agents [13,14] or grafting polymer chains [15–17] have been extensively reported. Surfactants are mainly used in water-containing systems and, without any covalent bonding, optimized interaction between the matrix and filler cannot be achieved [18]. By contrast, the covalent functionalization of SiO_2 becomes the hot topic because the resultant nanoparticles show strong interfacial adhesion between particle surface and polymer matrix

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[19]. However, covalent chemical reactions are usually carried out in organic solvents such as xylene, in which the hydrophilic SiO_2 nanoparticles are extremely prone to agglomerate with each other. Due to this severe aggregation of pristine nanosilicas, a desired resultant modified SiO_2 nanoparticles with small particle size and excellent compatibility to polymer matrix cannot be obtained by simply conducting subsequent covalent modification.

Thus the key objective of this work is to find a simple and efficient way to increase the efficiency of covalent functionalization of SiO_2 nanoparticles. For this purpose, we developed a combined approach of noncovalent and covalent modification process. The noncovalent step is expected to deagglomerate the SiO_2 aggregations, improve the dispersibility, and hence increase the exposure with the covalent functionalizing agent. TOAB, a kind of quaternary ammonium surfactant with four alkane chains, was selected to fulfill the noncovalent step along with ultrasonication. TOAB is commonly used as a phase-transfer reagent of Au nanoparticles from water into an organic phase [20]. However, in low-polar or nonpolar organic solvent, self-assembly could still be triggered through van der Waals interactions between polymer chains and TOAB, mainly by the polar interactions between the quaternary ammonium groups and polar groups, like hydroxyl or carboxyl, on the polymer chains [21]. Therefore, such characteristic makes TOAB a good candidate to assist the dispersion of pristine SiO_2 nanoparticles in organic solvents, thus creating a favorable environment for subsequent covalent grafting modification.

The modification effect of prepared SiO_2 nanoparticles was investigated and PMMA was selected as the matrix to synthesize nanocomposites. The practical dispersion situation of SiO_2 nanoparticles in the matrix was observed and efforts had been made to improve the mechanical properties of the polymer matrix using modified SiO_2 nanoparticles. Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), quasielastic laser light scattering (QELS) and thermogravimetric analysis (TGA) were used, while the mechanical properties of obtained nanocomposites were studied in detail.

2. Experimental

2.1. Materials

SiO_2 nanoparticles with an average diameter of around 20 nm were purchased from Zhoushan Mingri Nanomaterial Co. (Zhejiang, China). Tetraoctylammonium bromide (TOAB) was purchased from Alfa Aesar (China). The γ-methacryloxypropyl trimethoxysilane (KH570), utilized as the coupling agent, was supplied by Crompton Shuguang Organosilicon Co. (Nanjing, China). Methyl methacrylate (MMA) was procured from Kermel Chemical Reagent Co. (Tianjin, China) and purified by the standard treatment with 5% aqueous NaOH then deionized water, and followed by distillation at a normal pressure and then stored at low temperature prior to use. Benzoyl peroxide (BPO, analytical grade, Beijing Chemical Factory, Beijing, China) was used as an initiator. Hydroxyethyl cellulose (HEC, analytical grade, Heda Co. Ltd., Shandong, China) was used as a dispersant. Sodium dodecyl benzene sulfonate (SDBS, analytical grade, Tianjin Tianzhi Fine Chemical Co. Ltd., Tianjin, China) was used as a surfactant. Other reagents were all of analytical grade. Deionized water was used throughout.

2.2. Surface modification of silica nanoparticles

TOAB with varying proportions (0–25 wt%, based on original SiO_2) was dispersed in 150 mL xylene, and then the mixture was heated at 60 °C for 10 min to prepare TOAB xylene solution. Then 5 g SiO_2 was ultrasonically dispersed in TOAB xylene solution for 25 min to obtain a suspension of SiO_2. The as-prepared SiO_2 suspension was added to a flask followed by adding coupling agent (KH570) dropwise under continuous agitation. The reaction mixture was stirred for 8 h in boiling state. The particles were separated, washed and dried in vacuum for 12 h. Then the KH570 treated particles were redispersed ultrasonically in xylene to obtain a suspension of silica particles. Some initiator (BPO, 0.4 g) was added into the above suspension and the system was maintained under nitrogen atmosphere for 30 min to obtain a homogeneously dispersed system. Then MMA (40 g) was added dropwise into the mixture system. After the addition was completed, the reaction was performed for 5 h under stirring, and then cooled to room temperature. The precipitate was separated, washed and dried in vacuum for 12 h at 60 °C to obtain PMMA grafted SiO_2 in the presence of TOAB, which is named as SiO_2-g-PMMA(TOAB). PMMA grafted SiO_2 fabricated in the absence of TOAB were also prepared for comparison purpose, which is marked as SiO_2-g-PMMA.

2.3. Preparation of PMMA/SiO_2 nanocomposites

PMMA/SiO_2 nanocomposites were prepared by a typical *in situ* suspension polymerization: the mixture of 0.6 g modified SiO_2 (SiO_2-g-PMMA and SiO_2-g-PMMA(TOAB), respectively) and MMA monomer (60 mL) was ultrasonically dispersed, then diluted with distilled water (180 mL) containing 1.8 g HEC and 0.072 g SDBS. The mixture was then heated to the 75 °C, bubbled with nitrogen for 30 min under agitation. After initiator (BPO, 0.6 g) was employed to the system, the reaction was performed for 12 h with mechanical stirrer. The reaction products were repeatedly washed with distilled water, filtered and then dried in a vacuum oven overnight at 60 °C to obtain PMMA/SiO_2-g-PMMA and PMMA/SiO_2-g-PMMA(TOAB). *In situ* suspension polymerization of pure PMMA and PMMA/SiO_2, which stands for nanocomposites with unmodified SiO_2, were also synthesized for comparison.

2.4. Preparation of specimens for mechanical tests and TEM

Obtained polymer and nanocomposite microspheres were mixed with MMA by the mass ratio of 1:1 and introduced into the resin dough, which then was put into the mold and pressed in a pressing apparatus. The mold was placed in water and heated, finally the specimens were removed and polished, which were used for further mechanical tests and TEM after cooling to room temperature. The standard of tensile specimens was $50 \times 7 \times 2$ mm^3 and that of flexural specimens was $64 \times 10 \times 3.3$ mm^3.

2.5. Characterization

Before FTIR measurement, the modified SiO_2 were Soxhlet extracted with refluxing acetone for 48 h, then dried at 60 °C to remove the acetone. FTIR spectra of the samples were recorded by a Nicolet Magna Nicolet-5DX FTIR spectrometer with a resolution of 4 cm^{-1} and 32 scans in the range of 4000–400 cm^{-1} using KBr disk technique. The microstructure of the modified SiO_2 and the dispersion of SiO_2 in nanocomposite were observed by a Hitachi H-800 TEM. The specimens for TEM observations were prepared by microtoming with a Reicherte Jung Ultracut Microtome and mounted on 200-mesh copper grids. The average particle size and size distribution of SiO_2 were characterized by QELS with a Brookhaven Zetasizer at 25 °C. TGA was performed on a TA-50 thermogravimetric analyzer at a scan rate of 10 °C/min from 20 to 700 °C under a nitrogen atmosphere. The tensile and three-point bending tests were carried out at room temperature by using a Testometric Universal Tester M350–20 kN at a crosshead speed of