



Transparent and high permittivity films of poly(methyl methacrylate)-grafted 7 nm barium titanate particles prepared by surface-initiated atom transfer radical polymerization



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ABSTRACT

Transparent and high permittivity films were prepared by melt pressing poly(methyl methacrylate) (PMMA)-grafted 7 nm barium titanate (BT) particles. PMMA chains with molecular weights of 32–40 kDa were grafted on BT particle surfaces at a density of 0.2–0.7 chains nm⁻¹ through surface-initiated atom transfer radical polymerization of methyl methacrylate. This yielded BT/PMMA composites with BT volume fractions (φ) ranging from 3.2% to 10%. In melt-pressed BT/PMMA composite films, BT particles were well-dispersed and exhibited high transmittance at 550 nm, with the values standardized for 100 μ m thickness being 80%. The relative permittivity of the films at 1 kHz and 25 °C increased to 4.1 upon increasing φ to 10%, according to Lichtenecker's logarithmic mixture formula, while the loss tangent remained as low as 0.04.

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1. Introduction

Ceramic/polymer nanocomposites, in which high-permittivity metal oxide nanoparticles such as barium titanate (BT) are incorporated into high dielectric strength polymers, are high-performance dielectric materials [1–6]. However, simple incorporation of ceramic particles into a polymer generally yields inhomogeneous films, as inorganic nanoparticles tend to aggregate because of their low affinity for organic polymers as well as high surface energy. The dispersion of ceramic particles in polymers can be improved to some extent through the addition of surfactants, although residual free surfactants can cause high leakage current and dielectric loss. BT particles bonded with phosphonic acid surfactant on their surfaces can be dispersed in a poly(vinylidene fluoride-co-hexafluoropropylene) matrix, with the BT/polymer composite exhibiting a relative permittivity of 37 and high dielectric strength of 210 V μ m⁻¹. However, 30–50 nm particles formed 100 nm aggregates [2].

Aggregation of inorganic nanoparticles can be avoided by

grafting polymer chains on the particle surface in high density. Silica particles grafted with polymer chains having narrow polydispersity of molecular weight (chain length) can form arrays in solvents. The 100-nm-diameter particles exhibited structural colors in solvents due to Bragg reflection [7–9]. The 55-nm-diameter particles formed a hexagonal array in thin films, whereas 15-nm-diameter particles did not form an ordered array [10]. The 100-nm-diameter BT particles could be dispersed in a polymer matrix by grafting polymer chains on the particle surfaces [3–6]. While the permittivity of the composite increased to 77 upon increasing BT content to 40 vol% [3], the composite films should be opaque because of the large size of the particles although it was not reported. In contrast, transparent BT/polymer composites can be used to develop tough and light-weight capacitive touch panels for use in flexible devices as well as smartphones and tablets. The permittivity of glass required for use in capacitive touch panels is 4.5–6.9 [11]. Transparent BT/poly(methyl methacrylate) (PMMA) films can be obtained by grafting PMMA chains on smaller BT particles, resulting in larger permittivities than that of PMMA (3.1) and which might be comparable with that of glass.

In this study, we prepared BT/PMMA composites by grafting PMMA chains on the surface of 7 nm BT particles. The BT/PMMA

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composites were able to form free-standing films using a melt pressing method. The morphology, transparency, and permittivity of the composite films were examined. The fraction of BT ranged from 3.2 to 10 vol% upon increasing the number average molecular weight (M_n) of the grafted PMMA from 32 to 40 kDa. The BT particles were dispersed in matrices of the grafted PMMA such that the composite film exhibited high visible-light transmittance and a high relative permittivity of 4.1.

2. Experimental

2.1. Materials

The 7 nm BT particles were purchased from JGC Catalysts and Chemicals Ltd. (Kanagawa, Japan). Other chemicals were purchased from Tokyo Chemical Industry (TCI, Tokyo, Japan), Aldrich, and Wako Chemicals (Osaka, Japan). 2-Bromo-2-methyl-N-(3-(triethoxysilyl)propyl)propanamide (BrTEOS) was synthesized according to the procedure reported by Beltrán-Osuna et al. [12].

2.2. Preparation of BT/PMMA particles

PMMA-grafted BT (BT/PMMA) particles were prepared by surface-initiated atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) on BT particles (see Scheme 1).

BrTEOS was immobilized on BT particle surfaces to prepare ATRP initiator-modified BT particles (BT-Br). BrTEOS (1.0 g) dissolved in 2-methoxyethanol (2 mL) was added dropwise to a mixture of a dispersion of BT particles in 2-methoxyethanol (15.3 g) and 28% ammonia water (1.5 mL) at 40 °C and stirred overnight. BT-Br was collected by double centrifugation from the dispersion in 2-methoxyethanol and unreacted BrTEOS and ammonia were removed.

