

Acoustic Performance Enhancement in PVDF Speakers by Using Buckled Nanospring Carbon Nanotubes

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Abstract

A polyvinylidene fluoride (PVDF)-based film speaker is successfully fabricated with enhanced bass sound by incorporating buckled nanospring carbon nanotubes (NS-CNTs) as fillers. Various concentrations up to 1–7 wt% of uniformly dispersed buckled NS-CNTs are loaded to increase the beta (β)-phase fraction, crystallinity, and dielectric constant of the speaker, and this results in the bass part enhancement of about 19 dB full scale (dBFS) at 7 wt% filler loading of the piezoelectric film speaker.

Keywords: NS-CNTs, PVDF, acoustic performance, dielectric constant, dB full scale sensors

1. INTRODUCTION

As the demand for wearable devices is increasing, a large amount of research has been devoted to making electronic devices that are flexible, small, and lightweight. A conventional speaker is a dynamic speaker that operates from the interaction of the magnetic field of a permanent magnet and a voice coil. Although this type of speaker is widely used, its use is limited due to its weight, thickness, and rigidity. Thus, a new type of speaker that is light, thin, and flexible is required. One of the notable alternatives could be a piezoelectric film speaker, which can be made from a piezoelectric material with a thickness less than a few hundred μm , unlike the dynamic speaker that is thicker than 3 mm. In addition, unlike inorganic piezoelectric materials that have limited applications due to their brittleness and difficulty in processing to be used as flexible devices, organic piezoelectric polymers such as

polyvinylidene fluoride (PVDF) could be a good candidate. PVDF is a semicrystalline polymer consisting of the $-(\text{CH}_2\text{CF}_2)_n-$ repeating unit. Piezoelectricity in PVDF is caused by the changes in the dipole density in the polymer chain. The phases PVDF can form into depending on the chain configuration are the alpha (α), beta (β), and gamma (γ) phases [1]. Among these, the β -phase is the most useful due to its excellent piezoelectric and pyroelectric properties. These properties are attributed to the “all-trans (TTTT)” conformation. As the electronegative fluorine atoms are arranged in one direction, the β -phase shows the highest net dipole moment and hence a high piezoelectric property. PVDF in the β phase can be obtained from the α -phase by applying the mechanical drawing or electrical poling processes. Although film speakers have many advantages, poor acoustic performance in the low-frequency region is considered its main drawback. In order to overcome this problem, studies have been conducted to enhance the piezoelectric properties by increasing the polar β -phase content in PVDF. This results in the increase of strain in the thickness direction of the film and thus increases the sound pressure level in the entire frequency region. Polymer nanocomposites demonstrate great potential in this regard. Incorporation of various nanofillers into PVDF films that demonstrated higher β -phase content and dielectric properties have been reported, such as palladium nanoparticles [2], copper oxide nanoparticles [3], Fe-doped reduced graphene oxide [4], nanoclay [5], Ba-doped SiO_2 - TiO_2 hollow nanoparticles (Ba-HNPs) [6], urchin-like ZnO [7]. In this study, easily dispersible buckled nanospring carbon nanotubes (NS-CNTs) were loaded as nanofillers to enhance the acoustic performance of PVDF. In our previous work, easily dispersible NS-CNTs smaller than 30 nm

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were obtained and they showed a 492% increase in the relative dielectric constant (K) compared with that of pristine poly(vinylidene fluoride–trifluoroethylene) [P(VDF-TrFE)] with only a small dielectric loss tangent (D) of 0.06 [8,9]. Based on these excellent dielectric properties and the high dispersibility of NS-CNTs, the effect of adding nanofillers into the PVDF matrix was analyzed. In particular, the dielectric constant, β -phase fraction, and crystallinity were examined to investigate their effect on the acoustic characteristics.

