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Development of Stretchable PZT/PDMS Nanocomposite Film with CNT Electrode

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Abstract

The piezoelectric composite film of ferroelectric PZT ceramic ($PbZr_xTi_{1-x}O_3$) and polymer (PDMS, Polydimethylsiloxane) was prepared to improve the flexibility of piezoelectric material. The bar coating method was applied to fabricate flexible nanocomposite film with large surface area by low cost process. In the case of using metal electrode on the composite film, although there is no problem by bending process, the electrode is usually broken away from the film by stretching process. However, the well-attached, flexible CNT electrode on PZT/PDMS film improved flexibility, especially stretchability. PZT particles was usually settled down into polymer matrix due to gravity of the weighty particle, so to improve the dispersion of PZT powder in polymer matrix, small amount of additives (CNT powder, Carbon nanotube powder) was physically mixed with the matrix. By stretching the film, an output voltage of PZT(70 wt%)/PDMS with CNT (0.5 wt%) was measured.

Keywords : Flexible piezoelectric film, PZT, PDMS, CNT

1. INTRODUCTION

As a typical piezoelectric material, polycrystalline lead zirconate titanate (PZT, $PbZr_xTi_{1-x}O_3$) has been generally used since it was reported by Shirane and Suzukiin in 1952 [1]. PZT ceramics is becoming increasingly important, particularly in the field of sensors, actuators and nanogenerators, due to their outstanding piezoelectric and pyroelectric characteristics and their high dielectric constants [2]. However they were not only heavy and brittle, but also required expensive fabrication processes [3]. In the case of piezoelectric polymers such as poly (vinylidene fluoride) (PVDF), although they were flexible and tough materials with low mechanical impedance, critical problems of their long-term use were observed in various devices, because of their low and thermally unstable piezoelectric properties [4-6]. In this reason, many researchers have reported fabrication paper related on nanocomposite of piezoelectric ceramic and flexible polymer [7-10]. These approaches seem to be contribution to preparing high functional materials with both advantages induced from piezoelectric ceramic and flexible polymer.

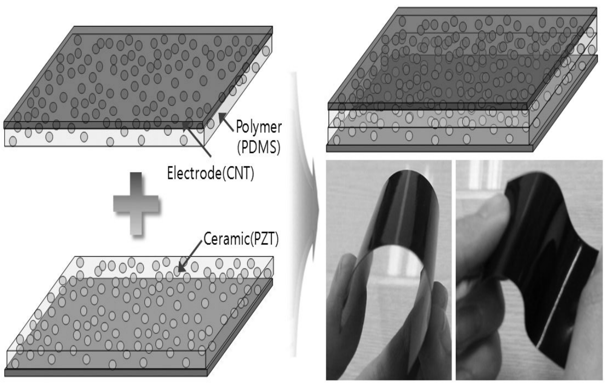

Fig. 1. Schematic diagram of the process for fabricating stretchable PZT/PDMS nanocomposite film and photograph of the flexible film.

Herein, the piezoelectric composite film of ferroelectric PZT ceramic and flexible polymer (PDMS, Polydimethylsiloxane) was prepared by bar coating method, and flexible CNT (Carbon nanotube) electrode was applied to the film. These stretchable nanocomposite films were fabricated with large surface area by bar coating method (low cost process), and had the improved characteristic of flexibility, especially stretchability, by

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applying CNT electrodes. The dispersion of PZT in polymer matrix was controlled by the amount of PZT and by adding small amount of additives. The generated voltage was obtained by applying a stretching impact to the nanocomposite films.

2. EXPERIMENTAL

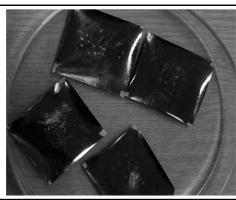
For preparation of electrode layer, CNT paste (Multi wall CNT, Applied Carbon Nano Technology Co.) was coated in polyimide film by bar coater, and cured at 100℃ for 1 hr. PDMS (Sylgard 184, Dow corning) and PZT powder (Sunnytec co., P-5H) were physically mixed with vigorous stirring for 1 hr, and applied on the CNT electrode with bar coater, and cured at 70℃ for 10 min in an oven. One quasi polymerized PZT/PDMS film on CNT electrode was placed in uniform contact with another quasi polymerized PZT/PDMS film on CNT electrode and fully polymerized at 100℃ for 1 hr under pressure. After polymerization, polyimide film was removed in PZT/PDMS nanocomposite film with CNT electrodes, and then the PZT/PDMS film was poled at 100℃ by applying an electric field of 5 V/mm for 1 hr, and aged for at room temperature 24 hr.

The structural properties of the nanocomposite film were analyzed by field-emission scanning electron microscope (FE-SEM; Jeol JSM-6700F). The PZT/PDMS composite film was cut in appropriated size (1 cm × 3 cm), and output voltage of the film was measured by oscilloscope (Teledyne LeCroy, WaveJet 322) depending on stretching the film by hand.

3. RESULTS AND DISCUSSIONS

Stretchable PZT/PDMS nanocomposite film with CNT electrodes in both sides was fabricated by uniform contact of two semi PZT/PDMS films with CNT electrode, as shown in Fig. 1. The bar coating method made a significant contribution to fabrication of this nanocomposite film with large surface area by a low cost process. In the case of using the metal electrode on the composite film, although there was no problem by bending process, the electrode was usually broken away from the film by stretching process. In the Table 1, various kinds of electrodes were applied to nanocomposite film by various methods. In the case of Ag paste drying at room temperature, there were advantages such as simple preparation process and low resistance, but there was also the critical problem of easy detachment from the film. The adhesive property of electrode and PZT/PDMS film was improved by Al or Ni sputtering, and there were not only benefits of low resistance and good bendability, but also drawback of poor stretchability. Even though resistance of the CNT electrode was little bit higher than that of metal electrodes, the CNT electrode had the outstanding merits of stretchability and good adhesion with the film. A well-attached CNT electrode on PZT/PDMS film seems to be a required condition for manufacturing flexible film, especially stretchable film. In the case of coating top CNT electrode layer on fully polymerized PZT/PDMS film with bottom CNT electrode layer, top CNT electrode layer was easily separated from the PZT/PDMS. The adhesion between the both CNT electrode layers and PZT/PDMS film was drastically improved by uniform contact of two semi

Table. 1. Preparation process and characteristics of various electrodes applied to PZT/PDMS film

Ag paste	Al	Ni	CNT
			
After applying, drying (room temperature, 1 hr)	Sputtering (5.0×10^{-6}Torr, Ar 30 sccm, 200 W, 2 hr, room temperature)	Sputtering (5.0×10^{-6}Torr, Ar 30 sccm, 200 W, 2 hr, room temperature)	After bar coating, drying (100℃ 1 hr)
Resistance: 1~2 Ω	Resistance: 1~4 Ω	Resistance: 10~35 Ω	Resistance: 600~800 Ω
Break-away from composite film	Good adhesiveness, Poor stretchability	Good adhesiveness, Poor stretchability	Good adhesiveness, Good stretchability

PZT/PDMS films with CNT electrode. As PDMS monomer was gradually polymerized, the PZT/PDMS composites strongly adhered to the surface of the CNT electrode film. The CNT electrode film thickness was about 40 ㎛, and the total thickness of the stretchable nanocomposite film was about 200~500 ㎛.

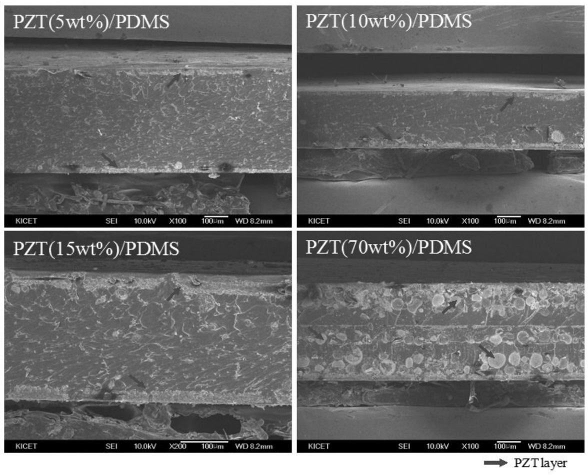


Fig. 2. SEM images of PZT/PDMS nanocomposite film with various weight ratio of PZT.

Fig. 2 indicated that the cross sectional images of PZT/PDMS film with various amount of PZT. In the case of small amount of PZT in PDMS matrix, the effect seems to be similar to the PZT bulk sample with low density, and it is difficult to expect good piezoelectric performance. In this reason, it was necessary to grow the amount of PZT powder for high performance. Furthermore, PZT powder was observed near the CNT electrode surface, because PZT particles were usually settled down in polymer matrix due to gravity of the weighty particle. This phenomenon seems to be a major cause of poor piezoelectric performance. To improve the dispersion of PZT powder in polymer matrix, small amount of additives (CNT powder) was physically mixed with the PZT/PDMS nanocomposite matrix. It is possible that CNT powder contribute to resistance to precipitation of PZT particle, as shown in Fig 3. Park et. al. reported that the $BaTiO_3$ nanoparticles can be well distributed by forming a complex mixture with CNT networks, and calculation results of the piezopotential distribution of the aggregated nanoparticle model show that the piezopotential of the aggregated nanoparticle model is inferior to that of a well-distributed nanoparticle model [10]. The SEM images of Fig. 3 support that one of CNT additives roles in the PZT/PDMS composites is improving the dispersion of PZT powder in polymer matrix.

Output voltage was measured when PZT (70 wt%)/PDMS film and PZT (70 wt%)/PDMS film with CNT (0.5 wt%) were stretched by hand, as shown in Fig 4. The voltage generated by stretching reached 0.82 V and 0.91 V when a larger impact was applied to the nanocomposite film. This was induced by piezoelectric effect driven transient flow of electrons under the external stimulus. The greater the stretchable impact applied to the film, the higher the output voltage generated. The nanocomposite film with better PZT dispersion due to addition of a small amount of CNT, had better piezoelectric characteristic.

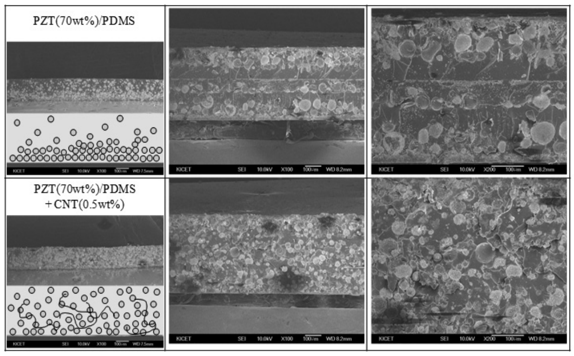


Fig. 3. Dispersion control of PZT in PDMS matrix by adding CNT.

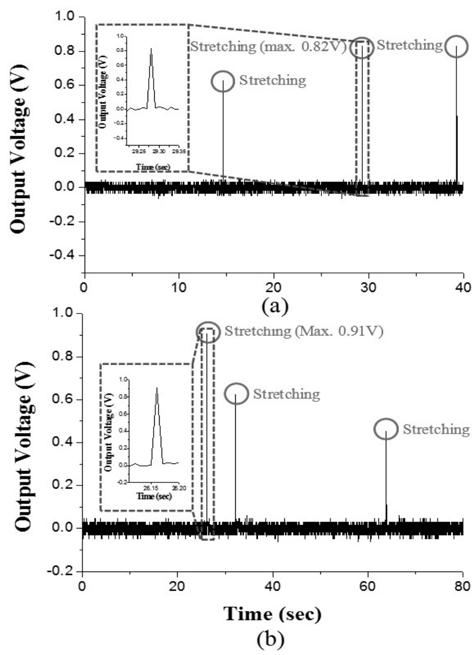


Fig. 4. Output voltage of stretching (a) PZT (70 wt%)/PDMS film and (b) PZT (70 wt%)/PDMS film with CNT (0.5 wt%).

4. CONCLUSIONS

Stretchable piezoelectric film can be achieved by applying CNT electrodes onto a nanocomposite film of ferroelectric PZT ceramic and flexible polymer (PDMS). The bar coating method, a low cost process, contributed to successful fabrication of a stretchable nanocomposite film with large surface area. The CNT electrode is a top candidate for electrodes, due to better adhesiveness and stretchability. The precipitation phenomena of PZT particles in the polymer matrix due to gravity of the weighty particle are improved by adding small amount of additives (CNT). The output voltage of PZT (70 wt%)/PDMS with CNT (0.5 wt%) created by stretching process can be increased to at least 0.91 V by applying a larger impact to the nanocomposite films.

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