



Short communication

Core-shell structured poly(methyl methacrylate)-coated zirconium dioxide nanoparticle and its dispersion stability



Min Ji Kim, Hyun Sik Chae, Hyung Jin Choi*

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

ARTICLE INFO

Article history:

Received 25 November 2013

Accepted 17 March 2014

Available online 25 March 2014

Keywords:

Core-shell structure

Dispersion stability

Organic-inorganic nanocomposite

ABSTRACT

To improve dispersion stability of ZrO₂ nanoparticles dispersed in a poly(4-vinylphenol-co-methyl methacrylate) (PVP-co-PMMA)/2-methoxyethanol solution, they were coated with poly(methyl methacrylate) (PMMA) by dispersion polymerization. Cross-linked PMMA-coated ZrO₂ particles were characterized by SEM and TEM. Chemical composition was examined by FT-IR spectroscopy. Mass ratio of PMMA to the ZrO₂ was analyzed by TGA. Density (1.97 g/cm³) of the PMMA coated ZrO₂ particles was much lowered compared to 5.46 g/cm³ of ZrO₂, and the improved dispersion stability of the coated particles in the PVP-co-PMMA/2-methoxyethanol solution was demonstrated using a Turbiscan.

© 2014 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

1. Introduction

Organic-inorganic hybrid materials including core-shell structured particles have attracted considerable attentions because of their advantageous characteristics resulted from combining properties of organic materials and inorganic materials [1,2]. Organic materials, mainly polymers, possess the flexibility, lightness and plastic mechanical properties with the concomitant ease of processing and structural diversity, while inorganic materials have the potential for wide electronic properties, magnetic and dielectric transitions, as well as thermal stability. Therefore these composite particles have been applied for a range of applications, such as bioseparation [3], gate insulator in electronics [3–6], and electrorheological and magnetorheological materials [6].

Meanwhile, polymeric gate dielectric materials have been developed to apply their mechanical flexibility and low-cost production to low-temperature processible gate dielectric materials for large-area electronics [7–9]. On the other hand, the high threshold voltage due to the low dielectric properties of polymeric insulators is one of the drawbacks that need to be overcome, and a variety of inorganic dielectric materials have been incorporated with polymeric systems for the organic-inorganic composites. Among the suitable inorganic materials, zirconium dioxide (ZrO₂) nanoparticles have attracted considerable attention because of

their optical and electrical properties with applications to electro-optic, piezoelectric and insulator [10].

As one of the polymeric gate insulators, the poly(4-vinylphenol) group has been studied as a gate dielectric [11,12] in terms of the solution processability, thin film quality, and surface chemistry. Furthermore, the poly(vinyl acetate)/clay composite increased the dielectric constant because of the high-*k* of the clay (Na⁺-montmorillonite) [13]. The dispersion stability of inorganic nanoparticles is important for achieving the excellent performance of these composites. The dispersion stability is affected by the particle volume fraction [14], density difference between the particles and medium [15], affinity between the particles and medium, etc. The surfactants can be used to disperse the aggregated nanoparticles uniformly, resulting in serious gate-leakage currents in organic thin film transistors to the solution mixture and composite film [16]. On the other hand, the surfactants reduced the dielectric constant of this system. The approach for designing and fabricating in a core-shell model has attracted considerable attention because nanoparticles with a well defined core and shell structures often exhibit improved physical and chemical properties compared to their single component counterparts. A range of methods have been reported for the fabrication of nanoparticles in a core-shell structured model over the past few decades. Some researchers reported that core-shell structured particles could be fabricated by the encapsulation of inorganic particles in a polymer shell [17,18]. The uniformly coated polymer shell provides an improvement in the affinity between the core-shell structured nanoparticles and polymer matrix.

* Corresponding author. Tel.: +82 32 860 7486.

E-mail address: hjchoi@inha.ac.kr (H.J. Choi).