2. EXPERIMENTAL

The synthesis process of NS-CNTs is illustrated in Fig. 1a. Firstly, linear single-walled carbon nanotubes (SWCNTs) were functionalized through acid treatment. After 12 h of ultrasonification, they were reacted with zinc acetate dihydrate, which was used as a template to make the NS-CNTs (Fig. 1a transmission electron microscopy (TEM) image). Subsequently, the inner zinc oxide nanoparticles were dissolved in HCl. Pristine PVDF thin films were made by the drop-casting method. PVDF and NS-CNTs were dissolved in DMF by stirring at 85 °C for 1 h to make composites. The solution was poured into a 5×5 cm glass substrate to make a free-standing film. The resulting composite was dried in a conventional oven for 5 h. The electrical

poling process was then conducted by applying a high DC voltage of 41 MV/m for 1 h in a heated silicon oil bath (ESI). Photographs of the fabricated nanocomposite films are shown in Fig. 1b. In order to deposit the electrodes of the piezoelectric speaker, silver paste was diluted in isopropyl alcohol and then spin-coated on the front and rear side of a film. Copper tapes were attached to the edges of the film to be used as contact electrodes.

As shown in Fig. 1c, the sound signal was delivered to an amplifier that had a 9 V battery as its power supply. The signal was delivered to the contact electrode attached on both sides of the film.

3. RESULTS AND DISCUSSIONS

Fig. 2a shows the dielectric constant (K) and the dielectric loss (D) values of the NS-CNTs/PVDF nanocomposites. The main problem of film speakers is poor acoustic performance in the bass region, which can be described using the dielectric permittivity spectrum as a function of frequency. The audible frequency range for humans is 20 Hz–20 kHz and shows the high dielectric loss value in the frequency range. The strain in the film thickness of the polymer film loudspeaker is described through the equation [10]

$$S = \frac{\epsilon_r \epsilon_0 E^2}{Y} = \frac{\epsilon_r \epsilon_0 V^2}{h^2 Y} \quad (1)$$

where s is the strain in thickness, Y is the elastic modulus of the polymer film, E is the strength of the electric field, ϵ_r is the relative dielectric constant of the polymer, ϵ_0 is the dielectric constant in a vacuum, h is the film thickness, and V is the applied voltage. As Equation (1) shows, achieving a high dielectric constant to increase the strain of the film is advantageous. Therefore, the relative dielectric constant and loss value of the fabricated NS-CNTs/PVDF films were measured at various filler contents. As shown in Fig. 2a, a bare PVDF film had a relative dielectric constant (K) of 1.84 at 1 kHz. As the relative weight content of NS-CNTs increased from 1 to 11 wt%, the K at 1 kHz showed a gradual increase, and after reaching a maximum value of $K = 3.58$ for 7 wt%, it decreased to $K = 2.91$ at 9 wt%. The increase in the dielectric constant in the NS-CNTs-incorporated PVDF films can be explained using the minicapacitor principle that has been reported [11,12]. Added fillers are assumed to act as nanoelectrodes and are separated by a polymer matrix that can be regarded as a nanocapacitor. A large number of distributed nanocapacitors enhances the dielectric constant of the polymer

