Dissipative particle dynamics simulation of phase separation in semiconducting/ferroelectric blend resistive films

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ABSTRACT

Organic semiconducting/ferroelectric blend films attracted much attention due to their cross-talk-free resistive property. Blend films were fabricated from the co-dissolved solution of both semiconducting and ferroelectric components. Spinodal decomposition induced phase separation which was the key structure for determination of resistive property in such blend films. However, till now only seldom work concerned the theoretic studies on phase separation process in semiconducting/ferroelectric blend systems. Here we reported our work on dissipative particle dynamics simulation of phase separation in such blend system. Phase separation morphology was evaluated as a function of the blending ratio of both components. Quantitative analysis method was developed for direct comparison of the domain sizes of semiconducting phase obtained from both simulated and experimental observations. Simulation work was well consistent with direct experimental results.

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1. Introduction

Organic materials and devices have shown great potentials in low-cost and flexible electronics, among which nonvolatile memories are one of essential modules for information storage. Resistive memory possesses those advantages of excellent scalability, fast reading and writing speeds and ease of production and has been regarded as a promising candidate for next-generation memory devices [1]. Resistive memory is usually structured by cross-bar array structure which also results in cross-talk problem, that is the misleading identification of high-resistance state during reading operation. One solution is to insert transistors or diodes into resistive structure to eliminate cross-talk problem which surely complicates the production process [2,3].

Semiconducting/ferroelectric blend polymer films present both resistive and rectifying properties and well solve the cross-talk problem [4]. Semiconducting/ferroelectric blend films are fabricated from their co-dissolved solution. With the evaporation of organic solvent, spinodal decomposition induces the occurrence of phase separation resulting in discrete semiconducting phase surrounded by continuous ferroelectric one. Semiconducting phase electrically connects with both top and bottom electrodes forming conductive filaments, whose conductivity is modulated by the polarization states of the adjacent ferroelectric phase. In such resistive blend films ferroelectric material is usually the copolymer of vinylidene fluoride and trifluoroethylene, P(VDF-TrFE), and the reported semiconducting materials include P3HT (poly (3-hexylthiophene)) [4–6], PFO (poly (9,9-dioctylfluorenyl-2,7-diyl) end-capped with dimethylphenyl groups) [7,8], PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) [9], F8BT (poly [(9,9-dinoctylfluorenyl-2,7-diyl)-alt-(benzo [1–3]thiadiazol-4,8-diyl)]) [10,11] and P3EPT (poly [3-(ethyl-5-pentanoate)thiophene-2,5-diyl]) [12,13].

Though phase separation structure in such blend films has been experimentally verified by various microscopic analysis techniques, such as scanning electron microscope (SEM) [7] [14], atomic force microscope (AFM) [10] [12] [14] [15] [16] and scanning near-field optical microscopy (SNOM) [14], and even the conducting filaments were also imaged by cross-section and energy filtered TEM [9] and synchrotron-based scanning transmission X-ray

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spectromicroscopy [15], so far theoretic simulation on phase separation in semiconducting/ferroelectric blend systems was only reported in seldom work [16]. Direct comparison between simulated and experimental results is further seldom mentioned. Here we reported our work on F8T2 (poly [(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(bithiophene)])/P(VDF-rFE) blend systems. Dissipative particle dynamics (DPD) method was used to simulate the evolution of phase separation with time and further to determine the dependence of phase separation morphology on the blending ratio of both components. Phase separation structure of F8T2/P(VDF-TrFE) blend films was further experimentally determined by SEM. Both results from simulation and experiment were directly compared and showed good consistency.

2. Background of dissipative particle dynamics simulation

Usually spinodal decomposition-induced phase separation in polymer blends is simulated based on phase-field simulation [17], Monte Carlo and DPD methods [18,19]. Here we use DPD method for our simulation work.

The DPD is a mesoscopic simulation method developed by Hoogerbrugge and Koelman [20] and usually used to simulate dynamic behavior of phase separation in multi-component system [21,22]. In DPD simulation, the whole fluid system is structured by a series of coarse-grained beads and each bead represents an entire functional group of atoms or molecules, thereby reducing the number of particles to be simulated [23]. The movement of each bead obeys the Newton's equation of motion and represents the collective behavior of a large number of atoms or molecules. The interaction force (F_{ij}) experienced by bead i with bead j includes three parts, the conservative force (F_{ij}^C), the dissipative force (F_{ij}^D), and the random force (F_{ij}^R) and is given by

$$F_i = \sum_{j \neq i} F_{ij} = \sum_{j \neq i} \left(F_{ij}^C + F_{ij}^D + F_{ij}^R \right) \tag{1}$$

here F_i is the total force experienced by the bead i. The F_{ij} has the same value, but the opposite direction with F_{ji}, thus ensuring the strict conservation of momentum. The interaction force between beads is confined within a certain cutoff radius r_c, which is usually taken as the dimensionless unit length in DPD simulation.

