Dynamic mechanical analysis of bucky gel actuator electrolyte by molecular dynamics simulation

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ABSTRACT

Bucky gel actuator is a kind of ionic electroactive polymer that bends when stimulated by an electric field. The mechanical properties of bucky gel actuator play a crucial role in its performance, determining the amount of displacement and blocking force. Dynamic mechanical analysis is performed by molecular dynamics simulation for the electrolyte layer that contains polyvinylidene fluoride as polymer membrane and 1-ethyl-3-methylimidazolium tetrafluoroborate as ionic liquid to study viscoelastic properties behavior of electrolyte at different strain frequencies. Calculated storage modulus increases and viscosity decreases while strain frequency increases in both tensile and shear modes. This is consistent with experimental result for pure polyvinylidene fluoride. Therefore, the presented molecular dynamics simulation method could be utilized for further studies to understand the ion transportation and bend mechanism of the bucky gel actuator.

1. Introduction

Bucky gel actuator (BGA) is a trimorph ionic electroactive polymer in which an electrolyte layer is sandwiched between two electrode layers (Fig. 1). The electrolyte consists of polyvinylidene fluoride (PVDF) as polymer membrane and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) as charge carrier. $EMIBF_4$ is an ionic liquid (IL) and its ions can move freely in PVDF membrane. When a voltage is applied to the electrodes, anions and cations migrate to the anode and the cathode respectively. Because of difference in ion size, a transfer of mass occurs resulting in the trimorph BGA bending towards the cathode [1].

The mechanical properties of BGA plays a key role in determining the amount of bending and blocking force, that is low mechanical properties leads to BGA bending more, and at the same time, creating less blocking force. Thus, mechanical properties of the electrolyte are one of the design parameters of BGA for each particular application. PVDF and the electrolyte layer are viscoelastic materials whose viscoelastic properties can be obtained from dynamic mechanical analysis (DMA). In DMA, a sinusoidal strain is applied to the specimen, and its stress is then measured. The measured stress is also sinusoidal but with some phase lag. Stress and strain of fully elastic materials are totally in phase, and stress of purely viscous fluid is with 90° lag relative to strain. Therefore, the phase lag between stress and strain indicates the amount of viscosity or damping factor in viscoelastic materials [2].

PVDF is a highly nonreactive thermoplastic fluoropolymer. Fluorine is the most electronegative element, and accordingly it forms strong bonds with hydrogen and carbon. In consequence, PVDF has specific properties such as mechanical, chemical, electrical, and thermal resistance due to its strong polar bonds [3]. PVDF polymer chains inherently form crystalline formations to decrease the energy level; but they are so long that some parts remain in the amorphous region. Hence, PVDF is a semicrystalline polymer. The crystalline region could be formed in different phases. The formation is mostly in α and β phase which are thermodynamically stable and polar, respectively [4].

There are limited researches on MD simulation of PVDF polymer, because it is a polar semicrystalline polymer with a complex structure. Chen and Shew [5] could be named as the first people who studied the conformational behavior of chain molecules containing polar groups by using Byutner and Smith's force field in 2003. Their results showed that the mean length of PVDF chains increases while temperature and dielectric constant increase. This increase of polymer length indicates the influence of polar groups on formational behavior of PVDF chains since the bond length and bond angles were constant.

Some researchers focused on MD simulation of PVDF composites. Bohlen and Bolton [6] in 2013 studied the effects of single walled carbon nanotubes on PVDF mechanical properties. They found that short single walled carbon nanotubes do not have a significant effect on bulk and shear moduli. In addition, they calculated interfacial shear stress and bonding energy between single walled carbon nanotube and PVDF polymer during simulated pullout test. Lee et al. [7] in 2014, evaluated the strength of the interface between PVDF binder and

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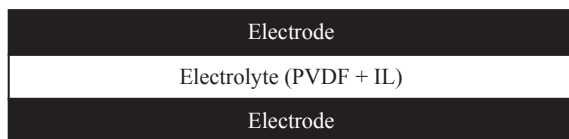| Electrode |
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| Electrolyte (PVDF + IL) |
| Electrode |

Fig. 1. Schematic of BGA; an electrolyte thin film layer containing PVDF and IL sandwiched between two electrode thin film layers.

graphite in opening and sliding modes. Their results indicated that failure occurs at interfacial region rather than inside PVDF or graphite. Some other researchers simulated the diffusivity of water molecules in PVDF by molecular dynamics (MD). For instance, in 2015, Bai et al. [8] studied the diffusion of water in PVDF/silica composite and observed that diffusion coefficient increases when silica concentration increases.

In the field of MD simulation of ionic liquids, although there is some research on pure IL [9–11], MD simulation for a combination of IL and polymers is limited. One of the early simulations was performed by Catlow and Mills [12] in 1995 that determined the structural and dynamical properties of the mixture of polyethylene oxide and Sodium iodide. Costa and Ribeiro [13] modeled polyethylene oxide and an ionic liquid in which the cations was 1-alkyl-3-methylimidazolium by MD simulation, showing that the ions remained dispersed in a polymer matrix. Diddens and Heuer [14] studied the lithium ion transport mechanism in ternary polymer composite containing polyethylene oxide, Lithium-bis(trifluoromethane) sulfonamide, and N-methyl-N-propylpyrrolidinium bis(trifluoromethane) sulfonimide. It was observed that the presence of IL lead to an increase of lithium diffusion. Raju et al. [15] examined the diffusivity of cations of N-alkyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide with different alkyl chain length in polyethylene oxide by MD simulation and found that cations with shorter alkyl length could diffuse more inside the polymer membrane. Other than ion transport in the polymer membrane, the combination of IL with other materials such as carbon nanotubes and graphene flakes [16], gases [17], water [18], and biomolecules [19] were also simulated by molecular dynamics.

