



# Use of unmodified SiO<sub>2</sub> as nanofiller to improve mechanical properties of polymer-based nanocomposites



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## ABSTRACT

SiO<sub>2</sub> nanoparticles without surface modification were used to prepare a polymer based nanocomposite: methyl methacrylate (MMA) was selected as the matrix, and copolymerized with a small amount of cationic functional comonomer 2-(methacryloyloxy)ethyltrimethylammonium chloride (MTC). The aim is to improve the dispersion of unmodified SiO<sub>2</sub> as well as the interfacial adhesion through electrostatic interaction between the positively charged copolymer matrix and negatively charged fillers, and ultimately to improve the mechanical properties. The chemical structure of P(MMA-co-MTC)/SiO<sub>2</sub> was characterized by <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR). The interaction between copolymer matrix and SiO<sub>2</sub> nanoparticles was investigated by zeta potential and Fourier transform infrared spectroscopy (FT-IR). Meanwhile, the morphologies of the synthesized microspheres were studied by scanning electron microscopy (SEM) and the dispersion of SiO<sub>2</sub> nanoparticles in P(MMA-co-MTC)/SiO<sub>2</sub> was observed by transmission electron microscopy (TEM). Finally, the mechanical properties of P(MMA-co-MTC)/SiO<sub>2</sub> was studied in detail and the tensile fracture surface was studied by SEM. The results indicate that, P(MMA-co-MTC)/SiO<sub>2</sub> has been successfully synthesized by *in situ* suspension copolymerization, and the mechanical properties, especially the flexural property, were remarkably improved due to the better dispersion state and stronger interfacial adhesion ameliorated through electrostatic interaction. When the content of MTC and SiO<sub>2</sub> is 10 wt% and 1.0 wt%, respectively, the optimal mechanical properties were obtained: compared to PMMA, the tensile strength was increased by 20.7% and the flexural strength was improved by as much as 140.7%. The whole process does not need surface modification, which makes this method more convenient and less costly.

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## 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<sub>2</sub> with several favorable advantages such as relatively inexpensive, nontoxic, biocompatible, high thermal resistant and especially its ability to reinforce polymer matrix's mechanical properties [4–6]. However, the high hydrophilicity of nano-structured SiO<sub>2</sub> surface can induce the nanoparticles to be easily agglomerated and hardly dispersible in polymer matrix. Thus, one of the greatest challenges in producing polymer/SiO<sub>2</sub> nanocomposites is to find an effective method for controlling the dispersion of the nanoparticles in polymeric hosts.

The most frequently used method is surface modification [7–9]. Indeed, in most cases surface modification is essential because the incorporation of unmodified SiO<sub>2</sub> cannot improve the property of

nanocomposites notably and sometimes can even deteriorate the property of nanocomposites [10–12]. For instance, in Zheng's work with the coworkers, compared with the pure epoxy resin, epoxy resin/unpretreated SiO<sub>2</sub> nanocomposite exhibits little improvement in its mechanical properties, while the mechanical properties of epoxy resin/pretreated SiO<sub>2</sub> nanocomposite are greatly improved [11]. In spite of the wide use of surface modification and its advantages, the process of surface modification is always tedious, energy-consuming and relatively less cost-effective, which becomes one of the greatest stumbling block to the large-scale production and commercialization of polymer/SiO<sub>2</sub> nanocomposites.

Therefore, there is still a need for research to obtain polymer/SiO<sub>2</sub> nanocomposites more efficiently. One possible and promising method is to disperse nanoparticles by electrostatic interactions [13]. As is well known, the surface potential of SiO<sub>2</sub> nanoparticles in aqueous system is negative due to the surface silanol groups' dissociation to form SiO<sup>-</sup>. If positive charge is introduced into the polymeric hosts, both the dispersion of SiO<sub>2</sub> and the interfacial adhesion between matrix and fillers could be improved through electrostatic interactions. Luna-Xavier et al. introduce positive charge into polymer matrix in emulsion polymerization by using

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a cationic initiator in order to build electrostatic interactions between nanoparticles and polymer. However, the SiO<sub>2</sub> they used was also pretreated [14,15]. Another idea of introducing positive charge is copolymerizing with cationic monomers. Chen et al. presented a novel method for preparation of raspberry-like organic–inorganic hybrid microspheres with PMMA as core and SiO<sub>2</sub> nanoparticles as shell. 2-(methacryloyl)ethyltrimethylammonium chloride (MTC) was used as an auxiliary monomer, and SiO<sub>2</sub> nanoparticles were deposited onto the surfaces of organic particles in aqueous medium via electrostatic interaction between SiO<sub>2</sub> nanoparticles and MTC. A possible formation mechanism of the raspberry-like hybrid microspheres was proposed on the basis of the results [16].

Although there are some examples of electrostatically driven reactions in literatures using the so-called colloidal assembly process, these researches were all carried out via emulsion polymerization and focused only on the morphology of resultant nanocomposites [14–16]. Up to date, there is no study about reinforcing the mechanical properties of synthesized nanocomposites by improving the dispersion of unmodified SiO<sub>2</sub> nanoparticles in polymeric host and enhancing the interfacial adhesion through electrostatic interactions.

