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Permittivity enhancement of transparent poly(vinylidene fluoride) nanocomposite films by loading titania-coated barium titanate nanoparticles

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Abstract

Barium titanate (BT) nanoparticles are coated by titania and modified by fluoroalkylsilane. The BT nanoparticles are incorporated into poly(vinylidene fluoride) (PVDF) films to obtain highly dielectric and transparent nanocomposite films at low filler loadings. Incorporation of BT nanoparticles having average sizes of 12 and 22 nm is performed. Incorporation of BT nanoparticles enhances the permittivity of PVDF films. Higher transparency of nanocomposite films is achieved by incorporating 12-nm nanoparticles compared to that by 22-nm nanoparticles. The polarisation mechanism in the nanocomposite films is examined using the Vo-Shi model. The result indicates that even a slight increase in the thickness of titania-coating layer on the BT nanoparticles increase the permittivity of the nanocomposite films. Comparison of the measured and calculated permittivities showed that the incorporation of BT nanoparticles coated with titania provides a practical approach to create transparent nanocomposite films having high permittivity.

Keywords : Barium titanate . Coating . Permittivity . Titania . Thin film . Polymers

1. Introduction

Incorporation of inorganic nanofillers into polymer films is a common technique to combine transparency of polymer films with specific functions derived from inorganic nanofillers (Subramani et al. 2016; Xia et al. 2017; Huang et al. 2017; Ojha et al. 2013; Dang et al. 2014; Parlak et al. 2011). For instance, the incorporation of magnetic or fluorescent nanoparticles can create transparent nanocomposite films having magnetism and fluorescence, respectively. The choice of nanofillers incorporated into polymer film and their content in the film are essential to determine the functionality of nanocomposite films. High flexibility and processability, which are important characteristics of polymer films (Rahman et al. 2017; Ghosh et al. 2016), however, are reduced by excessive loading of inorganic nanofillers. In other words, loading of inorganic nanofillers at > 50 vol% was reported to cause agglomeration among nanofillers accompanied by the formation of pores or voids in the fabricated nanocomposite films (Kim et al. 2009; Nagao et al. 2011; Abe et al. 2013).

Permittivity of polymeric films can be increased by incorporating highly dielectric nanoparticles into a polymer matrix. BaTiO₃ nanoparticles are commonly used as nanofillers to enhance the permittivity of polymeric films (Kanamori et al. 2016; Wang et al. 2015; Wang et al. 2016; Zhang et al. 2016; Hou et al. 2015; Hu et al. 2018a). Owing to their high surface-to-volume ratio and unique chemical properties, anisotropic and dielectric nanofillers including nanofibers (Wu et al. 2015), nanowires (Yao et al. 2017) and nanotubes (Pan et al. 2017) have also been employed for preparing nanocomposite films having high permittivity. Another approach to enhance film permittivity is coating dielectric nanofillers with organic molecules (Xie et al. 2017) or metal oxides (Huang et al. 2015) to introduce interfacial charges at the interface of the nanofiller/coating layer and the polymer matrix/coating layer. Xie et al. coated barium titanate (BT) nanoparticles with poly(dopamine) and successfully enhanced energy storage capacities of the corresponding nanocomposites (Xie et al. 2017). Rahimabady et al. employed core-shell-structured nanofillers comprising BT nanoparticles and titania shell for the P(VDF-HFP) polymer matrix and greatly enhanced the permittivity of the P(VDF-HFP) nanocomposite films (Rahimabady et al. 2013). More recently, Hu et al. reported that a relatively thin buffer layer of crystalline titania on BT nanoparticles could generate higher polarisation to increase dielectric constants of nanocomposite films (Hu et al. 2018b). However, no study to prepare transparent, highly dielectric nanocomposite films using the titania-coated BT nanoparticles has been reported thus far.

