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Investigation of Mechanical Properties of BaTiO3/PVDF Nanocomposites: a Molecular Dynamic Simulations

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Investigation of mechanical properties of $BaTiO_3$/PVDF nanocomposites: A molecular dynamic simulations

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Abstract

In the present research, MD simulations have been employed to study the mechanical properties of poly(vinylidene fluoride)-(PVDF) with and without reinforcement of barium titanate BTO by using Material Studio (MS) software. the stiffness matrix and mechanical parameters such as Young modulus, shear modulus, and bulk modulus of the unit cells were achieved after molecular dynamic (MD) optimizations and calculations. Finally, the mechanical properties for four different systems (PVDF-0, neat PVDF; PVDF-I, with 7.57 wt% BTO; PVDF-II, with 14.07 wt% BTO; PVDF-III, with 19.72 wt% BTO) were compared. The result shows that the mechanical properties of PVDF can be remarkably reinforced by being filled with a low volume fraction of BTO.

Keywords: PVDF, BTO, nanocomposite, Mechanical Properties, Materials Studio

1. Introduction

Poly (vinylidene difluoride) (PVDF) is a semicrystalline polymer and is widely used in fields where chemical resistance, abrasion and thermal stability are required. PVDF has been widely investigated since it exhibits many remarkable properties in terms of good mechanical properties, resistance to chemicals, high dielectric permittivity and unique pyroelectric and piezoelectric properties [1] in practical applications. The latter two are the most interesting in applications and derive from the two polar phases β and γ of PVDF. It is also the basic piezoelectric polymer and is used in smart structure sensors in spacecraft [2]. But pure PVDF cannot meet the requirements of mechanics, thermology and oxidation resistance completely. Many efforts have been under taken to improve the properties of PVDF. Incorporation of ceramic particles with high dielectric permittivity into the polymeric matrices is considered to be one of the most common and promising strategies, which takes the advantages of colossal permittivity of ceramic particles and good dielectric strength of polymers. Poly (vinylidene fluoride) (PVDF), a ferroelectric polymer with relatively high dielectric permittivity, was widely investigated in the formation of the dielectric composites with addition of ferroelectric ceramic fillers, such as $BaTiO_3$, $SrTiO_3$, and $Ba_{0.6}Sr_{0.4}TiO_3$ [3].

In recent years, the MD simulation has already been applied in the study of materials in a certain scale with the rapid advancement of computer technology. Therefore, the MD simulation becomes an important method to predict the mechanical properties of polymeric materials. Daan Frenkel and Berend Smit [4] have done a detailed summary of the physical knowledge involved in MD, introducing some applications and algorithms. Materials Science simulation software named Materials Studio, developed by American Accelrys is widely applied in the pharmaceutical, petrochemical, automotive, aerospace industrials and educational research department. The software is a comprehensive application of a variety of advanced simulation ideas and methods, such as quantum mechanics (QM), molecular dynamics (MD), Monte Carlo (MC) and dissipative particle dynamics (DPD) etc., the 3D molecular modeling and configuration optimization can be easily realized with it. Materials Studio using the Microsoft standard user interface, the appropriate parameter settings and the results analyzed can be achieved by each control panel.

2. Simulation details

2.1. Molecular models

PVDF, a semicrystalline polymer, has a variety of crystalline forms, among which the β-phase structure is desirable for dielectric composites due to its ferroelectric characteristic. Ruitian Bo. [5] used X-ray diffraction to study the diffraction of BT/PVDF composites for four crystalline phases of PVDF with different contents of BT, considering that β-phase crystalline structure of PVDF has the highest degree of polarization among all the crystalline forms, a macromolecular chain model of PVDF was constructed according to the β-phase crystalline structure (Figure 1(a)), which was composed of 100 structural units. The β-phase PVDF molecular chain conformation adopts the all-trans-(TTT) serrated conformation, as shown in Figure 1(b).