In this work, MMA and MTC were selected as the matrix and cationic functional comonomer, respectively. Efforts had been made to improve the mechanical properties of the matrix using unmodified SiO<sub>2</sub> nanoparticles. The positively charged copolymer was prepared by *in situ* suspension copolymerization of MMA with a small amount of MTC, and which could electrostatically adsorb the negatively charged SiO<sub>2</sub> nanoparticles simultaneously in the process of copolymerization to prepare P(MMA-co-MTC)/SiO<sub>2</sub> nanocomposites. <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) zeta potential, Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used, and the mechanical properties of obtained nanocomposites were studied in detail. The highlight of our research is that the whole synthesis process required neither surface modification of SiO<sub>2</sub> nanoparticles nor strict control of copolymerizing conditions.

## 2. Experimental

### 2.1. Materials

SiO<sub>2</sub> nanoparticles with an average diameter of around 20 nm were purchased from Zhoushan Mingri Nanomaterial Co. (Zhejiang, China). MTC was supplied by Alfa Aesar Chemical Reagent Co. (Tianjin, China). MMA was procured from Kermel Chemical Reagent Co. (Tianjin, China) and purified by the standard treatment with 5% aqueous NaOH and then deionized water, followed by distillation at a normal pressure and finally stored at low temperature prior to use. Benzoyl peroxide (BPO, analytical grade, Beijing Chemical Factory, Beijing, China) was used as initiator. Hydroxyethyl cellulose (HEC, analytical grade, Heda Co. Ltd., Shandong, China) was used as dispersant. Sodium dodecyl benzene sulfonate (SDBS, analytical grade, Tianjin Tianzhi Fine Chemical Co. Ltd., Tianjin, China) was used as surfactant. Other reagents were all of analytical grade. Deionized water was used throughout.

### 2.2. Preparation of copolymer and nanocomposite microspheres

Positively charged copolymer and nanocomposite microspheres were prepared by *in situ* suspension copolymerization in three necked, round bottom flask equipped with a reflux condenser, a nitrogen gas inlet and a stirrer. Unmodified SiO<sub>2</sub> nanoparticles with varying proportions (the content of SiO<sub>2</sub> varies from 0 wt% to

2.0 wt%, based on organic mixture) were added into organic mixtures (60 mL) of varying proportions of MMA and MTC (the content of MTC is 5 wt% or 10 wt%), and the obtained mixtures of SiO<sub>2</sub> and organic solution were ultrasonically dispersed and then were added to the three-neck flask followed by adding deionized water (180 mL) containing 1.8 g HEC and 0.072 g SDBS. The achieved mixtures were stirred at 300 rpm under a nitrogen atmosphere for 30 min to obtain homogeneous suspension systems. Then, the suspension copolymerization reactors were heated to 75 °C. After the addition of initiator, BPO (0.6 g), the reaction was performed for 6 h under stirring at 700 rpm. The products were repeatedly washed with deionized water and then filtered. Finally the obtained products were dried in a vacuum oven overnight at 65 °C to obtain the copolymer and nanocomposite microspheres, marked as P(MMA-co-MTC) and P(MMA-co-MTC)/SiO<sub>2</sub>, respectively.

The extra nanocomposite microspheres with 0 wt%, 7.5 wt% and 12.5 wt% MTC content (the content of SiO<sub>2</sub> is fixed at 1.0 wt%) were prepared respectively with the same procedure as described above, and the nanocomposite microspheres with 0 wt% MTC and 1.0 wt% SiO<sub>2</sub> are coded as PMMA/SiO<sub>2</sub>.

### 2.3. Preparation of specimens for mechanical tests

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

### 2.4. Characterization

The <sup>1</sup>H NMR spectra of P(MMA-co-MTC) and P(MMA-co-MTC)/SiO<sub>2</sub> were recorded using a UNITY plus-500 NMR spectrometer (Varian, USA) with CDCl<sub>3</sub> as the solvent. Chemical shifts were reported in ppm units with tetramethylsilane as an internal standard.

The zeta potential values of original SiO<sub>2</sub> nanoparticles, P(MMA-co-MTC) and P(MMA-co-MTC)/SiO<sub>2</sub> microspheres were measured by using a Brookhaven Zetasizer (Brookhaven Instruments Ltd., US). Zeta limits ranged from –150 to 150 V. Strobing parameters were set as follows: strobe delay –1.00, on time 200.00 ms, and off time 1.00 ms. The natural (unbuffered) pH of the aqueous samples was used. Each experiment was repeated at least four times and mean value was reported.

Before FT-IR measurement, PMMA/SiO<sub>2</sub> and P(MMA-co-MTC)/SiO<sub>2</sub> were Soxhlet extracted with refluxing acetone for 48 h, then dried at 60 °C to remove the acetone. FT-IR spectra of original and extracted SiO<sub>2</sub> samples were recorded by a Nicolet Magna Nicolet-5DX FT-IR spectrometer in the scan range of 4000–400 cm<sup>–1</sup> with a resolution of 4 cm<sup>–1</sup> using KBr disc technique.

Examination of the morphology of PMMA, P(MMA-co-MTC), PMMA/SiO<sub>2</sub> and P(MMA-co-MTC)/SiO<sub>2</sub> microspheres as well as study of the tensile fracture surfaces of PMMA, PMMA/SiO<sub>2</sub> and P(MMA-co-MTC)/SiO<sub>2</sub> was performed on a Philips XL-30 SEM. The examined surfaces of microspheres and fracture surfaces were sputter coated with a thin layer of gold prior to examination.

The dispersion of SiO<sub>2</sub> nanoparticles in PMMA/SiO<sub>2</sub> or P(MMA-co-MTC)/SiO<sub>2</sub> nanocomposite was observed by an H-800 TEM produced by Hitachi. The specimens for TEM observations were prepared by cryogenic microtoming with a Reichert Jung Ultracut Microtome and mounted on 200-mesh copper grids.

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