A MATLAB Program for Quantitative Simulation of Self-assembly of Polymer Blend Films with Nano-scaled Features

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Abstract

A MATLAB program has been developed for simulation of polymer blend self-assembly with nano-scaled features. The Cahn-Hilliard equation is implemented to calculate the free energy profile of the polymer blends. The Flory-Huggins type of energy is used to estimate the local free energy. The program is capable of quantitatively simulate the phase separation of polymer blends. The effects such as the substrate functionalization, solvent evaporation, and polymer materials properties are included in the program. The program can estimate the model parameters from the real experimental processing parameters and the material properties. The simulation results can be evaluated quantitatively and compared with the experimental results with analysis tools included in the program.

Introduction

Nano-manufacturing by polymer self-assembly is attracting interests in recent decades due to its wide applications [1]. The numerical simulation of this process can be used to research the mechanisms of phase separation of polymer blends and predict the unobservable process states and unmeasurable material properties. The mathematical principles and numerical simulation of self-assembly via phase separation has been extensively studied [2–11]. But few specific software toolkit have been developed to efficiently investigate this phenomenon.

A computer program is developed in MATLAB for the numerical simulation of the polymer blends phase separation. With this software, the mechanisms of the phase separation are investigated. Also the mobility, gradient energy coefficient energy, and the surface energy in the experiment are estimated with the numerical model. The software can evaluate the physical parameters in the numerical model by implementing the real experimental parameters and

materials properties. The numerical simulation results can be analyzed with the software and the results from the simulation software can be validated with the experimental results.
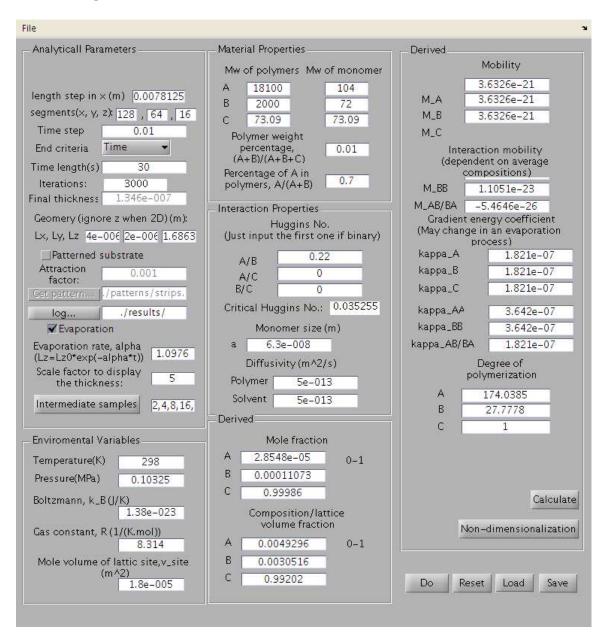
File

Analyticall Parameters

length step in x (m) 0.0078125
segments(x, y, z): 128 , 64 , 16
Time step   0.01
End criteria   Time
Time length(s)   30
Iterations: 3000
Final thickness 1.346e-007
Geomery (ignore z when 2D) (m):
Lx, Ly, Lz 4e-006 2e-006 1.6863
☐ Patterned substrate
Attraction factor: 0.001
Get pattern... ./patterns/strips.
log...   ./results/
☑ Evaporation
Evaporation rate, alpha
(Lz=Lz0*exp(-alpha*t)) 1.0976
Scale factor to display
the thickness: 5
Intermediate samples   2,4,8,16,

Enviromental Variables

Temperature(K)   298
Pressure(MPa)   0.10325
Boltzmann, k_B (J/K)
                  1.38e-023
Gas constant, R (1/(K.mol))
                   8.314
Mole volume of lattic site, v_site
(m^2)
                  1.8e-005

Material Properties

Mw of polymers Mw of monomer
A   18100   104
B   2000   72
C   73.09   73.09
Polymer weight
percentage,   0.01
(A+B)/(A+B+C)
Percentage of A in
polymers, A/(A+B)   0.7

Interaction Properties
Huggins No.
(Just input the first one if binary)
A/B   0.22
A/C   0
B/C   0
Critical Huggins No.: 0.035255
Monomer size (m)
a   6.3e-008
Diffusivity (m^2/s)
Polymer   5e-013
Solvent   5e-013

Derived
Mole fraction
A   2.8548e-05   0-1
B   0.00011073
C   0.99986
Composition/lattice
volume fraction
A   0.0049296   0-1
B   0.0030516
C   0.99202