Furthermore, organic–inorganic hybrid materials in a core–shell structure can be synthesized by dispersion polymerization [19], seeded polymerization [3] and Pickering emulsion polymerization [20] to decrease the inorganic particle density and improve the affinity between the particles and medium. This study examined the improvement in the dispersion stability of organic–inorganic composites.

2. Experimental

Zirconium dioxide particles (ZrO_2) (Aldrich, USA particle size <100 nm, density: 5.46 g/cm³) were used as a core inorganic material. Methacrylic acid (MAA) (Junsei, Japan) was used as a pre-treatment for the modification of ZrO_2 surface. Methyl methacrylate (MMA) (Junsei, Japan) and ethylene glycol dimethacrylate (EGDMA) (Aldrich, USA) were used as the monomer and a cross-linking agent, respectively. Polyvinylpyrrolidone (PVP) (Aldrich, USA, $M_w = 55,000$ g/mole) was used as a dispersion stabilizer. Azobisisobutyronitrile (AIBN) (Junsei, Japan) was used as the initiator for dispersion polymerization. Methanol (MeOH) (OCI, Korea) was used as the solvent. Poly(4-vinylphenol-co-methyl methacrylate) (PVP-co-PMMA) (Aldrich, USA, $M_w: 9000$ g/mole) and 2-methoxyethanol (Aldrich, USA) were used as a matrix polymer and solvent for the medium phase, respectively.

The cross-linked PMMA coated ZrO_2 particles were synthesized by dispersion polymerization, as shown in Fig. 1. The surface of the ZrO_2 nanoparticles was initially modified with MAA by sonication for 30 min to improve the affinity between MMA and ZrO_2 nanoparticles. The treated ZrO_2 was washed with methanol by centrifuge. The treated ZrO_2 was added to 100 g of methanol containing 3 g of PVP, and stirred for 30 min. At the same time, MMA and EGDMA were mixed with AIBN, and the mixture was then added to the dispersion. Dispersion polymerization was continued for 24 h at 60 °C at 300 rpm. After the reaction, the synthesized particles were washed sequentially with methanol and di-water, and freeze-dried. To prepare the thin films for the surface analysis of ZrO_2 and the cross-linked PMMA coated ZrO_2 suspensions, PVP-co-PMMA solution was prepared by dissolving the PVP-co-PMMA in 2-methoxyethanol at a rate of 5 wt% for the medium phase. To prepare the ZrO_2 suspensions and PMMA-coated ZrO_2 suspensions, the individual particles were dispersed in a PVP-co-PMMA solution with a fraction of 1 vol%. For higher dispersity, the suspensions were ultrasonicated for 1 h and homogenized for 3 min at 10,000 rpm using a homogenizer. Both pure ZrO_2 suspension and PMMA-coated ZrO_2 suspension were spin coated onto a cleaned silicon wafer at 1000 rpm for 30 s and then baked at 100 °C for 5 min. Subsequently, the sample was baked at 200 °C in a dry oven for 1 h to cure the polymer.

The synthesized ZrO_2 particles coated with cross-linked PMMA were characterized by scanning electron microscopy (SEM) (S-4300, Hitachi, Japan) and transmission electron microscopy

(TEM) (Philips CM200). In addition, average particle size and size distribution were analyzed by dynamic light scattering apparatus (DLS, ELS-8000, Otsuka, Japan). The prepared cross-linked PMMA-coated ZrO_2 particles' structure was analyzed by Fourier transform infrared (FT-IR) (Perkin Elmer System 2000) spectroscopy in the range from 400 to 4000 cm⁻¹. The amount of the polymer coating was measured by thermogravimetric analysis (TGA) (TA instrument Q50, USA) in nitrogen gas. The dispersion stability of pure ZrO_2 and the particles obtained in the PVP-co-PMMA solution was analyzed using a Turbiscan (Classic, MA 2000). The surface morphology of the spin coated film of pure ZrO_2 and cross-linked PMMA coated ZrO_2 dispersed in PVP-co-PMMA solution was analyzed by SEM and atomic force microscopy (AFM) (NS4A). The rheological properties of the cross-linked PMMA-coated ZrO_2 particles and pure ZrO_2 dispersed in a PVP-co-PMMA solution in 2-methoxyethanol at 1 vol% were observed using a rotational rheometer (MCR 300, Physica, Germany) with CC17 geometry.