Meanwhile, a cubic BTO structure with a space group of Pm3m was used to establish a spherical BTO particle model with a radius of 0.5 nm. The ball-and-stick model and scale model of BT spherical particles are shown in Figure 1(c). The cubic unit cells of mixtures of PVDF and BTO were built as five PVDF macromolecular chains and different amounts of BTO particles: 0, 1, 2 and 3. For convenience, we named the four systems PVDF-0, PVDF-I, PVDF-II and PVDF-III, respectively. at densities of 1.75 g cm^{-3} (for PVDF-0) and 1.8 g cm^{-3} (for PVDF-I, PVDF-II and PVDF-III) using the Amorphous Cell module. The characteristic features of the cubic cells of different systems are shown in table 1. The final periodic cells of these four models are shown in figure 2.

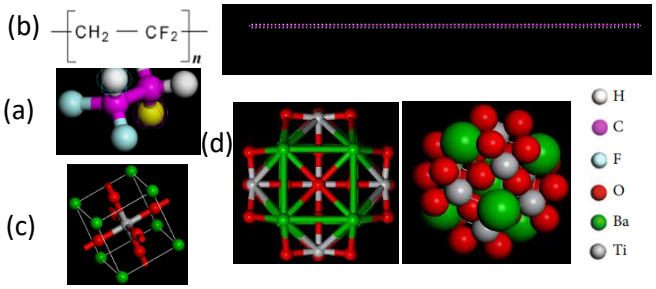

Fig. 1: The initial models of PVDF β-phase structural unit (a), PVDF macromolecular chain (b), crystal structure of BTO (c), and BTO spherical particle (d).

Table 1. Characteristics of the cubic unit cells in different systems.

System name	Components	Nº of atoms	unit cell size (Å)	Mass ratio of BTO
PVDF-0	5 PVDF chains	3010	31.2	0%
PVDF-I	5 PVDF chains + 1 BTO	3049	31.7	5,12%
PVDF-II	5 PVDF chains + 2 BTO	3088	32.5	9,74 %
PVDF-III	5 PVDF chains + 3 BTO	3127	33.3	13,93 %

2.2. Force field

All simulations were performed using the Materials Studio software packages from Accelrys Inc and the UNIVERSAL force field. The UNIVERSAL force field is the excellent general purpose forcefield. The parameters are generated from a set of rules based on element, hybridization and connectivity. The Universal forcefield was parameterized for the full periodic table and has been carefully validated for the main-group compounds, organic molecules and metal complexes. Universal is a purely diagonal, harmonic forcefield. Bond stretching is described by a harmonic term, angle bending by a three-term Fourier cosine expansion, and torsions and inversions by cosine-Fourier expansion terms. The van der Waals interactions are described by the Lennard-Jones potential. Electrostatic interactions are described by atomic monopoles and a screened (distance-dependent) Coulombic term.

2.3. Molecular dynamics details

Material Studio 2020 software was applied to carry out MD simulation by using the Forcite module. After constructing the initial models, the geometric structure was optimized by the Smart algorithm, which combined the steepest descent, conjugate gradient, and Newton minimization algorithm, and the convergence level was set to 0.0001 kcal/mol in a cascade manner. After the geometric structure was optimized, MD simulation was performed on the optimized model, 100 ps of isothermal-isobaric ensemble referred to as NPT ensemble simulation at 0.15GPa with a time integration step of 1fs, a temperature of 298K at room temperature was performed. The system has been compressed by increasing the pressure to increase the density via NPT simulation just for once in this paper.

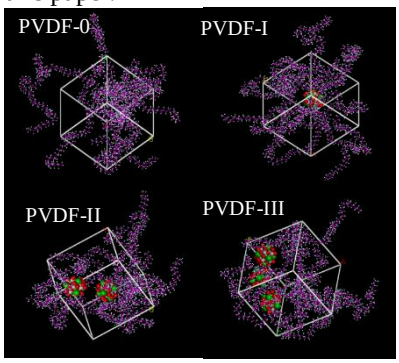

Fig. 2. Original periodic boxes of four different models used for simulation.

When the density was close to the experimental value, enough time of isothermal ensemble referred to as NVT ensemble simulation was performed to balance the system. For all the systems the cell configurations were saved every 10 000 steps; the volume–temperature properties and the elastic properties were analyzed based on the frames after the system achieved equilibrium. Curve of the cell density varies with time after simulation is shown in Fig.3.