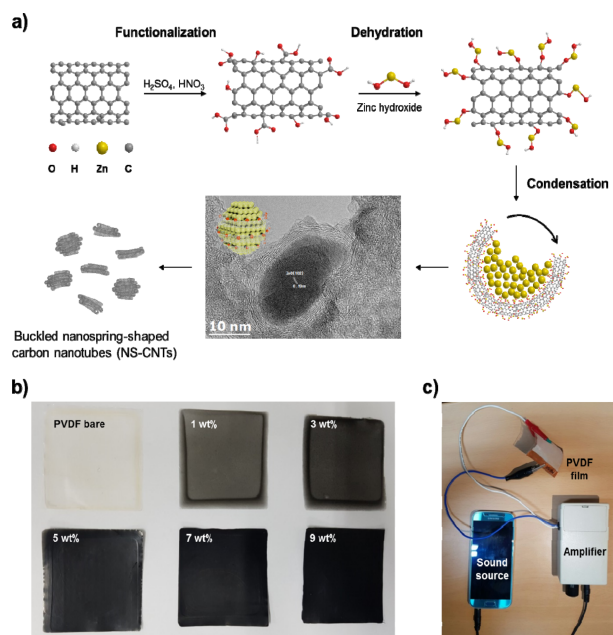


Fig. 1. (a) Synthesis process of NS-CNTs (b) photographic image of fabricated PVDF films with various concentrations of fillers (c) photographic image of PVDF film speaker and its set up to make it work.

nanocomposites with increased concentration of the nanofiller. In addition to this, a high dielectric constant was obtained because of homogenous dispersion of the NS-CNTs, which makes them difficult to be broken down. Regardless of the filler content, the dielectric constants decreased as the frequency increased. This can be interpreted as the lag of the dipole moment of the electric field at the higher frequencies. In the view of the molecular structure, molecular dipoles cannot be exactly oriented to follow the applied electric field at high frequencies. The dielectric loss values for various filler amounts are shown in the right y-axis of Fig. 2a. The loss value at 1 kHz was 0.005 for the pristine PVDF and showed similar or lower values until 5 wt% filler was added. Although it rapidly increased with the addition of 7 wt% NS-CNTs to 0.06, this value is also lower than 0.1, which is acceptable. A conclusion can be made that the fraction of the aggregated fillers was very small, unlike in the linear CNTs. The dielectric loss value showed an increase in lower frequencies near 100 Hz as well as at the high frequency of 1 MHz. Increasing the dielectric loss values near 100 Hz is attributed to the Maxwell-Wagner-Sillars (MWS) effect [13] and this is a feature of many crystalline polymers. MWS relaxation is caused by trapped charges at the interface between the insulator and conductor. The increase in dielectric loss at higher frequencies near 1 MHz is due to the Brownian cooperative segmental motion of the chain backbone [13,14]. As a result, the data indicate that the introduction of fillers enhanced the dielectric constant approximately twice while keeping the dielectric loss value low.

Another important factor in enhancing the acoustic property of piezoelectric polymer film speakers is the crystalline phase fraction, which was analyzed using Fourier transform infrared (FT-IR) spectroscopy and differential scanning calorimetry (DSC). Generally, different crystalline phases of PVDF display different vibration modes, which are reflected in FT-IR spectra. The absorption peaks at 764 cm^{-1} (CF_2 bending and skeletal bending), 796 cm^{-1} and 976 cm^{-1} (CH_2 rocking), and 1383 cm^{-1} are assigned to the α -phase; peaks at 840 cm^{-1} (CH_2 rocking, CF_2 stretching, and skeletal C-C stretching) and 1275 cm^{-1} correspond to the β -phase of the PVDF [15]. As Fig. 2b shows, the α -phase absorption peak at 764 cm^{-1} gradually decreased as the amount of filler increased, and the relative intensity of the β - and α -phase (I_β/I_α) ratio showed a maximum value of 6.52 at 5 wt%, that is, a 38% enhancement compared with that of the bare PVDF. When another filler amount was added, the peak corresponding to the α -phase increased again, leading to a I_β/I_α ratio of 3.89 at 11 wt% filler content. The calculated relative percentage of the β -phase ($F(\beta)$) using the Lambert-Beer law also indicated that the pristine