Derived
Mobility
                 3.6326e-21
M_A   3.6326e-21
M_B   3.6326e-21
M_C
Interaction mobility
(dependent on average
compositions)
M_BB   1.1051e-23
M_AB/BA   -5.4646e-26
Gradient energy coefficient
(May change in an evaporation
process)
kappa_A   1.821e-07
kappa_B   1.821e-07
kappa_C   1.821e-07
kappa_AA   3.642e-07
kappa_BB   3.642e-07
kappa_AB/BA   1.821e-07
Degree of
polymerization
A   174.0385
B   27.7778
C   1

Calculate

Non-dimensionalization

Do   Reset   Load   Save

Figure 1: Screenshot of the simulation program graphical user interface.

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Fundamentals

The numerical model for phase separation of polymer blends are established and validated with experimental results work [12]. The free energy profile during the phase separation in a inhomogeneous mixture is described by Cahn-Hilliard Equation [13–16], as shown below,

$$F(C_1, C_2, C_3) = \int_V \left\{ f(C_1, C_2, C_3) + \sum_{i=1,2,3} [\kappa_i (\nabla C_i)^2] \right\} dV \qquad (1)$$

where f is the local free energy density of homogeneous material, ϕ_i is the lattice volume fraction of component i, and κ_i is the gradient energy coefficient for the component i. The total free energy of the system is composed by two items as shown in Equation 1. The first item is the local free energy and the second is the composition gradient contribution to the free energy.

In our study, the local free energy is in the form of Flory-Huggins equation, which is well know and studied for polymer blends [17] The ternary Flory-Huggins Equation is shown as follows,

$$\begin{aligned} f(C_1, C_2, C_3) = \frac{RT}{v_{site}} \Big(&\frac{C_1}{m_1} \ln C_1 + \frac{C_2}{m_2} \ln C_2 + C_3 \ln C_3 \\ &\chi_{12} C_1 C_2 + \chi_{13} C_1 C_3 + \chi_{23} C_2 C_3 \Big) \end{aligned} \qquad (2)$$

where R is the ideal gas constant, T is the absolute temperature, v_{site} is the lattice site volume in the Flory-Huggins model, m_i is the degree of polymerization of component i, and C_i is the composition for the component i.

There are some parameters in the numerical model which can not be measured directly, such as the gradient energy coefficient and the mobility. These parameters have to be estimated from the experimental parameters.The gradient energy coefficient, κ, determines the influence of the composition gradient

to the total free energy of the domain. The value of κ is difficult to measure experimentally. Though efforts have been made by Saxena and Caneba [18] to estimate the gradient energy coefficient in a ternary polymer system from experimental methods, few experimental results are published for our conditions. Initially, the value of κ can be estimated by the interaction distance between molecules [19],

$$\kappa = \frac{RTa^2}{3v_{site}} \tag{3}$$

where a is the monomer size. A modified equation to calculate κ considering the effects of the composition is reported by Gennes, et al. [20].

$$\kappa_i = \frac{RTa^2}{36v_{site}C_i} \tag{4}$$

where the subscript, i, represents component i.

The mobility is estimated from the diffusivity of the components. The mobility of the polymer blends with long chains can be estimated by the equation as follows [20],

$$M_i = \frac{C_i}{m_i} \frac{D_m N_e v_{site}}{RT} \tag{5}$$

where m_i is the degree of polymerization as stated before, D_m is the diffusivity of the monomer, and N_e is the effective number of monomers per entanglement length. Because of the scarce experimental data for N_e, a more generalized form is employed for our study,

$$M = \frac{Dv_{site}}{RT} \tag{6}$$

The time evolution of the composition of component i can be represented as [5, 20–22],

$$\frac{\partial C_i}{\partial t} = M_{ii} \left[\frac{\partial f}{\partial C_i} - \frac{\partial f}{\partial C_3} - 2\kappa_{ii}\nabla^2 C_i - 2\kappa_{ij}\nabla^2 C_j \right]$$
$$+ M_{ij} \left[\frac{\partial f}{\partial C_j} - \frac{\partial f}{\partial C_3} - 2\kappa_{ji}\nabla^2 C_i - 2\kappa_{jj}\nabla^2 C_j \right] \tag{7}$$

where the subscripts i and j represent components 1 and 2, and

$$M_{ii} = (1 - \overline{C}_i)^2 M_i + \overline{C}_i^2 \sum_{j \neq i} M_j \qquad i = 1, 2; j = 1, 2, 3$$

$$M_{ij} = - \sum_{i \neq j} \left[(1 - \overline{C}_i)\overline{C}_j \right] M_i + \overline{C}_i\overline{C}_j M_3 \qquad i = 1, 2; j = 1, 2 \tag{8}$$

where $\overline{C}_i$ is the average composition of component i. To simplify the solution of Equation 7, $\kappa_{ii} = \kappa_i + \kappa_3$, and $\kappa_{12} = \kappa_{21} = \kappa_3$, where κ_i is the gradient energy coefficient in Equation 3.