Conservative force F_{ij}^C, dissipative force F_{ij}^D and random force F_{ij}^R can also be expressed as [24]:

$$F_{ij}^C = a_{ij} w^C(r_{ij}) \overrightarrow{e}_{ij} \tag{2}$$

$$F_{ij}^D = \gamma w^D(r_{ij}) (\overrightarrow{v}_{ij} \cdot \overrightarrow{e}_{ij}) \overrightarrow{e}_{ij} \tag{3}$$

$$F_{ij}^R = \sigma w^R(r_{ij}) \xi_{ij} \overrightarrow{e}_{ij} \tag{4}$$

here a_{ij} is a constant describing the maximum repulsion between interacting beads; $\overrightarrow{r}_{ij} = \overrightarrow{r}_i - \overrightarrow{r}_j$ and $\overrightarrow{v}_{ij} = \overrightarrow{v}_i - \overrightarrow{v}_j$, where $(\overrightarrow{r}_i(\overrightarrow{v}_i))$ and $(\overrightarrow{r}_j(\overrightarrow{v}_j))$ are the positions (velocities) of bead i and bead j, respectively; $\overrightarrow{e}_{ij}$ is the unit vector of $\overrightarrow{r}_{ij}$. The $w^C(r_{ij})$, $w^D(r_{ij})$ and $w^R(r_{ij})$ are the weight functions for the conservative, dissipative and random forces, respectively. The γ and σ are the coefficients of dissipative and random forces, respectively. The ξ_{ij} is a randomly fluctuating variable with Gaussian statistics. Conservative, dissipative and random forces are all along the center of the particle-particle, which ensures the conservation of linear momentum in DPD simulation.

In order to maintain a constant temperature T in DPD fluid system, following equations must be satisfied for γ and σ as well as for $w^D(r_{ij})$ and $w^R(r_{ij})$:

$$\gamma = \frac{\sigma^2}{2k_B T} \tag{5}$$

$$w^D(r_{ij}) = \left[w^R(r_{ij}) \right]^2 \tag{6}$$

where k_B is the Boltzmann's constant. In DPD simulation the interactive energy is denoted by $k_B T$, which is usually normalized to 1. The $w^D(r_{ij})$ and $w^R(r_{ij})$ are commonly selected according to

$$w^D(r_{ij}) = \left[w^R(r_{ij}) \right]^2 = \begin{cases} (1-r)^2 & , r < 1 \\ 0 & , r \geq 1 \end{cases} \tag{7}$$

The most important parameter in DPD simulation is the repulsive coefficient a_{ij} between beads. The a_{ij} describes the interactions between particles, which represents the complex interactions between atoms and molecules in the real system. The repulsion parameter between particles of the same type, a_{ii}, should be calculated according to the following equation:

$$a_{ii} = \frac{75 k_B T}{\rho} \tag{8}$$

where ρ is the reduced density. R. Groot et al. made plentiful discussions on the selection of the density ρ. They found that excess pressure was dominated by a single ρ^2 term over a large range of densities. For sufficiently large density, for example $\rho > 2$, excess pressure divided by $a_{ii} \rho^2$ tended to be independent of density ρ, implying a simple scaling relation [25]. Thus $\rho = 3$ is a reasonable choice in simulation [25,26]. The repulsive coefficient a_{ii} between beads of the same type is $25 k_B T$. The a_{ij} between beads of different types is approximated by the following equation

$$a_{ij} = a_{ii} + \Delta a \tag{9}$$

here $i \neq j$ and Δa is defined as the excess repulsion. Here Δa is a function of Flory-Huggins parameter χ_{ij}.

$$\chi_{ij} k_B T = D \Delta a \tag{10}$$

where D is a constant coefficient. The work from R. Groot indicated that $D = 0.306$ is a suitable value for accurate simulation of Schmidt number which is the ratio between the time for fluid particles to diffuse a given distance, to the time for hydrodynamic interactions to reach steady state on the same distance [25]. Since $k_B T$ is normalized to 1, thus we finally get [26].

$$a_{ij} = a_{ii} + 3.27 \chi_{ij} \tag{11}$$

The χ_{ij} is defined by

$$\chi_{ij} = \frac{V_{mol}}{RT} (\delta_i - \delta_j)^2 \tag{12}$$

where δ_i and δ_j are the solubility parameters of bead i and bead j, respectively, V_{mol} is the mean molar volume of the two beads [27] and R is the molar gas constant.

3. Experimental

The P(VDF-TrFE) (70/30 VDF/TrFE molar ratio) and p-type semiconducting F8T2 were bought from Kunshan Hisense