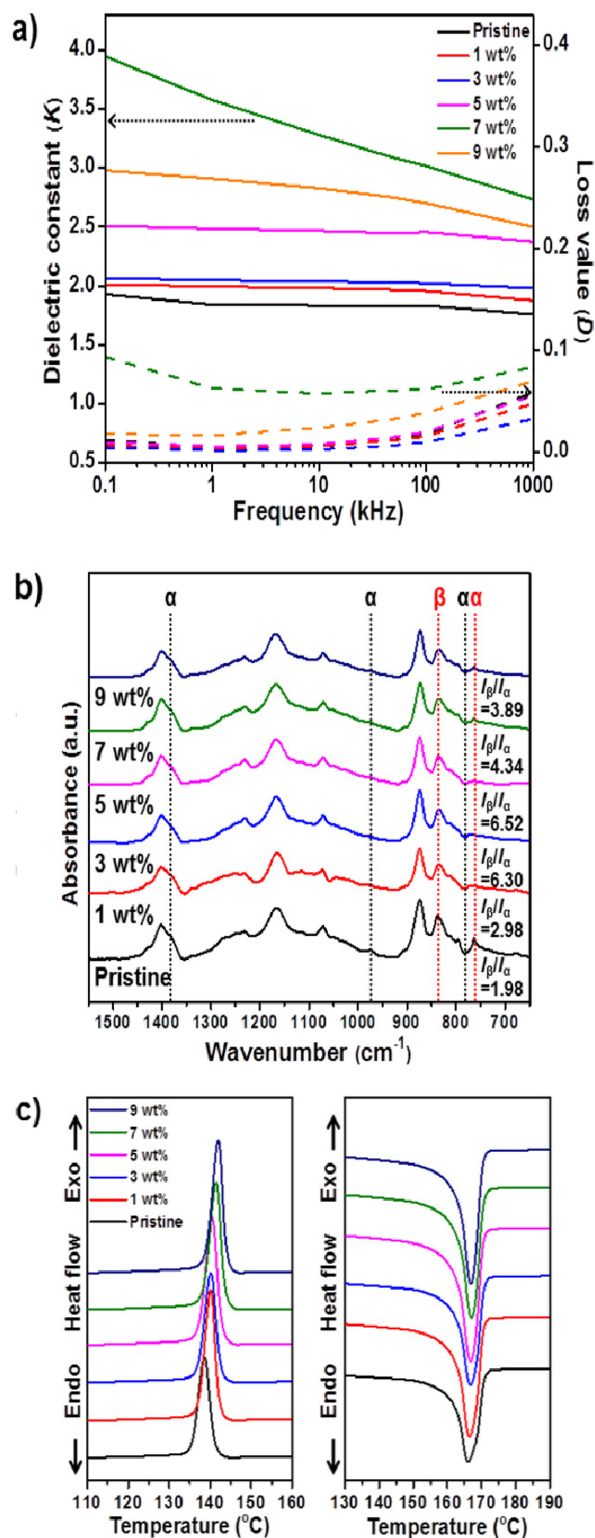


Fig. 2. (a) Dielectric constant (K) (left y-axis) dependence of NS-CNTs/PVDF nanocomposites and dielectric loss value (D) (right y-axis) with different filler contents on the frequency at room temperature. (b) The crystalline phase fraction which was analyzed by Fourier transform infrared (FT-IR) spectra and differential scanning calorimetry (DSC). (c) Crystallization temperature (left) and melting temperature (right) of filler loaded films from DSC data.

PVDF film showed the lowest value of 61%.

On the other hand, only an additional 1 wt% of filler increased the relative fraction of the β -phase to 70%, and with 5 wt% loading of the filler showed the highest value of 84% (ESI†). The piezoelectric property of the polymer nanocomposite was influenced by both the formation of the polar phase and the crystalline phase. The crystallinity of the nanocomposite film was confirmed using DSC. As shown in Fig. 2c, the crystallization temperature as well as the melting temperature shifted together to a higher temperature as the amount of loaded NS-CNTs increased. While the pristine PVDF showed a crystallization temperature (T_c) of 138.6 °C, it increased to 142.0 °C with the filler content of 9 wt%. Additionally, the melting point (T_m) showed a similar tendency, with a value of 166.0 °C for the pristine PVDF and 166.9 °C for 9 wt% NS-CNTs filler content. This indicates that the dispersed fillers act as a nucleating agent and they interrupt the segmental motion of the polymer chains that enhance the T_c and T_m of the polymer nanocomposites.

