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Investigation of microstructure and mechanical properties of polyvinylidene fluoride/carbon nanotube composites after electric field polarization: A molecular dynamics study

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ABSTRACT

Molecular dynamics (MD) simulation was used to investigate the microstructure and mechanical properties of pure polyvinylidene fluoride (PVDF) and PVDF/carbon nanotube (CNT) composites with and without a polarization process. After annealing, the trans percentages of non-polarized PVDF and composites are improved by about 25% compared to the initial model of α-phase PVDF. For PVDF and composites with polarization process, the PVDF trans percentages can be further enhanced by around 10% compared to those without the polarization process. The mechanical properties of pure PVDF can be improved by blending the PVDF with CNTs and with the polarization process. The local shear strain analysis shows that the strength of PVDF around the CNTs have been enhanced, leading to higher brittleness of the composites at increasing CNT weight fractions. During the tensile process, the trans percentage of PVDF increases in the non-polarized cases with increasing strain, but are less sensitive to polarized cases.

1. Introduction

Polyvinylidene fluoride (PVDF) is a popular polymer material for use as insulation in electrical wires [1] and filtration technologies [2], as well as in the biomedical field [3] because PVDF exhibits excellent chemical stability [4], thermal stability [5], corrosion resistance [6] and biocompatibility [7]. PVDF can display four different chain conformations arrangements, those of α-, β-, γ-, and δ-phases [8]. Among these four polymorphs, the α arrangement is the most common and stable phase with its dipole moments in random orientation, resulting in a zero system dipole moment. However, under a high electric field, PVDF in the α-phase is transformed to the polar β-phase, leading to the dipole moments aligning neatly in the electrical field direction. This β-phase PVDF polymorph has been widely applied to potential energy conversion applications [9] due to its excellent piezoelectric [10], ferroelectric [11], and pyroelectric [12] properties.

Electrospinning (ES) is a nanofiber production method which draws the polar polymer threads to nanofibers from polymer solutions under electric fields. Due to PVDF's excellent piezoelectricity, ES is the most commonly used production method. While most previous experiments dealt with pure PVDF only, some recent experimental results have shown that CNT/PVDF composite fibers display better mechanical and piezoelectric properties than those of pure PVDF. For example, Yu studied the influence of blending multi-walled carbon nanotubes (MWCNTs) and PVDF in the fiber β-phase on mechanical properties, output voltage and output power [13]. Their results showed that the PVDF fiber with MWCNT at 7 wt% exhibits the highest Young's modulus when the fraction of MWCNTs was varied from 0 to 10 wt%. The maximum output voltage and the average power for charging a capacitor are 6 V and 81.8 nW at the optimum concentration of 5 wt% MWCNT, 200% and 44.8% higher than those of pure PVDF nanofiber mats, respectively. This phenomenon can be explained by MWCNTs inducing the formation of a higher fraction of β crystalline phase during the ES process when compared with a pure PVDF mat. Baji investigated the improvement of the PVDF β-crystal content, as well as the dielectric and tensile properties for PVDF/CNT composite fibers of different MWCNT fractions [14]. When 3 wt% MWCNTs were incorporated into the PVDF fiber, the PVDF/MWCNT composite fiber exhibited the highest dielectric permittivity. Also the strength and stiffness were about 276 MPa and 1.64 GP, which are improved from 215 MPa to 1.25 GPa in the pure PVDF fibers. Near-field electrospinning (NFES) technology has been developed to produce polymer fiber with a nanoscale cross-section size for various sensing and actuation applications [15]. One of the current authors, Pan, studied the β-phase content and