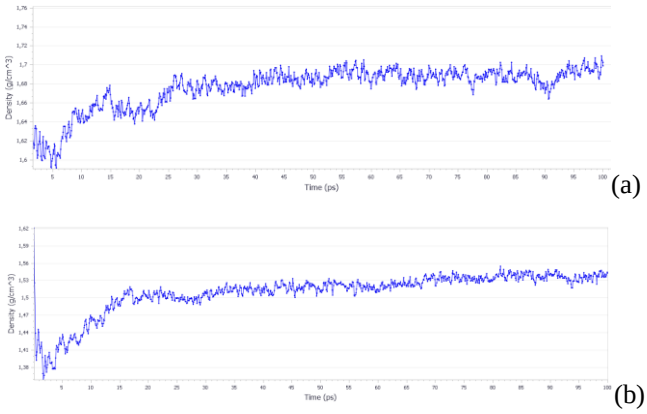

Fig.3 Curve of the cell density varies with time under **0.15GPa** of the PVDF-0 (a) and PVDF-III (b)

2.4. Mechanical properties

There are three main methods to evaluate the mechanical properties of nanocomposites by MD simulations, fluctuation formula, dynamics (constant-stress molecular dynamics), and static (constant-strain minimization) [6]. In the present work, the static method was used to calculate the mechanical properties of the system. Stress-strain behavior for linear elastic materials can be described by Hooke's law (Eq. 1):

$$\sigma_i = C_{ij}\varepsilon_j \qquad \text{Eq. 1}$$

Where, i, j=1, 2, 3. σ_i and ε_j is the 6-dimensional stress-strain vectors, and C_{ij} is the 6×6 stiffness matrix. The strain

amplitude was set to 0.005 to obtain the elastic constants. The stress components were calculated using the so-called virial expression (Eq. 2) [7].

$$\sigma_{ij} = -\frac{1}{V}\sum_{k}\left[m^{k}\left(u_{i}^{k}u_{j}^{k}\right) + \frac{1}{2}\sum_{i\neq j}\left(r_{i}^{kl}\right) f_{j}^{lk}\right] \qquad \text{Eq. 2}$$

Where V is the volume, m^k and u^k stand for the mass and velocity of the k^{th} particle, respectively, r^{kl} is the distance between k^{th} and l^{th} particles, and f^{lk} represents the force exerted on l^{th} particle by k^{th} particle. In microscopic view, the nano-particle reinforced Polymer Matrix composite is considered as the anisotropic material, while close to isotropic material on macro-level. So, it can be assumed that the material is close to isotropic. For isotropic material, the stress-strain relations can be completely described by two Lame constants λ and μ, which can be expressed as:

$$\lambda = \frac{1}{3}(C_{11} + C_{22} + C_{33}) - \frac{2}{3}(C_{44} + C_{55} + C_{66}),$$

$$\mu = \frac{2}{3}(C_{44} + C_{55} + C_{66})$$

The common elastic parameters such as elastic modulus E, Poisson ratio ν, bulk modulus K and shear modulus G can be expressed by the Lame constants:

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}, \quad \nu = \frac{\lambda}{2(\lambda + \mu)}, \quad K = \lambda + \frac{2}{3}\mu, \quad G = \mu.$$

3. Results and Discussion

The calculated mechanical properties of four systems obtained from the MD simulations as illustrated in Table 6. Table 2 represents the elastic stiffness matrix of pure PVDF which is obtained by the Forcite calculation available in the module tool of Material Studio software to calculate its mechanical properties. Similarly, tables 3, 4 & 5 elucidate the elastic stiffness matrix of nanocomposites for 1, 2, and 3 of BTO particles, respectively.