As NS-CNTs are added as fillers, their large surface area allows more PVDF molecules to be chemically adsorbed and this results in an increased crystallization temperature [4,16]. The possible mechanism for the increased β fraction can be explained by the interactions between the nanofiller and PVDF and the dispersibility of the fillers, which are consistent with a previous report by Ke *et al.* [17]. Because fluorine atoms in PVDF show a higher electronegativity compared with carbon and hydrogen atoms, they are highly electrophilic to sufficiently interact with the π electrons on the surface of the CNTs. This causes PVDF chains to form TT conformations. Furthermore, the functional groups remaining on the walls of the CNTs from the NS-CNTs synthesis process form hydrogen bonds with the fluorine atom of PVDF, which also help in the formation of the β -phase, as illustrated in Fig. 3a. In addition, good dispersibility allows more PVDF chains to be well adsorbed onto the surface of the CNTs and form a higher fraction of the β -phase. Because the adsorption energy of chains with the α -phase conformation (trans-gauche, TGTG') is much lower than for the β -phase conformation (all trans, TTTT), and the thermal stability of the α -phase is higher, the α -phase is frequently and easily formed after cooling from the melt state. Hence, the addition of nanofillers and the improved dispersibility can provide a much more effective surface area to align the PVDF, which results in the higher amount of the β -phase fraction as shown in Fig. 3b.

The fabricated film speaker was fixed to a baffle plate of 30 × 30 cm for measurement. The speaker and baffle plate were installed in a portable soundproofed box to avoid noise. A high

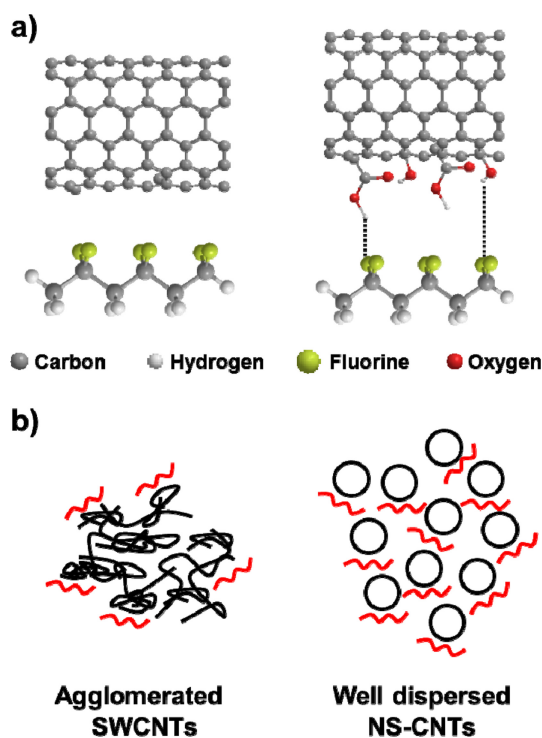


Fig. 3. (a) The scheme showing the role of NS-CNTs on the β phase formation in PVDF matrix. (b) Different dispersion of between agglomerated SWCNTs and NS-CNTs in the PVDF matrix. Red lines in (b) indicate the adsorbed PVDF chains on the surface of CNTs.

definition measurement microphone (M30 Earthworks, USA) was placed at a distance of 3 cm from the speaker. The dScope Series III (Prism Sound Co., UK) audio analyzer was used to analyze the acoustic performance from 20 Hz to 20 kHz. The film speaker and microphone were connected to the audio analyzer as shown in Fig. 4a. The acoustic performance of the film speaker at various weight percentages of NS-CNT is represented in Fig. 4b. The frequency response data confirmed that the acoustic characteristics were enhanced as the filler content increased compared with the pristine lab-prepared PVDF film. In particular, an approximately 19 dB full scale (dBFS) increase was observed in the low bass region as well as in the midrange and treble regions with the 5 wt% filler content. As the β -phase and crystallinity demonstrated a tendency to increase with increased filler content, the acoustic characteristics also improved evenly in both bass and treble regions.