In the present work, applicability of core-shell, dielectric nanofillers to a polymer matrix is examined to fabricate transparent

nanocomposite films having high permittivity. BT nanoparticles to be coated with titania are prepared as dielectric nanofillers using the sol-gel method and then are surface-modified with a fluoroalkylsilane, 3,3,3-trifluoropropylmethoxysilane (FPS), to attain high affinity of core-shell nanofillers with a polymer matrix of polyvinylidene fluoride (PVDF) (Kamezawa et al. 2015). FPS is a low-molecularweight fluoroalkylsilane-coupling agent that is commercially available and has C-F bonds similar to those of PVDF. Two different nanoparticle sizes of 12 and 22 nm are employed as the nanofiller to fabricate transparent nanocomposite films with high permittivity. Incorporations of the nanofillers are limited at 50 vol% or lower to retain polymer flexibility, because it was reported that a high loading of nanofiller inevitably led to inhomogeneity and aggregation of nanofillers in polymer matrices resulting in the deterioration of mechanical and dielectric properties (Kim et al. 2009; Hou et al. 2015). This is the first report on incorporation of the titania-coated BT nanoparticles to enhance permittivity of the polymer films with maintaining film transparency originated from the polymer.

2. Experimental details

2.1. Materials

Polyvinylidene fluoride (PVDF, average Mw = 180,000) and 3,3,3-trifluoropropylmethoxysilane (FPS) were obtained from Wako Pure Chemical Ind. They were used as the matrix polymer and surface modifier, respectively. Metallic barium (Kanto Chemical Co.) and tetraethylorthotitanate (TEOT, 97%, Tokyo Kasei Kogyo Co.) were used as raw materials for BT nanoparticles. Ethanol (EtOH, 99.5%), 2methoxyethanol (ME, 99.0%) and N-methyl-2pyrrolidone (NMP, 99.5%), as solvents, were also purchased from Wako Pure Chemical Ind. All the chemicals were used as received. Water was deionised to exhibit an electric resistance higher than 18 MΩ·cm. Indium tin oxide glass (Furuuchi Chemical Co.) and slide glass (Matsunami Glass Ind.) were used as substrates for dielectric and optical measurements, respectively.

2.2. Synthesis of BaTiO₃ (BT) nanoparticles and their titania-coating

The synthesis of BT nanoparticles has been reported in our previous studies (Kamezawa et al. 2015; Dang et al. 2014; Parlak et al. 2011). Typical experimental procedure of BT nanoparticles having an average size of 22 nm is as follows. AnME solution (60 ml) of metallic barium (0.0096 mol) and TEOT (0.0096 mol) was refluxed at around the boiling temperature of ME for 2 h under N₂ atmosphere. Then, the solution was mixed with an ME solution (60 ml) containing H₂O (15 M) to hydrolyse the double alkoxide of Ba and Ti. Hydrolysis and condensation were conducted for 5 h at 70 °C. The initial concentrations of [Ba] and [Ti] were both 0.08M. Synthesis of BT nanoparticles with an average size of 12 nm was performed via a similar procedure to produce 22-nm nanoparticles. The procedural differences lay in the solvent composition and H₂O concentration used. Instead of ME, a mixed solvent of ME and EtOH (volume ratio = 1:3) was used for the synthesis of 12-nm nanoparticles. Water concentration was adjusted to 5M. For using BT nanoparticles as cores in the next step of titania-coating, a combined process of centrifugation and redispersion was applied three times to wash the BT nanoparticles.

In the process of titania-coating, hydrolysis and condensation of TEOT were performed in a mixed solution of water and ME in the presence of BT nanoparticles at 0.1 vol%. The initial concentrations of TEOT and water were 0.025 and 0.25 M, respectively. The volume of reactions was 60 ml.

The surface of BT nanoparticles or titania-coated BT nanoparticles was modified using FPS. Before the addition of FPS, ultrasonication was performed to irradiate the suspension of nanoparticles for 30 min. The FPS added to the solution was 1.3 times as much as that required for monolayer coverage of the surface of nanoparticles. The reaction underwent for 1 h at 70 °C. FPS-modified nanoparticles were separated from the solution by centrifugation (20,000 rpm, 30min) and redispersion in N-methyl-2-pyrrolidone (NMP).

