Abstract

In the recent era, the mandate of energy in day-to-day life is gradually increasing with the growing population. Hence, emergence of a prudent, most fruitful, low cost and green energy method to fulfil the ever-growing energy demands in the daily life is one of the most promising tasks. Nevertheless, there are different energy sources in the surrounding environment from which energy can easily be harvested such as solar, thermal, chemical, biological and mechanical energies among which the most abundantly found in our ecosystem is mechanical energy. It is obvious that this energy is being debilitated during human body movement, walking, vibration, wind, flow of water and so on. Now-a-days, this accessible energy can be recycled for the use in wireless and portable electronic gadgets where minimal power is required. Generally, a source of power is battery for most of the electronic goods, but it has some circumscriptions. For instance, it has marginal life span. Hence, self-powered techniques naturally get more engrossment to resolve such above stated challenges. In the recent days, piezoelectric energy harvesters are employed to boost up the wireless and portable electronic gadgets. Currently, the only commercially successful piezoelectric polymers are poly (vinylidene fluoride) (PVDF) and its copolymers. PVDF has attractive electroactive properties, such as piezoelectricity, ferroelectricity and pyroelectricity. However, it has low coupling factor (0.30) and the dielectric constant (6 - 10). On the other hand, lead zirconate titanate (PZT) is the commonly used ceramic-based piezoelectric material due to its very lucrative properties like high electromechanical behaviour (coupling factor, 0.7), piezoelectric constant (d_{33} value lies between 250 to 700 pC/N) and the Curie temperature (>400°C). But in the recent era, the use of PZT has become limited due to its negative impact towards the environment because of the presence of toxic lead content in its structure (more than 60 wt.% Pb). To overcome the above said problems of PVDF and PZT based piezoelectric materials, in the present thesis work, a lead free flexible PVDF/potassium sodium niobite (KNN) nanocomposite based piezoelectric materials have been developed by different methods (solution cast, electrospinning, and melt extrusion).

KNN has been chosen as filler material in the present study to develop PVDF polymer-based nanocomposites. As a first step, KNN nanorods have been synthesized via hydrothermal method by varying the process parameters (mole ratio of KOH and NaOH, autoclave filling volume, reaction temperature, rection time). The synthesis parameters have been optimised (i.e., 1/5 KOH and NaOH molar ratio, 180 °C reaction temperature, 80% autoclave filling volume) having constant reaction time (8 hours) to achieve KNN nanostructures in the form of

nanorods with an average aspect ratio of ~8.5 as calculated by Image J software. Moreover, to confirm the morphological structure of synthesized KNN NRs, SEM analysis has been carried out. In addition, XRD result of the synthesized KNN nanorods has confirmed the orthorhombic crystal structure which has higher piezoelectric properties as per the reported literature. After successful synthesis of KNN nanorods, different nanocomposite based piezoelectric materials have been prepared using KNN nanorods (KNN NRs) as filler materials in PVDF polymer by different methods. At first, PVDF/KNN NRs nanocomposite-based film has been prepared by solution cast method followed by fabrication of piezoelectric nanogenerator. The percentage of KNN nanorods into PVDF matrix has been varied systematically to observe its direct effect on energy harvesting efficiency of the nanogenerator. Interestingly, it has been observed that 10% KNN NRs @ PVDF nanocomposite film possesses the highest electroactive (β-crystal) phase (~98%) as compared to other KNN incorporated samples. In addition, 10% KNN NRs @ PVDF nanocomposite film is capable to generate 3.4 V open circuit voltage and 0.100 μA current by applying repeated compressive forces on to it. The developed nanogenerator has shown the current density of 0.025 $\mu A/cm^2$. However, some agglomeration of KNN nanorods has been observed from the morphological view of the PVDF/KNN based nanocomposite films. To minimize the agglomeration by improving the distribution of KNN NRs throughout the PVDF polymer matrix and to enhance the compatibility between the KNN and PVDF, the surface of KNN NRs has been modified by using surface modifying agents. Herein, KNN nanorods have been surface modified by three diverse surface modifiers such as 3-aminopropyltrimethoxysilane (APS), polyaniline (PANI) and polyvinylpyrrolidone (PVP) for resolving the agglomeration problem of the nanorods and to look for their effects on the micro-structural growth including nucleation of polar crystals of PVDF. The nanocomposite films have been developed simply by solution cast method. The growth of electroactive phases (β and γ) of the PVDF polymer has been observed to be improved significantly by incorporation of surface modified KNN nanorods. The beta fraction (F(β)) and gamma fraction (F(γ)) as calculated by the FTIR spectrum (98% and 99%) are maximum for the silane and PVP modified KNN nanorods incorporated PVDF polymer. A PVDF/SM-KNN nanocomposite based nanogenerator has shown ~5.6 V output voltage and ~0.306 μA current, respectively.

