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学位論文題目	Research on development of smart nanocomposites with shape memory and piezoelectric effects （形状記憶と圧電効果を有するスマートナノ複合材料の創製に関する研究）
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論 文 内 容 の 要 旨

Piezoelectric materials and shape memory materials are the two classes of smart materials widely used in different fields such as aerospace, medical care, automobile and daily necessities. Over recent decades, their composites extra attract many researchers' attentions because the material performances are able to be remarkably improved by combining fillers and matrices, and the synthesis and applications of the composites have made great progress. However, the composites just have only one kind of smart effect, piezoelectricity or shape memory property. Here, we introduce a group of smart composites consisting of lead zirconate titanate (PZT) particles with the average diameters of 400 nm and shape memory polyurethane (SMPU) matrices, aiming to combine piezoelectric effect and shape memory effect into one composite. The resultant composites, PZT / SMPU composites, are prepared by the solution blending method, and three kinds of these composites, PZT 60% (%), PZT 70% (%) and PZT 80% (%), succeed in obtaining both the two smart effects. The above three composites all show recovery rates of above 94% in the third cycle. Compared with the pristine SMPU, PZT / SMPU composites show that the maximum recovery stresses are enhanced by at least 133%, elastic moduli are improved to more than 166% and yield stresses are increased by no less than 32%. Besides, the strong potential in nanopositioning is revealed by the results of nanoscale displacement measurements under step voltages because the displacements with 1 nm resolution can be achieved in a common laboratory without any control of the environmental parameters. Taking the advantage of shape memory effect makes the film actuators made of PZT / SMPU composites easy to be deformed into a variety of designed shapes. As a consequence, the shaped actuators are capable of generating much more displacements which is several times, even dozens of times, more than that of the corresponding unshaped film actuators, while the positioning errors remain the same (still within ± 5 nm). This promising merit partly profits from the softness of SMPU matrices which, to some extent, could protect PZT particles from ambient noise. Thus, PZT / SMPU composites have the ability to output displacements with the positioning errors within ± 5 nm without the requirement for a controlled environment. This ability implies the possibility of reducing the costs of nanopositioning and, even, nanomachining and nanofabrication.

Although a large number of shape memory composites (SMCs) have been reported, the variations in recovery rates of SMCs induced by fillers are also discovered and several simples reasons for the variations of recovery rates are also given, a thorough analysis, so far, has not been presented yet. To understand the essence of shape memory behaviors of SMCs, the molecular mechanism of SMCs is proposed on the basis of that of shape memory polymers (SMPs) by identifying the differences lying in the molecular motions of SMPs and SMCs. The analysis on molecular motions in consideration of the motions of fillers discloses the positive and negative effect of fillers on recovery rates and the decisive role of interfaces between fillers and matrices in the above two effects. Besides PZT / SMPU composites, another group of SMCs, TiO_2 / SMPU composites, are tested likewise to make our conclusions more general. For directly verifying the role of interfaces, the recovery rates of SMCs with good interfaces are compared with that of SMCs with poor interfaces. The experimental results prove that interfaces are both benefit and harmful for recovery rates at the same time. Besides, the limit of programming ability of SMPs and SMCs are experimentally demonstrated too. Some conclusions on the relations between recovery rates and interfaces are given, and then are applied to explain the changes in recovery rates of other reported SMCs. Moreover, the conclusions are able to qualitatively predict the recovery rates of SMCs with more fillers or less fillers.

Besides recovery rates, the influences of interfaces on piezoelectric effect and relative permittivity are analyzed as well. As a result, PZT / SMPU composites with poor interfaces exhibit lower relative permittivity because of the existence of the free spaces between piezoelectric fillers and SMPU matrices, and the piezoelectric effect is critically dependent on whether the interfaces are good or poor. The experimental results testify that PZT / SMPU composites with poor interfaces are unable to produce any displacement. This inability of producing displacements could be explained by the microscopic mechanism for actuation behaviors of PZT / SMPU composites. Moreover, PZT fillers exhibit effective improvement in storage moduli, but very little effect on the glass transition temperature.

Interdigitated electrodes are made on the surfaces of PZT / SMPU composites to utilize the piezoelectric effect along the longitudinal direction. PZT / SMPU composites with interdigitated electrodes demonstrate the ability to generate bending displacements and harvest energy from external vibrations. The experimental results of energy harvesting show that PZT / SMPU composites can produce electric voltages continuously which imply the potential for powering electric devices sustainably.

Finally, silver nano particles are added into PZT / SMPU composites and the resulting composites, Ag / PZT / SMPU composites, show an increase in piezoelectric charge constants. The values of piezoelectric constant of Ag / PZT / SMPU composites are at least twice as many as those of PZT / SMPU composites.