BT-Br was subsequently used for copper-mediated ATRP of MMA. Three BT/PMMA particles with different volume fractions of BT were prepared by changing the weight ratio of MMA to BT-Br and the polymerization period, as listed in Table 1. Herein the prepared composites are identified as BT/PMMA- ϕ , where ϕ corresponds to the volume fraction of BT as a percent. BT/PMMA-3.2 was prepared as follows. A mixture of MMA (6.0 g), BT-Br (0.50 g), N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, 0.079 g), and dimethylformamide (DMF, 15 g) was sonicated for 3 min in an ice bath, degassed immediately through three freeze-pump-thaw cycles, and charged with nitrogen. This was followed by addition of Cu^IBr (0.045 g). Polymerization was performed by heating the mixture at 70 °C for 3 h. Next, the solution was diluted with THF, poured into methanol, and the BT/PMMA particles were washed-centrifuged three times in methanol (4500 rpm, 15 min) to remove unreacted monomer. Finally, the particles were dispersed in a mixture of acetone and an aqueous solution of ethylenediaminetetraacetic acid (EDTA) to remove the Cu catalyst. The molecular weight and polydispersity index (PDI) of the grafted PMMA were estimated by size exclusion chromatography (SEC) of PMMA cleaved from the BT/PMMA particles [10].

2.3. Methods

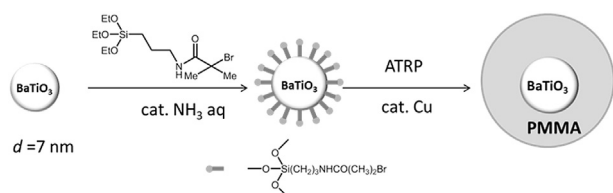
SEC was performed on a JASCO system equipped with polystyrene gel columns using CHCl₃ as the eluent following calibration with a PMMA standard. Differential scanning calorimetry (DSC) measurements were conducted using a Perkin–Elmer DSC 7 under dry nitrogen flow. X-ray photoelectron spectroscopy (XPS) was performed on a JEOL JPS-9010 spectrometer. Diffuse reflectance infrared (DRIR) spectra were measured using a JASCO FT-IR4200 spectrometer equipped with a DR PRO410-M attachment. Thermal gravimetric analyses (TGA) were performed using a Rigaku ThermoPlus Evoll TG8120 under dry nitrogen flow. Visible (Vis) spectra were measured using a Jasco V570 spectrophotometer. Small-angle X-ray scattering (SAXS) patterns were measured using Cu K α radiation with a Bruker AXS Nano-STAR-U equipped with a Vantec-2000 detector. Ultra SAXS (USAXS) measurements were performed at the BL-03XU beamline in SPring-8, Harima, Japan using a Rigaku R-AXIS VII as a detector at a camera length of approximately 8 m. The X-ray radiation wavelength (λ) was either 0.15 or 0.20 nm. The SAXS and USAXS intensities were corrected by transmission and subtraction of background scattering and plotted against the scattering vector ($q = (4\pi \sin \theta)/\lambda$). The corrected SAXS intensity was fitted to the Percus–Yevick model using Bruker Nanofit software. Transmission electron microscopy (TEM) was performed using a Hitachi H-7650 Zero A microscope. The dielectric properties were measured at 25 °C using a Solartron 1255B frequency response analyzer equipped with a Solartron 1296 dielectric interface. A disk-shaped sample (0.5 mm thickness and 15 mm diameter) was set in a SH2-Z sample holder equipped with 10 mm diameter electrodes (Toyo Corp., Tokyo, Japan).

3. Results and discussion

3.1. Characterization of BT/PMMA particles

Modification of the BT surface with BrTEOS was confirmed by XPS and DRIR spectroscopy. Fig. 1 shows the XPS of the BT and BT-Br particles. In the O1s region shown in Fig. 1a, the BT particles exhibited a peak at a binding energy of 533.8 eV, whereas the corresponding peak of the BT-Br particles appeared at a slightly smaller binding energy of 530.8 eV. This decrease in the binding energy of O1s is associated with the transformation of the carboxylic acid (O=C–O–H) on the BT particle surface to an ester (O=C–O–C) upon reaction with BrTEOS [13]. BrTEOS may react preferentially with the more acidic carboxylic acid group rather than hydroxyl group. In the C1s region shown in Fig. 1b, both BT and BT-Br particles show two peaks at 288.8 and 285.7 eV that can be attributed to the O=C–OH and C–H species, respectively [13]. The BT particles exhibited a stronger peak at 288.8 eV and a weaker peak at 285.7 eV compared with the BT-Br particles, which can be ascribed to the ester bond formation in BT-Br particles upon reaction of BrTEOS with carboxylic acid groups on the BT particle surface. The DRIR spectrum of BT-Br includes absorption peaks at 1116 and 1020 cm⁻¹, which are associated with Si–O and Si–O–Si groups, respectively, demonstrating that siloxane moieties are attached to the BT-Br particles (compare Fig. 2a and b).

PMMA brushes were densely grafted on BT particles through surface-initiated ATRP. The DRIR spectrum of the BT/PMMA particles includes absorption peaks at 2962 cm⁻¹ (C–H groups), 1730 cm⁻¹ (C=O groups), and 1263 cm⁻¹ (C–O groups), indicating the presence of PMMA chains. The relative amount of PMMA was estimated from TGA thermograms (Fig. 3). Upon increasing the temperature to 410 °C under a nitrogen atmosphere, PMMA decomposed completely, whereas BT and BT-Br decreased in weight by less than 10%, even though surface-adsorbed water and



Scheme 1. Preparation of BT/PMMA Particles.

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