2.3. Preparation of nanocomposite films incorporating BT nanoparticles or TiO₂-coated BT nanoparticles

To prepare the suspension used for spin-coating, PVDF was added to the suspension of surface-modified nanoparticles and stirred at 70 °C for 5 h. Subsequently, the suspension was spin-coated on the substrates at 1500 rpm for 30 s, before the coated substrates were heated on a hotplate at 100 °C for 30 min. Before heating treatment, no dry processes were conducted to avoid agglomeration of BT nanoparticles. The thickness of the nanocomposite films was in the range 0.4–0.7 μm. The contents of nanofiller incorporated into the nanocomposite films were experimentally obtained with thermogravimetric analysis in which the films that were dried overnight under reduced pressure were heated in a range of room temperature to 550 °C. The measurement of nanofiller content included experimental

errors within several percentages of the nanofiller volume contents.

2.4. Characterisation

XRD measurement (Ultima IV, Rigaku Co.) was conducted to examine the crystallinity of nanoparticles formed in sol-gel reactions. The chemical compositions of coated nanoparticles were measured with inductively coupled plasma mass spectrometry (ICP-MS, SPS7800, Seiko Instruments). The transmittances of nanocomposite films were characterised on a UV-Vis spectroscope (UV-3010, Hitachi High-Technologies). Capacitances of the prepared films were measured by an LCZ meter (ZM2335, NF Electronic Instruments) at a frequency of 10 kHz. Dielectric constant of the film was calculated from the capacitance of composite film, the thickness of nanocomposite film, and the area ($7.07 \times 10^{-4} \text{ cm}^2$) of the circular Au-electrode by sputtering. The thickness of nanocomposite films was measured using AFM (NPX200, Seiko Instruments). Nanoparticles with and without titania-coating were characterised using transmission electron microscopy (STEM, Hitachi HD-2700) and dynamic light scattering (DLS, ELSZ-2, Otsuka Electronics). To prepare samples for STEM observation, a small amount of suspension was directly introduced on a collodion microgrid (Cu200A, JEOL) and dried at room temperature.

3. Results and discussion

Figure 1a, b shows TEM images of BT nanoparticles prepared via the sol-gel method at water concentrations of 15 and 5 M, respectively. Averaged sizes of the BT nanoparticles in Fig. 1a, b were 22 and 12 nm, respectively. The peaks in XRD patterns for BT nanoparticles, which are presented in Fig. S1 of Supporting Information, are attributed to the perovskite cubic phase of BaTiO_3 . From the (110) peaks of the pattern, the crystal sizes of the BT nanoparticles were estimated to be 16.3 and 9.1 nm for the BT nanoparticles (Fig. 1a, b), respectively, using the Scherrer equation. Because crystal sizes were close to those measured by TEM images, the formed nanoparticles were likely to comprise single crystals in sol-gel reactions.

The hydrolysis and condensation of TEOT in ME solvent at $[\text{H}_2\text{O}] = 250 \text{ mM}$ were conducted in the presence of BT nanoparticles to form a titania shell on them. Figure 1c, d shows the obtained particles after coating reactions. BT nanoparticles were apparently coated by some precipitates that were observed as low-density substances, from Fig. 1c, d. The coated nanoparticles were dissolved in concentrated sulphuric acid to measure their chemical compositions using ICP-MS. The ratios of Ti/Ba for the nanoparticles, as shown in Fig. 1c, d, were 2.03 and 1.82, respectively, which were stoichiometrically consistent with those used in the synthesis of BT nanoparticles and their coating.

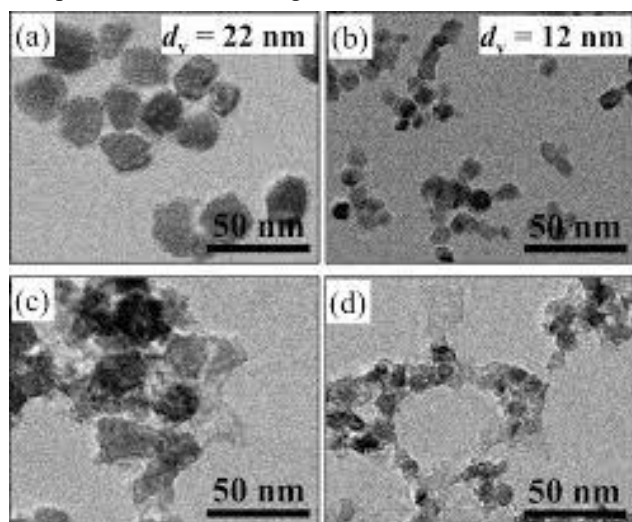


Fig. 1 TEM images of BT nanoparticles with different average sizes of 22 nm (a) and 12 nm (b). BT nanoparticles obtained by titania-coating of the particles a and b are shown in the images of c and d, respectively