Table 2 The elastic stiffness matrix of PVDF-0-unit cell

Cij(GPa)	1	2	3	4	5	6
1	28.9997	15.0136	14.2503	0.4811	0.1126	0.4057
2	15.0136	28.5822	13.7818	0.0265	0.0027	0.5443
3	14.2503	13.7818	23.0743	-0.7474	-0.2659	-0.2030
4	0.4811	0.0265	-0.7474	5.9126	-0.3497	0.1834
5	0.1126	0.0027	-0.2659	-0.3497	7.6371	0.2359
6	0.4057	0.5443	-0.2030	0.1834	0.2359	9.7928

Table 3 The elastic stiffness matrix of PVDF-I-unit cell

Cij(GPa)	1	2	3	4	5	6
1	22.8363	13.1283	13.6079	-0.0089	-0.8817	0.1639
2	13.1283	22.4870	12.1256	-0.1214	-0.0988	0.2665
3	13.6079	12.1256	17.8147	0.3211	-0.1023	0.9749
4	-0.0089	-0.1214	0.3211	4.1398	0.2007	-0.3112
5	-0.8817	-0.0988	-0.1023	0.2007	5.5402	-0.1074
6	0.1639	0.2665	0.9749	-0.3112	-0.1074	5.6415

Table 4 The elastic stiffness matrix of PVDF-II-unit cell

Cij(GPa)	1	2	3	4	5	6
1	20.5617	9.5544	9.8416	0.0345	-2.0727	0.4216
2	9.5544	15.6972	8.0312	0.2702	0.6677	0.2339
3	9.8416	8.0312	15.0205	0.5211	-3.3232	0.2123
4	0.0345	0.2702	0.5211	3.2892	0.2466	-0.3432
5	-2.0727	0.6677	-3.3232	0.2466	6.5269	0.0533
6	0.4216	0.2339	0.2123	-0.3432	0.0533	5.8525

Table 5 The elastic stiffness matrix of PVDF-III-unit cell

Cij(GPa)	1	2	3	4	5	6
1	12.5306	6.6015	6.5862	0.7967	0.0279	-0.6802
2	6.6015	14.3826	5.9996	0.1467	0.1481	-0.0034
3	6.5862	5.9996	12.8918	0.4570	-0.4212	0.2406
4	0.7967	0.1467	0.4570	3.1203	0.2982	0.0554
5	0.0279	0.1481	-0.4212	0.2982	3.7756	0.2926
6	-0.6802	-0.0034	0.2406	0.0554	0.2926	4.2962

It can be seen from Table 2-5 that the values of Cij (i = 1,2,3; j = 4,5,6) are close to zero, which indicates that the polymer model simulated by molecular dynamics is not extreme anisotropic material. The values of C_{11}, C_{22} and C_{33}; C_{12}, C_{13} and C_{23} ;and C_{44}, C_{55} , C_{66} are similar which indicate that the model is close to the isotropic material. So, it can be assumed that the material is isotropic. According to the mechanical stability conditions the composite is stable mechanically, and this agreed with research [8]

Table 6. Mechanical Properties of Pure PVDF, PVDF-I, PVDF-II and PVDF-III

	Young's Modulus (E)			Bulk Modulus (K)			Shear Modulus(G)		
	Ex	Ey	Ez	Reuss	Voigt	Hill	Reuss	Voigt	Hill
Pure PVDF	17.9	18.2	13.9	18.2	18.5	18.3	6.8	7.1	6.9
PVDF-I 7.57 Wt%	11.2	12.9	8.2	15.2	15.6	15.4	4.3	4.6	4.5
PVDF-II 14.07 Wt%	12.3	9.1	7.8	10.8	11.7	11.3	3.9	4.7	4.3
PVDF-III 19.72Wt%	7.8	10.1	8.7	8.5	8.6	8.6	3.4	3.6	3.5

Comparing the data in table 6, it can be observed obviously that the young's modulus, bulk modulus and Shear Modulus with the W_t of 7.57%, 14.07% and 19.72% were decreased than that of pure PVDF.

4. Conclusions

Molecular modeling of BTO/PVDF nanocomposites has developed to determine the elastic constants such as Young's modulus, bulk modulus, shear modulus. In this study, the MD simulation approach with UNIVERSAL force-field has been effectively applied to simulate the PVDF nanocomposites with different wt% of BTO. The constant strain approach has been used to calculate the mechanical properties of nanocomposites.

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