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Enhanced Dielectric Properties of Electrospun Titanium Dioxide/Polyvinylidene Fluoride Nanofibrous Composites

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Abstract: Titanium dioxide/polyvinylidene fluoride (TiO_2/PVDF) composite was prepared by electrospinning process to enhance the dielectric properties for application as a gate insulator in organic thin-film transistors (OTFTs). Scanning electron microscopy, thermogravimetric analysis, and X-ray diffraction were employed to characterize the as-prepared samples, and then their dielectric constants were investigated by impedance analysis. The impedance results show that the dielectric constant of the electrospun TiO_2/PVDF nanofibers is higher than those of other samples, demonstrating that electrospun TiO_2/PVDF composite can be a proper candidate for gate insulators in OTFTs.

Keywords: Polyvinylidene fluoride, Titanium dioxide, Electrospinning, Dielectric properties

Introduction

In recent years, organic thin-film transistors (OTFTs) have received increasing interest for printable electronics, portable displays, patchable electronics, and smart cards, because of their suitability for disposable, light, and flexible devices [1-4]. Low operating voltage is a crucial factor for various OTFT-based applications, but there are major problems, such as high working voltage due to the low charge carrier mobility of organic semiconductors, and the insufficient dielectric properties of the organic gate dielectrics for OTFTs [5,6]. The requirements for the dielectric in OTFTs are much broader, and include processability, high capacitance, high dielectric strength, high on/off ratio, and low hysteresis [7]. The dielectric properties of dielectrics are influenced by thermodynamic stability, film morphology, interface quality, compatibility with the currently used or expected materials, and process compatibility [8]. It is important to obtain an organic insulator with a high dielectric constant for OTFTs to run at low working voltage.

The dielectric properties of polymer dielectric materials have been investigated [9-11]. However, these materials have been unsuitable as gate dielectrics due to their relatively lower dielectric constants in applications demanding low operating voltage. To improve the dielectric constant, various polymer/inorganic nanocomposites made by incorporating inorganic nanoparticles with high a dielectric constant into an organic matrix have been studied [12-14]. In polymer-based nanocomposites used for dielectrics, it is important to maintain the superior mechanical properties of polymers and to uniformly disperse the inorganic nanoparticles into the polymer matrix.

In this study, a composite of titanium dioxide and polyvinylidene fluoride (TiO_2/PVDF) was prepared by electrospinning. Electrospinning is a simple method for forming PVDF nanofibers that have ferroelectric characteristics directly using an electrospinning PVDF solution. Electrospun PVDF nanofibers made by electrospinning solutions of PVDF dissolved in proper solvents under an applied electric field have been reported [15]. We choose mixed solvents of hexafluoroisopropanol (HFIP)/N,N-dimethylformamide (DMF) as an appropriate solvent for electrospinning PVDF and TiO_2/PVDF. HFIP is a suitable solvent for the electrospinning process, because of its higher volatility than those of other solvents, such as formic acid/meta-cresol. DMF has been empirically found to be helpful during the electrospinning process and the formation of electrospun nanofibers [16]. TiO_2 nanoparticles have also been used to increase dielectric constants [17-19]. In order to confirm the influence of the preparation methods, an impedance analyzer was used for investigating the dielectric properties.

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Experimental

Materials

PVDF, HFIP, titanium (IV) butoxide, potassium chloride (KCl), and 2-Methoxyethanol were purchased from Sigma-Aldrich. DMF was obtained from OCI Company, Ltd.

Preparation of TiO_2 Nanoparticles

0.1 M KCl solution was poured into ethanol with stirring. Then, titanium (IV) butoxide was added into the as-prepared solution with stirring for 20 min, and this solution was placed in ambient air at room temperature to obtain a precipitation of the TiO_2 nanoparticles. After washing and drying the product, to obtain crystalline TiO_2 nanoparticles, the as-prepared TiO_2 nanoparticles were annealed at 600 ^oC, and maintained at this temperature for 3 h.