Since the sample preparation for TEM observation included a drying process to induce assembling of the nanoparticles on a sample grid, it was difficult to judge the colloidal stability of coated particles from low-magnification TEM images, as shown in Fig. S2. Colloidal stabilities of the coated nanoparticles in NMP were examined using dynamic light scattering. Figure S3 presents size distributions of the coated nanoparticles with and without surface-modification by FPS. The surface-modification improved colloidal stability of the coated nanoparticles in NMP and reduced the dispersion size of the coated nanoparticles.

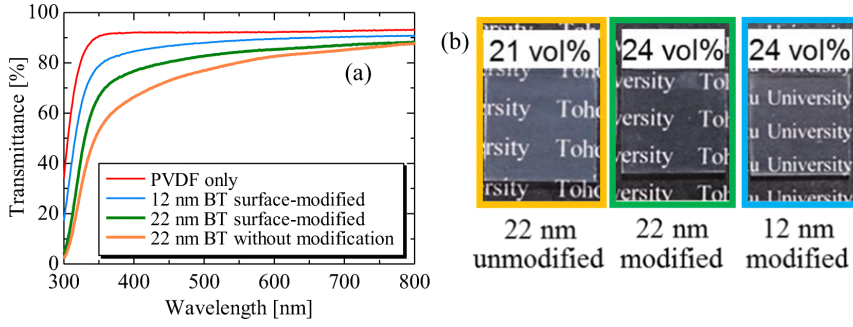


Fig. 2 **a** Transmittance spectra of PVDF nanocomposite films incorporating the titania-coated BT nanoparticles surface-modified with FPS. The blue and green lines show spectra of the films for BT nanoparticles sizes of 12 and 22 nm, respectively, at the BT contents of 24 vol%. The red line indicates that of films without incorporation of the nanoparticles. The orange line shows no surface-modification for the coated nanoparticles with the size of 22 nm at 21 vol%. **b** Appearances of the nanocomposites films corresponding to the three spectra indicated with the different colours

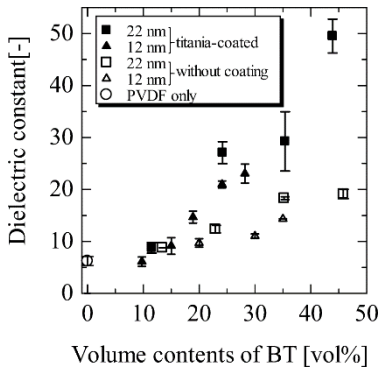


Fig. 3 Dielectric constants of nanocomposite films. All the nanoparticles were surface-modified with FPS for homogeneous incorporations of the nanoparticles into PVDF

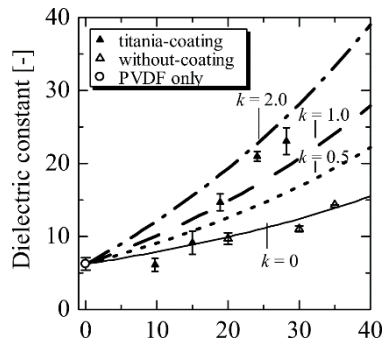


Fig. 4 Dependence of nanocomposite permittivity on interface volume constant k between BT and PVDF matrix in Vo–Shi model at fixed ϵ_{int} and ϵ_{BT} of 103 and 100, respectively. The average BT nanoparticle size is 12 nm

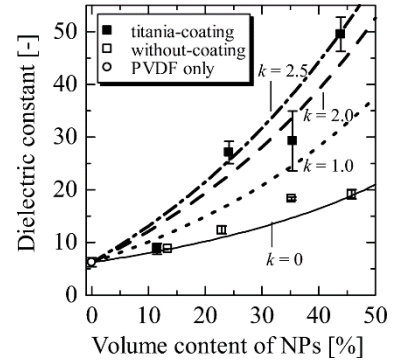


Fig. 5 Dependence of nanocomposite permittivity on interface volume constant k between BT and PVDF matrix in Vo–Shi model at fixed ϵ_{int} and ϵ_{BT} of 103 and 150, respectively. The average BT nanoparticle size is 22 nm

