Nanomanufacturing and Analysis of Novel Continuous Ferroelectric PVDF and P(VDF-TrFE) Nanofibers

By

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Poly(vinylidene fluoride) (PVDF) and PVDF copolymers are well known for their ferroelectric and piezoelectric properties. Currently, they are mainly used in applications in the form of films. Thin PVDF films have been shown to possess unique ferroelectric properties in the nanoscale range. However, their two-dimensional nature limits their applicability in active engineering materials and structures. One-dimensional PVDF nanofibers can be expected to combine ferroelectric behavior with enhanced mechanical properties and ultrahigh flexibility providing critical advantages for applications. In this work, novel continuous PVDF nanofibers were nanomanufactured and systematically studied for the first time. Nanofibers from PVDF and P(VDF-TrFE) copolymer with several molecular weights and co-polymer compositions were manufactured by electrospinning. The method consists of spinning polymer solutions in high electric fields. Effects of process parameters on nanofiber diameters and morphology were studied. Resulting nanofibers were characterized by FE-SEM, TEM, XRD, FTIR, DSC and TGA. Effects of annealing on copolymer nanofibers were analyzed. Nanofiber-reinforced composites were manufactured and their polarization behavior studied using a specially designed experimental device. A number of pioneering observations and discoveries were made as a result of this analysis. For example, analysis of crystalline

structure of PVDF nanofibers showed that the initial α phase of the PVDF raw material was converted to β phase during electrospinning. This result is very encouraging as the β phase is primarily responsible for the piezo- and ferroelectric behavior of PVDF polymers. It was also shown for the first time that nanofabricated P(VDF-TrFE) nanofibers exhibited distinct Curie points and different structures than their raw materials. Annealing was shown to be an effective way to modify properties of P(VDF-TrFE) co-polymer nanofibers.

Overall, the results demonstrated for the first time flexible nanomanufacturing of continuous PVDF and co-polymer nanofibers exhibiting a number of unusual ferroelectric properties. The developed continuous nanofibers can be used in a broad range of applications spanning smart and active composites, multifunctional coatings, functional textiles, ultrafast/sensitive sensors, tailorable miniature actuators, MEMS/NEMS, energy conversion devices, and many others.

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Chapter 1 Introduction

1.1 Material and nanomaterial

Materials influence every segment of our everyday lives, such as clothing, food production, housing and transportation. Historically advancements of human societies have been initiated by the introduction of new materials. The early civilizations are even classified by the level of their material development (e.g. Stone Age, Brone Age). In modern society, new materials play an increasingly important role in the technological breakthroughs.

Materials can be grouped in a variety of ways. For example, Materials can be classified as polymers, metals and ceramics by their atomic structures and chemical makeup, nanomaterials and macromaterials by their dimensions, and various functional materials such as active materials, biomaterials and energy related materials.

Current research in material science focuses on nanomaterials. A nanomaterial is a material with at least one dimension less than 100 nm. Usually nanomaterials can be classified as zero-dimensional nanomaterials (i.e. nanoparticles and nanodots), one-dimensional nanomaterials (i.e nanotube, nanowires and nanofibers) and two-dimensional matierals (i.e. nanodiscs and nanofilms). Nanomaterials possess many unique features such as small size coupled with high specific surface area, unique physical and chemical properties and quantum confinement. Nanomaterials are the basis of nanotechnology, which creates useful materials, devices and systems through control of matter on the nanometer-length scale and explores novel properties and phenomena developed at that scale. Nanotechnology is expected to significantly redevelop existing technology and create new