Preparation of TiO_2/PVDF Composites

The experimental method is shown in Figure 1. In a

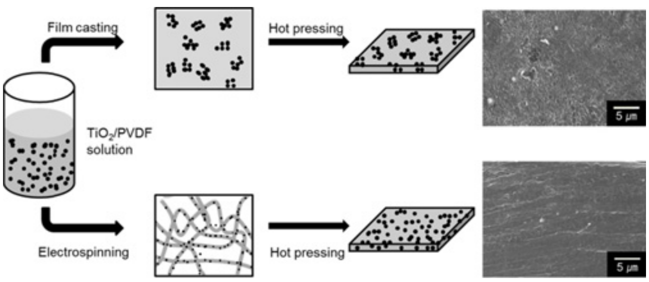

Figure 1. Schematic illustration of the preparation and SEM images of electrospun TiO_2/PVDF nanofibers and film-casted TiO_2/PVDF.

typical procedure, TiO_2 nanoparticles were added to 2-methoxyethanol and then sonicated for 1 h. PVDF was added to mixed solutions of DMF/HFIP (8:2 by weight) and stirred at 50 °C for 2 h. The weight ratio of TiO_2 to PVDF was fixed at 1:20, which is the optimal condition in this study. The TiO_2 suspension was slowly dropped into PVDF solution with stirring, and the mixed solution was stirred vigorously for 30 min. During electrospinning, the distance between the capillary tip and the collector (aluminum foil) was 20 cm, and a voltage of 35 kV was applied. After electrospinning, the final TiO_2/PVDF electrospun mat was prepared by hot-pressing at 160 °C for 15 min. To examine the differences between the preparing methods, a TiO_2/PVDF film-casted mat was prepared by the same method, but without the electrospinning process.

Characterization

The morphology of the samples was determined by field emission scanning electron microscopy (FESEM, S-4300, Hitachi, Japan) at an accelerating voltage of 15 kV. X-ray diffraction (XRD, Rigaku, DMAX-2500, Japan) was used to characterize the samples through a diffractometer with reflection geometry. Thermogravimetric analysis (TGA, Q50, TA instruments, UK) was conducted at temperatures ranging from 20 to 800 °C.

Measurement of Dielectric Properties

An impedance Analyzer (HP4294A, Agilent, USA) was used to measure the dielectric constants of the samples between 10^2 Hz and 10^8 Hz. For this measurement, the samples were cut into 0.5-mm squares, and layers of Pt were deposited on the top and bottom of the square samples with a magnetron sputtering system (E-1030, Hitachi, Japan).

Results and Discussion

Figure 2 shows the XRD pattern, TGA data, and SEM image of the as-prepared TiO_2 nanoparticles used in this experiment. As shown in the XRD pattern, the diffraction peaks of the as-prepared TiO_2 nanoparticles were mainly revealed at 2θ values of 25.2 °, 37.1 °, 37.8 °, 48.1 °, 54.0 °, 55.1 °, 62.7 °, and 68.8 °, which means the crystalline phases correspond to (101), (103), (004), (200), (105), (211), (204) and (116), respectively [20]. These crystalline phases indicate that the as-prepared TiO_2 nanoparticles have anatase-type crystalline structure, which is known to have a dielectric constant of about 31. TGA data shows that the as-prepared anatase-type TiO_2 nanoparticles have outstanding thermal stability in air, and the SEM image shows that these anatase-type TiO_2 nanoparticles had diameters of tens to hundreds of nanometers.

Figure 3(a) shows the appearance of electrospun PVDF nanofibers, which had an average diameter of 240±100 nm (N=30). For electrospun TiO_2/PVDF nanofibers, we were able to confirm that electrospun TiO_2/PVDF had an average diameter of 220±70 nm (N=30), which are similar to that of electrospun PVDF nanofibers, as shown in Figure 3(b). To disperse the TiO_2 precursor, TiO_2 particles, and metal precursor, 2-methoxyethanol has been used as a solvent in various investigations [21,22]. The TEM image of the inset in figure 3(b) shows that the TiO_2 nanoparticles were incorporated with nanofibers.

Figure 4 shows the XRD patterns of electrospun PVDF nanofibers, film-casted PVDF, electrospun TiO_2/PVDF nanofibers, and film-casted TiO_2/PVDF. As shown in Figures

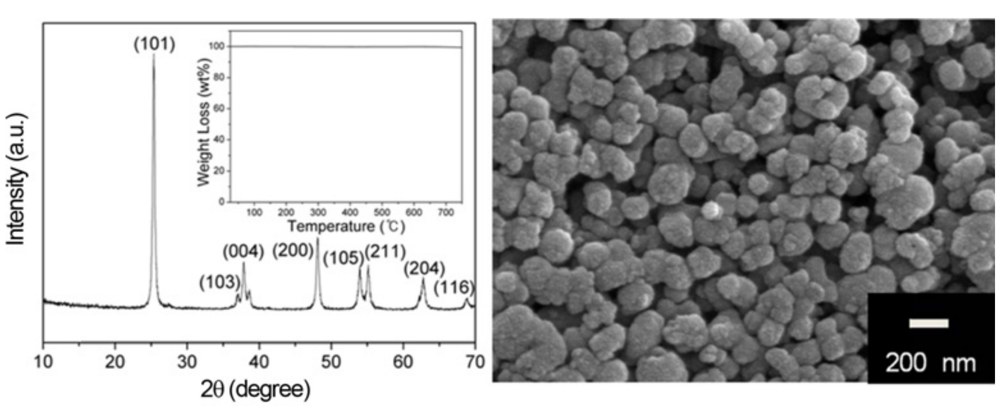

Figure 2. XRD pattern, TGA curve, and SEM image of TiO_2 nanoparticles.

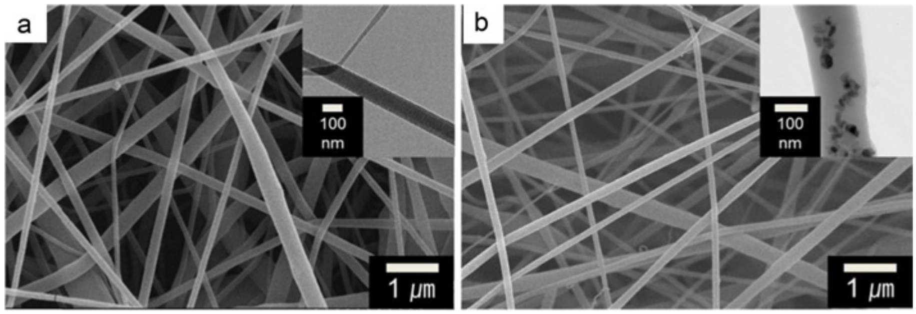

Figure 3. SEM and TEM images of (a) electrospun PVDF and (b) electrospun TiO_2/PVDF.

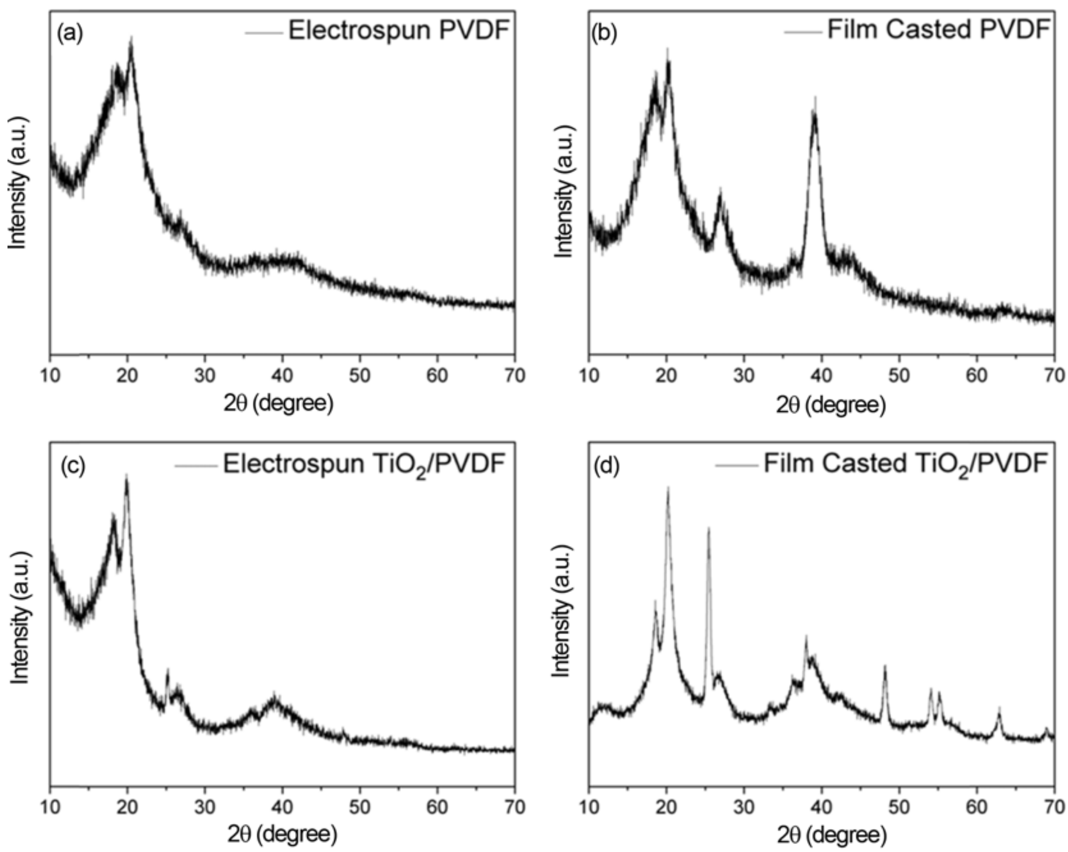

Figure 4. XRD patterns of (a) electrospun PVDF, (b) film-casted PVDF, (c) electrospun TiO_2/PVDF, and (d) film-casted TiO_2/PVDF.

4(a) and 4(b), there are differences in the peaks between electrospun PVDF nanofibers and film-casted PVDF. The film-casted PVDF showed clear diffraction peaks at 2θ values of 20.0^{o}, which corresponds to (200)/(110) reflections of the beta-phase, and at 18.4^{o} and 26.7^{o}, which correspond to (020) and (111) reflections of the alpha-phase [23]. However, electrospun PVDF nanofibers showed broad peaks unlike the film-casted PVDF, around 25^{o} and 45^{o}. The dielectric constant is higher for the samples predominantly containing the beta-phase, and decrease with increases in the amount of the alpha-phase [24]. Because electrospun PVDF nanofibers had beta-phase predominant structure in comparison to film-casted PVDF, it has a decisive effect on the dielectric constant. In Figures 4(c) and 4(d), electrospun TiO_2/PVDF nanofibers and film-casted TiO_2/PVDF showed peaks of anatase-type TiO_2 nanoparticles, because of the incorporation with TiO_2 nanoparticles.

To confirm the incorporated contents of TiO_2 nanoparticles, the TGA analysis of electrospun TiO_2/PVDF nanofibers and film-casted TiO_2/PVDF is presented in Figure 5. We were able to confirm that the weight ratio of TiO_2 in TiO_2/PVDF composites was about 4 wt%, regardless of the preparation methods.

Figure 6 shows the dielectric constants of electrospun

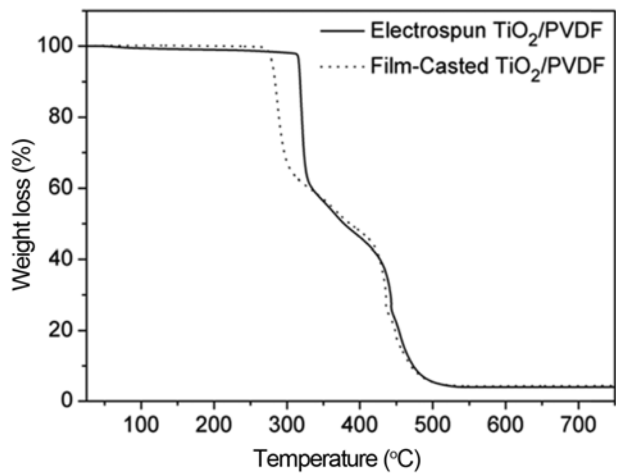

Figure 5. TGA curves of (a) electrospun TiO_2/PVDF and (b) film-casted TiO_2/PVDF.

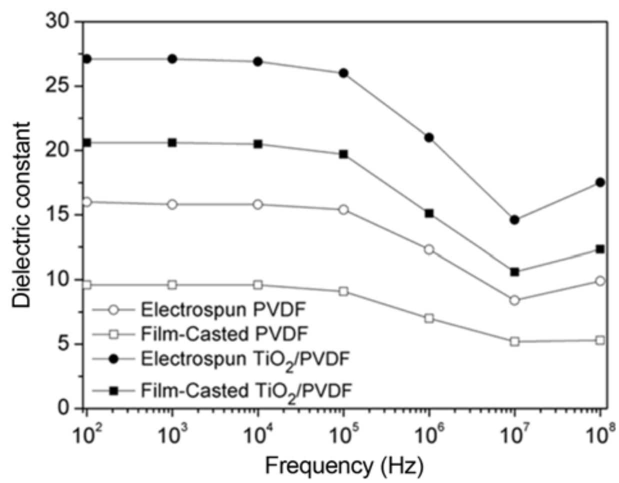

Figure 6. Dielectric constants of electrospun PVDF, film-casted PVDF, electrospun TiO_2/PVDF, and film-casted TiO_2/PVDF.

PVDF nanofibers, film-casted PVDF, electrospun TiO_2/PVDF nanofibers, and film-casted TiO_2/PVDF. In a previous related work, An *et al*. reported on TiO_2/PVDF film prepared by spin-coating process on a silicon substrate (100) for electroactive properties [25]. According to their report, the dielectric constant of the spin-coated PVDF film was about 8 at 100 Hz, and the dielectric constant of TiO_2/PVDF film (10 at 100 Hz) was higher than that of PVDF film, because of the enhanced dielectric property by TiO_2 incorporation. In this study, electrospun PVDF nanofibers had a higher dielectric constant (16.0 at 100 Hz) than those of film-casted PVDF (9.6 at 100 Hz) and spin-coated PVDF. We suggest that electrospun nanofibers have an advantage compared to materials prepared by casting and coating methods. The dielectric constants of electrospun TiO_2/PVDF nanofibers (27.1 at 100 Hz) and film-casted TiO_2/PVDF (20.6 at 100 Hz) were increased compared to those of the samples without TiO_2 nanoparticles incorporated. Electrospun TiO_2/PVDF nanofibers had a higher dielectric constant than film-casted TiO_2/PVDF. We suggest that electrospinning yields an advantage compared to film-casting regarding the dispersion of TiO_2 nanoparticles, as shown in Figure 1, demonstrating that electrospun TiO_2/PVDF nanofibers are a proper candidate for use as gate insulators in OTFTs.

Conclusion

We have prepared electrospun TiO_2/PVDF nanofibers by electrospinning, and their dielectric properties have been investigated. Anatase-type TiO_2 nanoparticles were obtained by solution chemical processing and thermal annealing and confirmed using XRD patterns. Both the electrospun TiO_2/PVDF nanofibers and film-casted TiO_2/PVDF had similar TiO_2 contents of about 4 wt%. The dielectric constant was improved by incorporating anatase-type TiO_2 nanoparticles. Electrospun TiO_2/PVDF nanofibers had a large dielectric constant (27.1 at 100 Hz), because TiO_2 nanoparticles were well dispersed by the electrospinning method, demonstrating that electrospun TiO_2/PVDF nanofibers are suitable candidates for use as gate insulators in OTFTs.

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