In this paper, the electrolyte layer is studied by MD simulation as the primary and basic step of determining mechanical properties of the three-layered BGA. This is the first time (to the best of our knowledge) that the combination of PVDF and $EMIBF_4$ is simulated by using molecular dynamics and its viscoelastic properties are determined via DMA at different strain frequencies. Firstly, dynamic modulus of pure PVDF for a variety of systems including different numbers of chains with different lengths is calculated to understand the polymer chain effects on mechanical properties. Secondly, dynamic modulus is determined for pure PVDF at different strain frequencies and the viscoelastic behavior via frequency change is verified with experimental results. Lastly, dynamic modulus of PVDF/$EMIBF_4$ is obtained at different strain frequencies and compared with pure PVDF dynamic modulus to investigate the effect of ionic liquid on mechanical properties and therefore, on the displacement and blocking force of BGA.

2. Method

Materials simulated in this paper are PVDF as polymer and $EMIBF_4$ as ionic liquid. A PVDF chain with three repeat units (monomers) and $EMIBF_4$ ions are shown schematically in Fig. 2. Initial configuration of polymer atoms is created by randomly growing the polymer chains segment by segment while considering their interactions with positioned atoms at 293 K and density of 1 g/cm^3. In this way, the cell configuration would be more realistic rather than starting the simulation from crystalline formation. Simulation cells of Bohlen and Bolton [6] and Lee et al. [7] consisted of 60 chains with 12 monomers and 20 chains with 20 monomers, respectively. To study the effect of chain size on PVDF properties, different cells are constructed i.e. 10 chains with 100 monomers, 100 chains with 10 monomers, and 4 chains with 250

monomers. In all cases, the number of atoms are approximately equal and around 6000 and the periodic boundary condition is applied.

For initial configuration of atoms for PVDF/$EMIBF_4$ cell, similar to pure PVDF cell, 10 chains with 100 monomers are grown randomly segment by segment at 293 K and density of 0.8 g/cm^3 while 325 ion pairs exist in the cell. Total number of atoms are 13,820 and the boundary condition is periodic. Fig. 3 shows the PVDF/$EMIBF_4$ cell including 10 polymer chains with 100 monomers and 325 ion pairs. The density and the length of the cubic cell are 0.8 g/cm^3 and 64.383 Angstroms respectively. A brief information about different systems created here is presented in Table 1.

In the literature, some efforts have been made to develop a proper force field for PVDF and $EMIBF_4$. Karasawa and Goddard [20] were the first researchers that presented the first force field for PVDF in 1992. The force field was nonpolar and applicable only for crystalline PVDF. After that, several studies were performed to improve the force field, for instance, Byutner and Smith [4] in 2000 introduced a force field for PVDF that could simulate the amorphous phase. Although the force field was nonpolar, modified partial charges compensated the polarity effect. Hence, the force field presented by Byutner and Smith is utilized in several MD simulations [5,7,22,23]. In 2015, Lachet et al. [24] developed a general force field for hydrofluorocarbons by modifying Byutner and Smith's force field. However, for PVDF, Byutner and Smith's force field is still more accurate [24].

The first force field for imidazolium based ionic liquid was introduced by Hanke et al. [25] in 2001 in which united atoms were used for methyl and methylene groups. After examining the force field, they concluded that the force field was not accurate enough for simulating ion diffusion. De Andrade et al. [26] affirmed that the hydrogen bonds between anions and hydrogen atoms existing in imidazolium rings should also be considered. So, they modified the previous force field by using all atoms instead of the united atoms approach. In their force field, De Andrade et al. assumed that the imidazolium ring is symmetrical and therefore, the bond length and angles are symmetrical as well. Canongia Lopes et al. [27] revealed that there is a significant difference in imidazolium ring bonds and angles. They presented a new force field in which the imidazolium ring was asymmetrical. This force field was used widely by researchers for MD simulation of ionic liquids [28–30]. It was adequate for predicting thermodynamic properties, however the calculated diffusion coefficient and electrical conductivity were inconsistent with experimental results. Borodin et al. [31] presented a polar force field based on quantum chemistry in 2009 for a wide range of ionic liquids, capable of predicting the diffusion coefficient of ionic liquids more precisely.

The force field developed by Byutner and Smith [21] is utilized here for PVDF polymer. For ionic liquid, Del Popolo et al. [32] found that structural properties of 1,3-dimethylimidazolium chloride are almost similar for both polar and nonpolar force fields. Therefore, for simplicity, a nonpolar force field based on de Andrade et al. [26] work is applied in this paper for $EMIBF_4$. Details of the force field could be found in the supplementary materials. The interactions between PVDF and $EMIBF_4$ atoms are non-bonded in which the van der Waals parameters are taken from Table S6 (supplementary materials). Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code is used for all simulation in this paper.

Next, the created cell with initial configuration would be equilibrated in 5 steps as below:

1. Geometry optimization: energy of the system is minimized by using conjugate gradient algorithm.
2. Canonical (NVT) ensemble at 500 K for 1 ns: firstly, residual stress caused by bad dynamics is removed (the initial density is lower than the actual). Secondly, the temperature above melting point (177 °C) gives high energy to chains to move towards equilibrium configuration in a shorter simulation time.
3. Isothermal-isobaric (NPT) ensemble at 500 K and 1 atm for 0.5 ns: