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Highly enhanced electromechanical properties of PVDF-TrFE/SWCNT nanocomposites using an efficient polymer compatibilizer

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ABSTRACT

PVDF-TrFE/SWCNT nanocomposites with outstanding electromechanical properties were produced using P3HT-PMMA block copolymers as a compatibilizer between PVDF-TrFE and SWCNT. P3HT-PMMA block copolymer coated SWCNT (PTMCNT) was first prepared to utilize π-π stacking interactions between SWCNT and the P3HT block segment. The obtained PTMCNTs are highly compatible with the PVDF-TrFE matrix due to strong hydrogen bonding interaction between the polymer matrix and the PMMA block segment on the surface of SWCNT, leading to a very low percolation behavior at 0.05 wt% of SWCNT in PVDF-TrFE. The obtained electroactive PVDF-TrFE/SWCNT nanocomposites showed ca. 50 times increased electromechanical thickness strain, ca. 3200 times increased elastic energy density, and ca. 460 times increased electrical-to-mechanical energy conversion rate in comparison to those of pristine PVDF-TrFE at the relatively low electric field (50 V_{pp}μm-1). These outstanding properties result from the ultra-low percolation of SWCNT along with uniform local field distribution in PVDF-TrFE, which kept not only intrinsic properties of PVDF-TrFE such as all-trans formed crystalline phase and softness but also enhanced electrical properties including dielectric constant.

1. Introduction

Various dielectric polymers such as silicone elastomers, acrylic copolymers, polyurethane (PU), and polyvinylidene difluoride (PVDF), and PVDF based copolymers have been known as electroactive polymers (EAPs), which are often employed for electromechanical applications such as next-generation compact actuators, sensors, artificial muscles, and micro-robotics, owing to sizeable electromechanical deformation, high energy density, fast response time, and facile processability [1–9]. In order to elucidate the electromechanical system of electroactive polymers, two key mechanisms are generally considered: (1) electrostatic strain [$S = 0.5K\varepsilon_0E^2(1+2\sigma)/Y$, where K is the dielectric constant, ε_0 is the vacuum dielectric permittivity (8.85×10^{-12} F m^{-1}), E is the applied electric field, σ is the Poisson's ratio, and Y is the elastic modulus]; (2) electrostrictive strain [$S = ME^2$, where M is the field related electrostrictive coefficient, which is proportional to the square of the dielectric constant (K)] [10]. These two mechanisms can be independently or complementarily adopted for electromechanical performance according to types of EAPs. The electrostatic strain mechanism can be applied for most polymers under the certain electric field, which is particularly more enhanced with soft rubbery polymers such as acrylate-polymers, styrene-butadiene rubber (SBR), and silicon rubber due to their lower elastic modulus (Y) [11,12]. In addition, the case of polymers with high dielectric constant such as PVDF and its copolymers can be further expected the electrostrictive strain mechanism due to a significnat change in the polarization in a material under constant stress [10,13,14]. However, these EAPs have suffered from the needs of relatively high electrical stimulation (>100 V μm^{-1}). Thus, the large deformation at reduced operating voltage is a very important issue to be overcome in EAPs, which will be achieved by control of the electric and the mechanical properties of EAPs such as increase of dielectric

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constant and a decrease of elastic modulus, respectively. Nanocomposites with a conducting filler or a softener (plasticizer) in EAPs are relatively easy way to increase the dielectric constant or to decrease the elastic modulus, respectively, where control of the electrical property with conducting filler is more suitable than that of the mechanical property, because most plasticizers with small molecular weight hydrocarbon and oil are electrically inactive and can be flowed out during the operation.

PVDF and its copolymers have been widely studied as EAPs because of their high dielectric constant, high dipole density, and fast reversible polarization switching properties originated from the all-trans form crystalline phase in comparison to other electrostrictive polymers [7–9]. However, its electromechanical performances are still not enough to apply for various soft actuator applications because of its relatively small deformation. Nanocomposites with conducting fillers ($K > 1000$) are thus considered to increase dielectric constant, which is usually maximized near percolation threshold [15–17]. However, an introduction of the conducting filler near percolation threshold inevitably leads to an increase of elastic modulus, even at the presence of 1 wt% conducting fillers. In accordance with the electromechanical mechanisms, elastic modulus can influence the field-induced strain in a deprecating manner. Zhang et al. reported electrostriction-driven electromechanical performance of PVDF-TrFE composites with copper-phthalocyanine (CuPc) (40 wt%), which showed 23-times enhanced the field related electrostrictive coefficient (M, $113.0 \times 10^{-4}\ \mu\mathrm{m}^2\ \mathrm{V}^{-2}$) in comparison to that of pristine PVDF-TrFE ($4.9 \times 10^{-4}\ \mu\mathrm{m}^2\ \mathrm{V}^{-2}$). However, such high quantity of the conductive filler could lead to many drawbacks involving an increase of elastic modulus (from 400 MPa to 750 MPa) and a decrease of breakdown strength (ca. $10\ \mathrm{V}\ \mu\mathrm{m}^{-1}$) because of low-quality composites originated from a poor dispersion of the conducting filler [10]. Gong et al. also reported that ca. 50-times enhanced electromechanical properties based on the field related electrostrictive coefficient with poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (PVDF-TrFE-CFE) terpolymer composite with chemically modified graphene ($77.5 \times 10^{-4}\ \mu\mathrm{m}^2\ \mathrm{V}^{-2}$) in comparison to that of PVDF-TrFE-CFE ($1.5 \times 10^{-4}\ \mu\mathrm{m}^2\ \mathrm{V}^{-2}$), which also led to a large increase of elastic modulus by more than 9-times in comparison to pristine PVDF-TrFE-CFE terpolymer [18]. In general, if these two aforementioned composites exhibit the percolation phenomena at lower conductive filler quantity, we can easily assume that much larger electromechanical strain will be obtained because of the elastic modulus effects on the electrostatic strain. For this, the percolated nanocomposites should be made with the low quantity of conducting fillers (<0.1 wt%).

Herein, we demonstrate highly enhanced electromechanical properties using ultra-low percolated polymer composites (0.05 wt %) containing the crystalline PVDF-TrFE copolymer matrix and P3HT-PMMA block copolymer coated single-wall carbon nanotube conducting filler (TMSWCNT). Obtained PVDF-TrFE/TMSWCNT (PTMCNT) composites showed excellent dispersion stability of single-wall carbon nanotube (SWCNT) both in solution and in film states by the aid of the P3HT-PMMA block copolymer compatibilizer because the P3HT block segment strongly interacted with SWCNT through π-π stacking interaction, and the other PMMA block segment was highly compatible with PVDF-TrFE through hydrogen bonding interaction [7,17]. Obtained PTMCNT composites with 0.05 wt% of TMSWCNT exhibited a large increase in dielectric constant by 8-times (76.3 at 10 Hz) in comparison to that of pristine PVDF-TrFE (9.6 at 10 Hz) with a great benefit of close elastic modulus (540 MPa) to pristine PVDF-TrFE (450 MPa), which is proper to higher electromechanical performance. In addition, the PTMCNT composites dominantly showed all-trans polar crystalline phase (74.2%) than that of PVDF-TrFE (64.5%). Based on the aforementioned properties of PTMCNT composites provided the highly enhanced electromechanical performance, exhibiting 5.1% of electromechanical strain and $0.84\ \mathrm{J\ cm}^{-3}$ of elastic energy density at $50\ \mathrm{V_{pp}}\ \mu\mathrm{m}^{-1}$. As comparing with pristine PVDF-TrFE, these results indicated substantial enhancement about a 50 times increase for electromechanical strain and more than 3000 times increase for elastic energy density. Furthermore, its electrical-to-mechanical energy conversion exhibited 460 times increase at $50\ \mathrm{V_{pp}}\ \mu\mathrm{m}^{-1}$ in comparison to that of the pristine PVDF-TrFE.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich and used without purification process unless mentioned otherwise. P3HT-PMMA block copolymer was prepared by using reported synthetic method [19–22]. Single-wall carbon nanotubes (SWCNT) (ASP-100F) was purchased from Hanwha chemical of Korea, and PVDF-TrFE (70/30 mol%) was purchased from Solvay Solexis of Belgium, and used them as received.

2.2. Preparation of TMSWCNT

The P3HT-PMMA block copolymer coated SWCNT (P3HT-b-PMMA to SWCNT = 1:1 mass ratio) was prepared following the modified our previous report [23]: 10 mg of P3HT-b-PMMA ($M_\mathrm{n} = 24{,}000$, PDI = 1.25, 68 wt% of PMMA) was dissolved in 100 mL of chloroform for an hour, and 5 mg of SWCNTs was dispersed by mixing with prepared P3HT-b-PMMA solution, followed 30 min of sonication. In order to achieve fully P3HT-b-PMMA coated SWCNTs, the solution was retained with stirring for 12 h. Thereafter, several times centrifugation with chloroform was performed to remove the non-reacted SWCNTs, and then took the solution part. Thereafter, 100 mL of chloroform was added the solution for dilution. The free P3HT-b-PMMA was removed by simple filtration with chloroform rinsing to give solid TMSWCNT.

2.3. Preparation of the PTMCNT composite film

The obtained TMSWCNT was applied for composite with PVDF-TrFE matrix. TMSWCNT (10 mg) and PVDF-TrFE (5 g) were dispersed in THF with mild stirring at 50 °C for overnight, followed by gentle sonication for 10 min before precipitation. The well dispersed solution was slowly poured into the methanol, and then obtained precipitates were dried at 50 °C for 48 h, yielding a PTMCNT composite. The PTMCNT composite films were prepared by applying the solution-casting process for the investigation of the electromechanical studies. 3 wt% solution of the PTMCNT composite in THF was prepared with stirring for overnight and followed by sequential sonication for 10 min before casting. Thereafter, the clear solution was poured onto the Teflon dish, and then dried at room temperature for overnight. The resulting films were dried again under vacuum at room temperature for an hour. Thereafter, gold electrodes were coated on the both surface of the film by using gold sputter about 20 nm in a thickness.

2.4. Preparation of PCNT and PTM composite films

PVDF-TrFE/SWCNT (PCNT) and PVDF-TrFE/P3HT-*b*-PMMA (PTM) reference polymer composites were prepared following the coagulation method. 5 g of PVDF-TrFE was dissolved in 100 mL of THF involving 5 mg of SWCNT or 5 mg of P3HT-*b*-PMMA with sonication for an hour. As-prepared mixture solution was then rapidly poured into water, and thereafter the filtrated precipitates