The fabrication of PVDF nanocomposite films was conducted using the coated nanoparticles. Transmittance spectra of the films with and without incorporation of 24 vol% nanoparticles surface-modified with FPS are shown in Fig. 2. The spectrum without surface-modification is also presented for 22-nm nanoparticles. Surface-modified nanoparticles with FPS exhibited higher transmittance than that of unmodified nanoparticles lower than 24 vol%, which is probably due to the difference in the dispersion sizes of nanoparticles, shown in Fig. S3. Transmittance > 75% in the visible range of wavelength was attained in the surface-modification of titania-coated nanoparticles. The spectra of nanocomposite films at different contents of BT nanoparticles are presented in Fig. S4. The transparency of the films can be visually confirmed in film appearances of Fig. 2b and the optical microscope images of Fig. S5, indicating that the 12-nm and 22-nm nanoparticles with surface-modification were homogeneously dispersed in the films.

We measured the dielectric constants of the films incorporating titania-coated BT nanoparticle content lower than 40 vol% for 12-nm nanoparticles and those with content lower than 50 vol% for 22-nm nanoparticles. The dielectric constants of films are shown in Fig. 3, wherein dielectric constants of films without titania-coating are also plotted. All the nanoparticles in Fig. 3 were surface-modified by FPS to be homogeneously incorporated into the PVDF films. Although all the dielectric constants in Fig. 3 were increased by incorporating BT nanoparticles, which was independent of their sizes, the incorporation effect on permittivity with 22-nm nanoparticles was slightly stronger than that with 12-nm nanoparticles. As shown in Fig. 3, distinct increase in dielectric constants with the titania-coating was observed for both sizes of particles. Although similar enhancements of dielectric constants were already reported in some previous reports (Wang et al. 2015; Huang et al. 2015), our results in Figs. 2 and 3 prove that the titania-coating is effective for permittivity enhancement and the maintenance of high transparency in nanocomposite films.

To examine the polarisation mechanism in the nanocomposite films, the permittivity enhancement of nanocomposite films was analysed using an empirical model reported by Vo and Shi. An interface volume constant (k) between fillers and the polymer matrix

was introduced to account for filler–polymer interaction strength (Vo et al. 2002). As shown in Fig. S6, experimental permittivities for 12-nm nanoparticles were plotted together with those calculated using the Vo–Shi model at a fixed filler permittivity of 100 (Kobayashi et al. 2009). The calculated permittivity of nanocomposite films exhibited a weak dependence on the interfacial permittivity ϵ_{int} in the range of 10^2 – 10^4 . Conversely, as presented in Fig. 4, the interface volume k for a fixed filler permittivity strongly affected the permittivity of nanocomposite films in a narrow k range of 0.5–2.0, indicating that even a slight change in the volume of the TiO₂ coating of BT nanoparticles affected the permittivity of nanocomposite films. Similar to the comparison with the experimental permittivities, as shown in Fig. 4, a strong dependence on the interface volume k was observed for 22-nm nanoparticles, shown in Fig. 5, wherein experimental permittivities were plotted with those that were calculated in the k range of 1.0–2.5 at a fixed filler permittivity of 150. The permittivities of nanocomposite films, thus, were mainly dominated by the interfacial polarisation mechanism.

Although the optimum thickness of titania layer that appropriately balanced high permittivity and transparency was not determined in the present work, the comparison of experimental and calculated data indicated that the coating of a titania layer with an appropriate thickness can be an effective pathway to fabricate nanocomposite films having high permittivity and transparency.

4. Conclusion

Titania-coating of BT nanoparticles that were homogeneously dispersed into a polymer matrix was a practical approach to enhance the permittivity of nanocomposite films and to maintain their high transparency. The comparison between experimental and calculated permittivities via the Vo–Shi model indicated that the titaniacoated BT nanoparticles are reliable nanofillers to increase the permittivity of transparent nanocomposites. In addition, titania-coated BT can also be effective for fabricating transparent nanocomposite films having high permittivity.

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Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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