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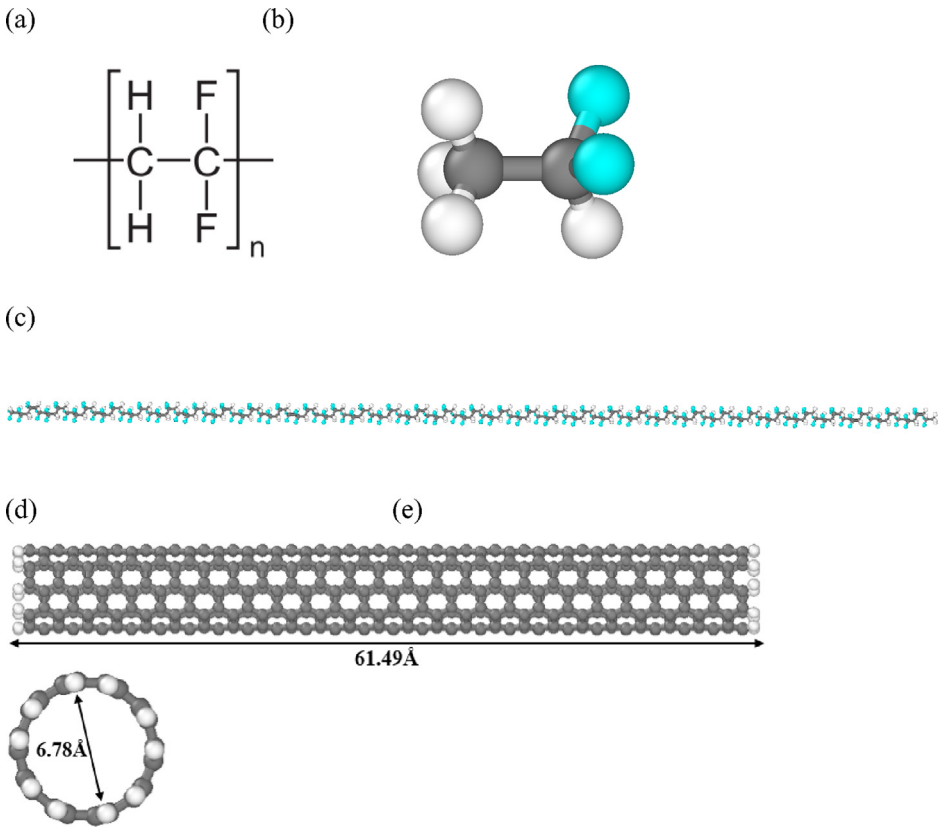

Fig. 1. Schematic diagrams of (a) molecular formula of PVDF, (b) the monomer of PVDF, (c) a α-PVDF chain with 100 repeated units, (d) lateral section and (e) cross section of (5,5) CNT. Atoms: gray (C), white (H), light blue (F). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Parameters of materials used in the simulations.

Name	CNT type	Length (Å)	MW (amu)	Repeat units	Number of atoms
SWCNT	(5,5)	61.49	6025.66	–	520
PVDF	–	252.09	6405.42	100	602

Table 2
System information in the simulations.

CNT weight fraction (%)	Number of PVDF chains	Number of CNTs	Total atom numbers
0	80	–	48,160
4.49	80	4	50,240
9.34	73	8	48,106
13.23	74	12	50,788

Table 3
Comparison of PVDF properties between experiment and this work.

Properties	Pure PVDF (experiment)	Pure PVDF (this work)	Error (%)
Density (g/cm^3)	1.78 [91]	1.66	6.7
Solubility parameter (MPa$^{1/2}$)	23.2 [92]	21.52	7.2

the mechanical properties of PVDF/MWCNT nanofiber fabricated by NFES technology [16]. Their results showed an enhancement in the Young's modulus of the PVDF fiber from 0.026 to 0.1 GPa after 0.03 wt % MWCNT was incorporated into the PVDF fiber. X-ray diffraction (XRD) analysis showed the XRD peak at $2\theta = 20.8^\circ$ for this 0.03 wt% MWCNT content was the highest, indicating that the fraction of crystalline β-phase was enhanced by the incorporation of MWCNT.

These aforementioned experimental studies proposed that the improvements in dielectric permittivity and mechanical properties compared to PVDF were due to the incorporation of CNTs, which induced more β-phase configurations as well as reinforcing the PVDF. However, it is relatively difficult to investigate the change in local atomic arrangement after the incorporation of CNT into PVDF by the experimental approach. The alternative is to use reliable numerical methods to investigate phenomena which are difficult to observe by direct empirical approach. Molecular simulation methods such as molecular dynamics (MD) [17], molecular statics (MS) [18], and the Monte Carlo method [19] are powerful numerical tools to investigate material behaviors from the atomic scale and help clarify the physical insights found in experimental results. They can also be used to predict the related properties of materials prior to corresponding experiments in order to save time and money. For example, Bohlén used MD simulation to investigate the effect of different single wall carbon nanotube (SWCNT) alignments within the PVDF on mechanical properties [20]. Their simulation results showed that random orientation of 4 wt% SWCNTs in PVDF matrix does not significantly affect the Young's modulus, which is about 3.1 GPa for the composite and 3.0 GPa for the pure PVDF. However, when the SWCNT are aligned along a tension direction, the Young's modulus can be enhanced by about 33% compared to that of pure PVDF. Miao adopted MD simulations to analyze the relaxation processes at 300 K which occur after thin electrospun nanofibers of poly(vinylidene fluoride) were formed [21]. Simulation results indicate that the first such relaxation process gives rise to twist defects due to the rapid rotation of chain segments along longitudinal axes of the chain. In the second process, which happens more slowly, the twist defects migrate along the chain until they become adjacent to other similar defects. Erdtman used MD to study the melting behaviors of α- and β-PVDF [22]. They indicated the melting point of β-PVDF is higher than that of α-PVDF, with the predicted melting points of both