In the next experiment, PVDF/KNN NRs nanocomposite based nano fibrous web has been prepared by electrospinning method. A unique nanogenerator has been fabricated using nanorods (aspect ratio~ 8.5) of lead-free potassium sodium niobate (KNN) incorporated poly (vinylidene fluoride) (PVDF) based nano fibrous web. The unique dimension of synthesized nanorods with a very low loading (only 3%) have bestowed somewhat surprisingly a negative effect on beta nucleation but subdued this effect by their significant positive contribution towards piezoelectric response by self-orienting the dipoles at the electrospinning process itself. Finally, the developed nanogenerator has showed a higher open circuit output voltage of ~17.5 V, output current of ~ 0.522 μA and current density ~0.13 μA/cm^2 under a repeated finger tapping and has also able to light up a light emitting diode (LED) of 2 V practically. Nevertheless, this nanocomposite based fibrous web again shows the distribution issues of the nano fillers inside the matrix like solution cast film. To resolve this problem, silane modified potassium sodium niboate (SM-KNN) has been incorporated in poly (vinylidene fluoride) (PVDF) for developing PVDF/SM-KNN electrospun nanogenerator. PVDF/3% SM-KNN nanocomposite has generated remarkably high output voltage of ~21 V, output current of ~22 μA, current density of ~5.5 μA/cm2 and power density of ~115.5 μW/cm^2. For further improving the piezoelectric performance, other semiconductive (ZnO) and conductive (CNT) fillers have also been added along with KNN nanorods in the PVDF polymer. The output voltage and current for the PVDF/KNN/ZnO based nanogenerator have been noted as ~25 V and 1.81 μA (when pressure is applied by the finger tapping mode) and 8.31 V and 5 μA (when pressure is applied by a sewing machine). A power density of 11.31 μW/cm^2 (finger tapping mode) and 10.38 μW/cm^2 (pressure applied by a sewing machine) have also been recorded as exhibited by this nanogenerator. Whereas, in the case of PVDF/KNN/CNT based nanogenerator, 0.1% incorporation of CNT in the nanogenerator has demonstrated a significant improvement in piezoelectric performance with an output voltage of ~23.24 V, current ~9 μA and power density of 52.29 μW/cm^2 on finger tapping vis-à-vis voltage of ~12 V, current of ~18 μA and power density of 54 μW/cm^2 on the application of mechanized compressive force.

In a separate study, a flexible nanogenerator based on melt-spun nanocomposite filament has also been successfully prepared. A nanogenerator has been made of PVDF/4% KNN NRs based filament which has exhibited the highest $F(\beta)$ value (i.e., 26% polar β phase). The PVDF/4% KNN NRs filament based nanogenerator could also generate around 3.7 V voltage and 0.326 μA current, respectively. Finally, the structural characteristics, morphology, and piezoelectric performance of various nanogenerators fabricated by different methods (solution cast, electrospinning, and melt-extrusion) have been compared. At the end, it has been concluded that the electrospinning method (wherein the best piezoelectric performance has been achieved) is the best technique for developing PVDF/KNN NRs nanocomposite based flexible piezoelectric materials as compared to solution cast and melt extrusion processes.