3. Results and discussion

Fig. 2 shows SEM images of both pure ZrO_2 particles (a) and synthesized cross-linked PMMA coated ZrO_2 particles (b). In Fig. 2(a), pure ZrO_2 particles exhibited a fairly smooth surface and polydispersed size distribution. After encapsulating the ZrO_2 surface with PMMA, the surface morphology became rough, as shown in Fig. 2(b). The synthesized PMMA-coated ZrO_2 particles were larger than the pure ZrO_2 particles. Fig. 2(c) and (d) presents TEM images of the pure ZrO_2 particles and synthesized cross-linked PMMA-coated ZrO_2 particles, respectively, with a spherical shape. After the coating process of PMMA, the core and shell of the synthesized particles were ZrO_2 , which was more opaque, and PMMA, which was more transparent, respectively, as shown in Fig. 2(b). The density of the synthesized PMMA-coated ZrO_2 particles was 1.97 g/cm³, which was lower than that of pure ZrO_2 (5.46 g/cm³). As shown in Fig. 2(b), the product was not coated as a single particle because of the aggregation force of the pure particles. Therefore, the particle size distribution was large.

Average particle size and size distribution of cross-linked PMMA coated ZrO_2 particles are indicated in Fig. 3. Fabricated PMMA coated ZrO_2 particles are widely distributed over a range of 430 nm–2 μm, with the maximum intensity positioned at about 998 nm which is regarded as an average particle size. This wide range size distribution depends on how many particles are aggregated in the process of coating with PMMA and coating thickness of PMMA layer.

Fig. 4 shows the FT-IR spectra of pure ZrO_2 particles (a) and cross-linked PMMA coated ZrO_2 particles (b). The two peaks at 2997 cm⁻¹ and 2952 cm⁻¹ can be assigned to the C–H bond stretching vibrations of the –CH₃ and –CH₂– groups, respectively, while the peak at 1444 cm⁻¹ can be attributed to the bending vibration of the C–H bond of the –CH₃ group. The two peaks at

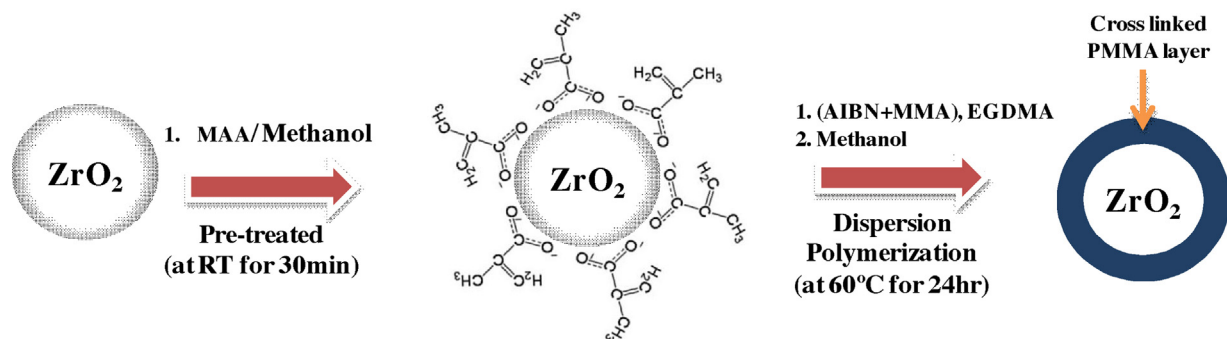


Fig. 1. Schematic diagram for the synthesis of crosslinked PMMA coated ZrO_2 particles.

Download English Version:

<https://daneshyari.com/en/article/226893>

Download Persian Version:

<https://daneshyari.com/article/226893>

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