For detailed discussion and practical scientific cases with this software can be found in our previous works [22–24].

The MATLAB Program for Simulation of Polymer Phase Separation

Design Principles

The program is developed in MATLAB m-code. A graphical user interface (GUI) is implemented in the program created with MATLAB GUI editor. MATLAB is widely used in scientific computation and has many toolkits and commonly used mathematical functionalities. But implementing the software in MATLAB the efficiency of development is greatly improved. Also, by developing the program in MATLAB, the program is cross platform.

The software is designed for daily usage of simulation and experiment scientists. The program is light weighted and programmed with high computation efficiency so that it can produce significant science results in a common PC. It also extensible to a parallel version or implement code to use the high computation performance of GPU. The GUI is implemented so that the users can conveniently input the experiment parameters. The results as well as the user settings can be saved and revisited by the program. Also, for better assistance to a real productive environment, the simulation model is carefully designed, so that the users provide the real processing and material parameters and the program will produce quantitative results comparable to experimental results. Analytical tools are also provided with the program for post-processing of the results.

Numerical Methods

To solve the partial differential equation, the discrete cosine transform spectral method is employed. The discrete cosine transform (DCT) is applied to the right hand side and left hand side of Equation 7. The partial differential equation in the ordinary space then transformed into an ordinary differential equation in frequency space. When the ODE in frequency space then is solved, the results are transformed back to the ordinary space.

Comparing to conventional finite element method, the spectral method is more efficient and accurate. This method enabled the program to solve the equation in a reasonable computation time to investigate the changes of the phase separation during an real time span long enough to observe the phase evolution. The spectral method is only applied to the spatial coordinates since the time length of the evolution is not predictable. Actually the real time for phase evolution is usually one of the major concerns as the result of the simulation.

The DCT takes a considerable portion of the computation time. Especially

in a 3-dimensional numerical model, the 3-dimensional DCT function with conventional approach has a complexity of $O(n^3)$, which can not be practical for real application on a PC. To overcome this computational difficulty, the code can either be translated to C code embedded in MATLAB m scripts, or a different mathematical approach can be implemented as well. In this program, the DCT is calculated from the fast Fourier transform (FFT) which is optimized in MATLAB.

Quantitative Simulation with Real Experimental Parameters

Many of previous numerical simulations in the self-assembly with polymer blends phase separation are qualitative other than quantitative. The results can only be used to provide non-quantitative suggestions to the experiments. While this program implemented a numerical model which quantitatively simulates the experimental results with the real processing and material parameters. Most of inputs in to this program can be directly measured and read from the instrument or material labels. For some of the physical parameters such as κ and the mobility, the program can provide a start value from the calculation with the theoretical model. The user may need to validate the value by comparing the simulation results to the experimental results. Eventually, a more accurate estimation can be find with optimization methods by setting the difference between the simulation and experiment results as the cost function.

Besides the parameters in Cahn-Hilliard equation, other effects such as the evaporation, substrate functionalization, and the degree of polymerization are also implemented with the real conditions. The final results are saved and summarized. The characteristic length of result pattern from simulation and its compatibility with the substrate functionalization are calculated. These numbers can be used to compare with the experimental results.

Data Visualization and Results Analysis

When running the program, the message from the software will be output to the working console of MATLAB. The messages will show the current state and real time results of the simulation. Also, when the simulation is started, the phase pattern will be plotted in a real time plot window. Users can set the frequency of real time plot and the scale factor on the domain of the contour plot in the GUI. The results of the simulation will be saved to a folder designated by the user. The real time plot will be saved to the result folder. The quantitative results will be saved as several comma separated values (CSV) text files. The result folder can be loaded into the analysis toolkit of the program and the user can view the assessment values such as the characteristic length, the compatibility parameters, and the composition profile wave in depth direction with convenient plotting tools. Usually these results such as the composition profile in each direction in the domain are difficult to observe in experiment results.

