Lead free ceramic/polymer based hybrid piezoelectric nanocomposites as mechanical energy harvesters

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ABSTRACT

Energy harvesting from easily available mechanical vibrations in our surroundings has gained attractive substantial attention for its application in the field of artificial skins (electronic skin), shoes, wearable electronics, foldable displays and environment monitoring. Polar Poly(vinylidene) fluoride (PVDF) and its copolymers are the most responsive piezoelectric polymers that can be used as self-powered flexible energy harvesters due to its strong piezoelectric response, chemical and mechanical durability. Consequently, different strategies have been developed to enhance electroactive polar phase fraction of PVDF such as development of specific processing technology, inclusion of specific fillers, mechanical stretching, electrospinning, electrical poling, etc. Therefore, different types of ceramic fillers such as PZT, $BaTiO_3$, $LiNbO_3$, $KNaNbO_3$, $ZnSnO_3$ etc. have been used to fabricate the PVDF composites. In this regard, Zinc Oxide (ZnO) incorporated PVDF composites are very promising materials in this field owing to the inherent piezoelectric property of ZnO as well as environment benign nature. The nucleation and stabilization of the polymer depends upon shape, size as well as concentration of filler. Therefore, in order to investigate the morphological influence of ZnO on the stabilization of β phase of PVDF as well as dielectric, ferroelectric and piezoelectric properties of PVDF based composites, two types of morphologically different ZnO i.e. wet chemically synthesized ZnO particles and hydrothermally synthesized ZnO nanorods were incorporated into PVDF to fabricate their respective composite films. One dimensional (1D) rod shape structure was found to be more effective in enhancing the dielectric, ferroelectric, energy storage and energy harvesting performance PVDF compared to particle like structure of ZnO. Furthermore, to study the effect of aspect ratio of ZnO nanorod on the electrical properties of PVDF, ZnO nanorods with different aspect ratio were synthesized and incorporated into PVDF matrix to fabricate the resulting composite film. ZnO filler with high aspect ratio increased the polar phase fraction of PVDF composite which triggered the enhancement of dielectric properties along with ferroelectric and piezoelectric properties. Thereby, the aspect ratio of ZnO nanorods was tuned to achieve the performance enhancement of the resulting PVDF based composites. For further enhancement of electrical performances, third phase conductive filler such as multi-walled carbon nano tube (MWCNT) was impregnated in the flexible ZnO/PVDF composites. MWCNT has supported homogeneous dispersion of ZnO in PVDF matrix by reducing compatibility issues. This uniform dispersion of filler in the matrix improved the polarity of the matrix by enhancing the interfacial interaction between $-CH_2$ dipoles of PVDF and surface charges of fillers, which lead to the enhancement of dielectric, ferroelectric, energy storage density and mechanical energy harvesting performance of the composite. ZnO filler was further modified by incorporating Al^{3+} ions into the ZnO host lattice, which lead to the

modification of the surface charge of the nano-filler and reduced oxygen point defects. Use of Al^{3+} ions incorporated ZnO as filler in PVDF matrix enhanced the dielectric constant of the composite with a considerably low dielectric loss and reduced the leakage current value. The enhanced surface charge of ZnO filler improved the polar phase, dielectric permittivity, energy storage density and mechanical energy harvesting performance of the resulting PVDF-HFP based composite films. 10 wt% Al@ZnO loaded poled PVDF-HFP (10PALZO-P) composite was considered as the most suitable candidate to design the energy harvester owing to its best performance in terms of dielectric, ferroelectric, piezoelectric properties as well as output performance i.e. output voltage, current and power density. In order to achieve the real life applicability of the fabricated energy harvester, it was used to harvest energy from different types of human body motions such walking, running, hand or wrist movement etc. This piezoelectric energy harvester (PZEH) has also been utilized as an efficient height-monitoring sensor. Thereby, the present thesis work established the feasibility of using ZnO-based composites towards low cost, flexible as well as wearable piezo-electric energy harvesting devices.

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