博　士　論　文　の　内　容　の　要　旨

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論文題目	Research on nanofiber-based multifunctional composites with shape memory and piezoelectric effects for energy harvesting (形状記憶と圧電効果を有するエネルギー収集用多機能ナノファイバーコンポジットに関する研究)

(博士論文の内容の要旨)

Smart piezoelectric and shape memory materials are widely used in many fields such as sensing, energy harvesting, automobile, aerospace and health monitoring. In recent years, both piezoelectric materials and shape memory polymer-based composites have attracted increasing attention owing to the favorable shape memory and piezoelectric effects. Among these applications, the popularity of flexible energy harvesters receives extensive investigation because of their high flexibility, which enables them to be applied in wearable and implantable devices. Flexibility and functionality are key issues for their applications. However, most reported flexible composites only exhibit one kind of smart performance, and there are few reports on flexible multifunctional nanofibers for energy harvesting. Herein, multifunctional nanofibers from lead zirconate titanate (PZT) particles and shape memory polyurethane (SMPU) are prepared by electrospinning and melt spinning in this study. The developed nanofibers have shown both piezoelectric and shape memory effects, and their potential applications in sensing and energy harvesting were investigated.

PZT particles were modified by the silane coupling agent to improve the dispersity in the SMPU matrix and the interfacial bonding. Through the observation on surface morphology, it was demonstrated that the silane coupling agent was coated on the surface of PZT particles, significantly increasing the dispersion effect of PZT fillers in the SMPU polymer matrix. Compared with the unmodified random nanofiber, the modified nanofiber appeared great enhancement of mechanical properties caused by higher dispersion effect of PZT particles in tensile strength (increased by at least 9.36%), yield stress (growing by at least 5.47%) and break strain (rising by at least 5.03%). The shape recovery rates of developed nanofibers were all above 84% in the first cycle and over 95% in the third cycle, even under the condition that the PZT content reached up to 80 wt%. Additionally, the modification also helped transfer the stress to PZT particles, more efficiently, through the improvement of the interface, leading to stress growing and higher voltage. The output voltage of the modified 80wt% PZT/SMPU random nanofibers reached 120.3 mV, the maximum value.

Although a large number of nanofiber-based shape memory composites as well as energy harvesters have been reported, there is still no report related to the influence of alignment degree on mechanical property, shape memory and energy harvesting. In order to understand the mechanism of how the alignment angle of nanofibers affected the shape memory behavior, the alignment degree of nanofibers got controlled and designed as 0°, 45° and 90°. The dynamic mechanical analysis and the thermo-mechanical analysis were carried out below and above glass transition temperature (Tg). They disclosed that, above Tg, the higher volume of nanofibers along the tensile direction enhanced the elastic modulus of aligned nanofibers and stored more energy during deformation, further influencing shape recovery and fixity ratio. The aligned SMPU nanofibers with 0° alignment degree achieved the obvious improvement of shape recovery stress (increased by 728%) and shape recovery rate (increased by 2.5%) under the comparison with the random SMPU nanofiber. The similar phenomenon was also found in the test of energy harvesting. The output voltage generated by the PZT/SMPU

based energy harvester was proportional to the increment of acceleration, displacement and frequency. By changing the nanofiber alignment degree in the aligned PZT/SMPU nanofiber, P/S-0 (with a nanofiber direction parallel to the strain direction) was able to generate 421 mV voltage at the displacement of 10 μm, increasing by 5.4 times than that of the random nanofibers based energy harvester. Taking advantage of the shape memory effect, it was capable of deforming the PZT/SMPU energy harvester into various curved shapes in order to match complex structures while the harvester maintained its original piezoelectric characteristics, consequently enhancing energy harvesting from curved surfaces. This advantage helped the SMPU based energy harvester firmly match the complex structures and prevent debonding between the harvester and curved surfaces, followed by more effective energy harvesting. The pre-deformed energy harvester with a curved shape generated an output voltage of 84.3 mV, 3.21 times as high as that of the non-pre-deformed energy harvester.

Through the optimization of the alignment angle of nanofibers, aligned PZT/SMPU nanofibers could be used as wearable device to improve the efficiency of energy harvesting from different types of body movement, including bending, twisting and applying pressure. These types of human movement induced mechanical vibration from different directions. The aligned PZT/SMPU nanofibers based wearable device exhibited various output voltages, responding to the mechanical vibration from different directions. The PZT/SMPU energy harvester with 0°, 45° and 90° alignment degrees generated output voltages as high as 23 mV, 55 mV and 36 mV, respectively, during twisting motion, but reached 537 mV, 231 mV and 78 mV, respectively, during bending motion. These results provided insights and methods for the optimal arrangement of nanofibers in wearable device, which facilitated the efficiency improvement of energy harvesting from the movement of different body parts.