Examples

To demonstrate the capability of this program, example simulation cases are shown in this paper. The results of numerical simulation have been validated with the experimental results in our previous work [12]. To compare the simulated results with a real experimental system, we directed the morphologies of polystyrene (PS) / polyacrylic acid (PAA) blends using chemically heterogeneous patterns. More specifically, alkanethiols with different chemical functionalities were patterned by electron beam lithography, which were then used to direct the assembly of PS/PAA blends during the spin coating from their mutual solvent [25]. The experimental conditions are implemented into the numerical simulation. The effects such as the substrate functionalization and the solvent evaporation are involved in the numerical modeling. The parameters
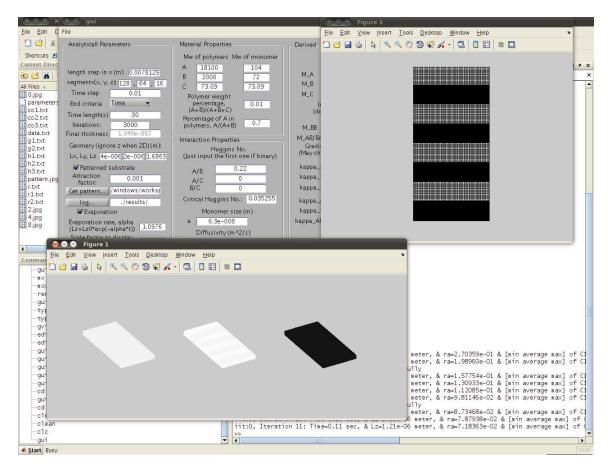
Figure 2: The simulation is running with the real time plot of the current ternary phase morphology.

difficult to measure are acquired with the optimization methods [22].

Sophisticated techniques are required to investigate the composition profile in the depth of the polymer film [26]. While the numerical simulation results can provide the composition profile in each position of the file, the composition profile change in depth direction can be easily accessed. To investigate the composition wave allow the direction perpendicular to the film surface, a thick film is implemented to the numerical simulation. This kind of film is not only difficult to fabricate and characterize in experiments, however in the numerical modeling, the user only needs to change the mesh grid domain size. The depth profiles with different substrate functionalization are shown in Figure 3, where $|f_s|$ denotes the surface energy term from the substrate functionalization. This

term will be added to the total free energy on the interface of the polymer film and the substrate. The initial thickness of the film is 1 mm and decreases to 8 μm due to the evaporation of the solvent. The thickness results are scaled by 0.5 to fit in the figures. It can be seen that a higher surface interaction force can result in a faster substrate directed phase separation in the film. A stronger substrate interface attraction force can direct the phase separation morphology near the substrate surface. While with a lower surface energy, the phase separation dynamics in the bulk of the film overcomes the substrate attraction force. It can be seen that at 30 seconds, the substrate functionalization has little effects on the morphology on the substrate surface. Also, the checker board structure can be seen near the substrate surface with a higher surface energy [11].

To investigate the effects of a more complicated pattern, a larger domain is simulated. The pattern on the substrate applied on the substrate surface is shown in Figure 4. The substrate pattern is designed to investigate the effects of various shapes and contains components such as squares, circles, and dead end lines in different sizes. The initial surface dimensions of the model are changed to $12\mu m \times 12\mu m$. The initial thickness of the film is 1mm and shrinks during the solvent evaporation. The elements in the modelling is $384\times384\times16$. The average composition ratio of PS/PAA is changed to 38/62 to match the pattern. The result patterns from the simulation can be seen in Figure 5.

It can be seen that in a larger domain with complicated substrate patterns, the attraction factor has to be increased to obtain a better replication. In general, the increase of the attraction factor will increase the refinement of the pattern according to the substrate pattern. But since the substrate pattern has geometrical features in different sizes, the attraction factor has to be strong enough to force the intrinsic phase separation with unified characteristic length to match the substrate pattern in different sizes. This would be the main challenge to the replication of complicated patterns. It has been reported