The addition of 7 wt% filler showed the better bass performance, as could be observed through the high crystallinity and dielectric properties, but the frequency response of the middle and treble ranges decreased due to the decrease in the relative ratio of the β -phase. The lower frequency response of the lab-made film

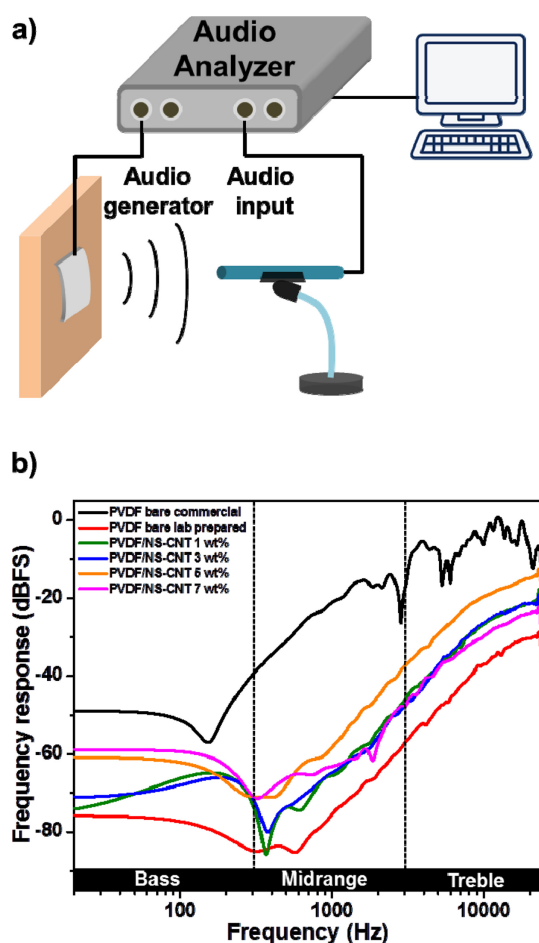


Fig. 4. (a) Schematic illustration of acoustic performance measurement setup (b) Frequency responses of NS-CNTs loaded PVDF thin film speakers at different weight percent of fillers.

compared with that of the commercial film was because the lab-made PVDF films had a lower density. PVDF films that are cast from *N,N*-dimethylformamide (DMF) easily form porous structures due to the water vapor from humidified air [18].

4. CONCLUSIONS

The effect of NS-CNTs in PVDF films on the sound pressure characteristics was demonstrated by varying the content of the filler. Enhanced acoustic performances of filler-added PVDF thin films were correlated to the improved dielectric constant, loss value, enhanced fraction of the β -phase, and the high degree of crystallinity. The highest improvement of the bass region was observed at approximately 19 dBFS at 7 wt% filler loading due to the greatly improved dielectric constant and loss characteristics. The addition of 5 wt% filler demonstrated improved acoustic

characteristics in the overall frequency region, caused by the high crystallinity, β -phase fraction, and dielectric constant. However, the improvement of the β -phase is the most important factor, as it increased the acoustic performance. The linear shape of the carbon nanotubes improves the β -phase of PVDF, but NS-CNT has structural difficulties to improve the β -phase. Additionally, the comparison of PVDF and PVDF-TrFE showed that PVDF-TrFE contains relatively high amounts of hydrogen. Therefore, hydrogen interacting with the oxygen of the PVP that surrounds the surface of NS-CNTs enhances the dispersibility of the films. As a consequence, the conclusion is that the enhanced dBFS in NS-CNTs/PVDF hybrid films was largely influenced by the crystallinity and relative fraction of the β -phase.

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