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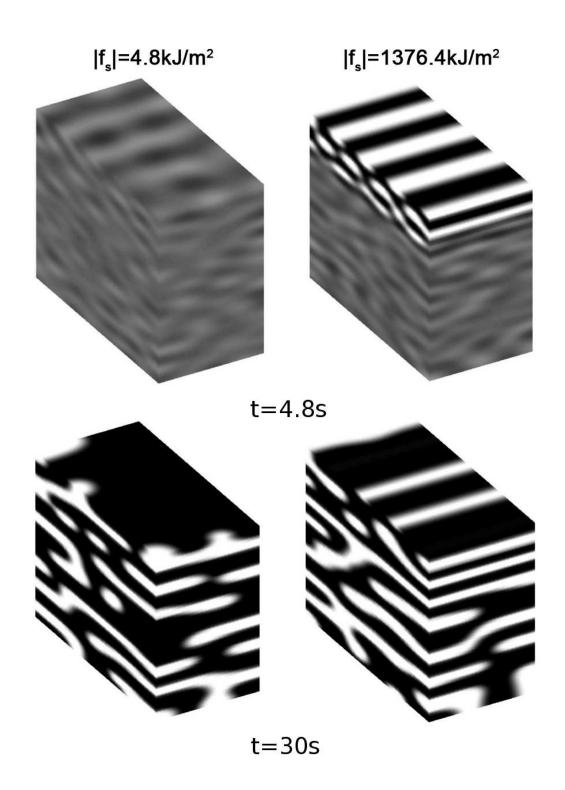|f$_s$|=4.8kJ/m² |f$_s$|=1376.4kJ/m²

t=4.8s

t=30s

Figure 3: The phase separation in a thick film.

Figure 4: The substrate pattern with complicated features.

by Ming et. al. [25] that the addition of the copolymer can improve the refinement of the final patterns in experiments. The reason is that the PAA-b-PS block copolymer will concentrate in the interface of the PS and PAA domains in the phase separation, therefore decreasing the mixing free energy. Fundamentally, the addition of the block copolymer increased the miscibility of the two polymers. To simulate these phenomena, the Flory-Huggins interaction parameter is decreased from 0.22 to 0.1 to increase the miscibility of PS/PAA

|f_s|=4.8kJ/m² |f_s|=137.8kJ/m² |f_s|=1378.4kJ/m²

|f_s|=13764.9kJ/m² |f_s|=13764.9kJ/m² with copolymers
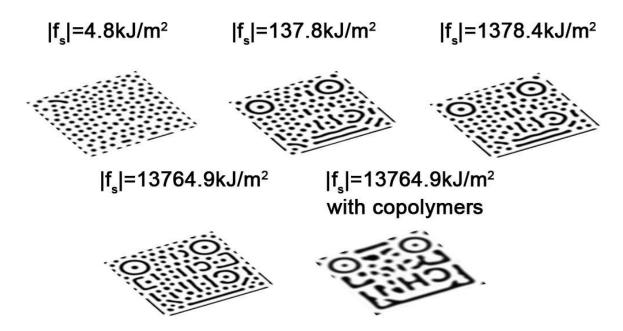
Figure 5: The effects of complicated substrate patterns.

in the modelling. The result pattern is also shown in Figure 5, in comparison to the cases without the addition of block copolymers. It can be seen that the refinement of the phase separated pattern is improved by the addition of the block copolymer. The C_s values of the phase separation with complicated patten are measured and plotted in Figure 6.

A assessment parameter, C_s, the compatibility parameter is introduced to evaluate the replication of the morphology to the substrate pattern, where a higher C_s value denotes a better replication of the polymer film morphology according to the substrate pattern It can be seen in Figure 6 that the C_s value for the system with block copolymer is 7.69E-01, which is higher than the system without the block copolymer when attraction forces are the same. The decrease of the Flory-Huggins interaction parameter increases the miscibility of the polymers, which will decrease the miscibility gap of the polymers, as can be seen in Equation 2. The two phase at equilibrium will be less concentrated in different types of polymer. This is an issue may need to be concerned when the interaction parameter of the two polymers is changed.
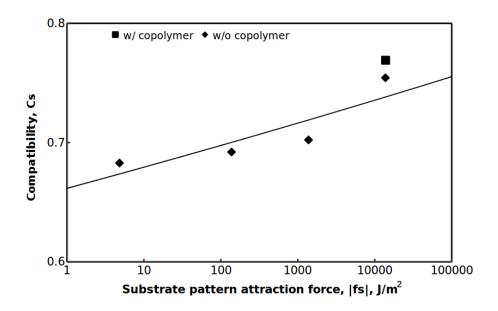
Figure 6: The effects of complicated substrate patterns.

Conclusion

A computer program for simulation of polymer self-assembly with phase separation is introduced. The program is developed in MATLAB m code and designed to assist the scientists in real working environments. The program is able to simulate the experiment results quantitatively with real experimental parameters. The unmeasurable physical parameters such as the gradient energy coefficient and the mobility can be estimated with the program. The program provides a graphical user interface and analytical toolkits. This program can help the scientists in research in polymer phase separation mechanisms and dynamics with high efficiency, convenience of usage, quantitative results analysis,

and validated reliability.

Acknowledgement

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