



Mathematical Modelling and Phase Separation Kinetics of Polystyrene/Polyvinylmethylether Blend

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ABSTRACT

A mathematical model based on the Cahn-Hilliard non-linear theory of phase separation has been developed. The model equation has been solved using a discrete cosine transform spectrum method to provide dynamic spatial concentration field of a polymer blend and predicting the morphology evolution during the course of a temperature-induced phase separation process. The model shows an accurate qualitative agreement with experimental observation using parameters of the polystyrene/polyvinylmethylether blend and different initial concentrations of the blend have been tested in relation to the microstructure, transient and later stages of blend morphologies. It has been observed that kinetics and morphology of the phase separated blend are affected by the initial concentration of the blend. In this study, different types of microstructures, e.g., droplet-like and rod-like morphologies have been identified. It is concluded that the initial concentration of each component of the blend and temperature are the most important variables which control the kinetics of phase separation and blend morphology. The mathematical model provides a suitable tool for better understanding of the kinetics and phase separation process as well as the microstructure of the polymer blends. The discrete cosine transform method for solving a high non-linear partial differential equation is considered as a suitable numerical approach where the other conventional mathematical numerical methods such as finite element and finite volume methods require many computational facilities. The model is very useful for studies of the early and later stages of phase separation process and provides information on concentration profile of the separated phases which would be useful in the determination of the interfacial properties.

Key Words:

Cahn-Hilliard theory;
mathematical modelling;
phase separation;
polymer blends;
spinodal decomposition.

INTRODUCTION

Polymer blends are a very important class of engineering materials with specialized applications [1,2]. Different types of polymer and their combinations introduce a broad variety of polymer blends with very diverse mechanical and physical properties [3,4]. Polymer blend performance depends on the morphology of the blend and it is

important to address the desired structure by selecting a suitable polymer type and grade and the processing methods [4,5].

In most processes for manufacturing polymer blends, usually, two polymers would be mixed and melted to meet the required properties. The degree of miscibility of the two polymers at molten state,

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their compatibility and also the quenching procedure determine the formation, structure, properties and application of the polymer blend.

In a lower-critical-solution-temperature (LSCT) blend, temperature increase leads to separation of two miscible or partially miscible polymers into two distinct domains where the process is called temperature-induced phase separation (TIPS) [6]. The morphology of the final polymer blend is either a droplet-matrix structure (in which droplet-like region of one phase may be dispersed in the matrix or in the continuous region of the other phase) or a bicontinuous of rod-like regions, a morphology constituted of two coexisting polymer phases [6].

Several research works have been focused to explore experimentally and determine the extent of compatibility of polymer blends [7-9], morphology evolution [10-12], final properties [13,14], and the effects of operation variables such as temperature and concentration on polymer blends [15-18]. However, it is interesting to develop a quantitative realistic model to predict the polymer blend system, capture the desired morphology and at best to control the extent of phase separation.

The Cahn-Hilliard non-linear theory has been successfully used for quantitative simulation of the dynamics of temperature-induced phase separation of polymer blends [7,10,11] and polymer solutions [16-18]. The challenge has been the complexity of the mathematical procedure for solution of the fourth order Cahn-Hilliard differential equation. In addition, another important aspect is the use of appropriate form of free energy function for polymer blends. If the densities of the two polymers do not differ, the incompressibility assumption holds true and the well-known Flory-Huggins lattice model of polymers may be successfully applied [8].

There are some research works on modelling of phase separation of polymer blends but many of them are limited to the use of properties related to symmetrical blends in which the chain length of the two polymers are quite equivalent [7]. In blending, using two polymers with different chain lengths or different molecular weights as an unsymmetrical blend, would build a phase diagram of the blends skewed towards one polymer concentration, creating some complexities in the numerical calculation

of the spatial concentrations. Thus, the theoretical description of the polymer blend phase separations with respect to the real life polymer behaviour is industrially and academically essential.

The aim of this work is to provide a mathematical framework to model the dynamic behaviour of temperature-induced phase separation of unsymmetrical polymer blends.

MODELLING

According to the Cahn-Hilliard theory [10,11] for a blend of two polymers A and B, the total free energy as the sum of both homogeneous and non-homogeneous parts is as follows:

$$F(\phi) = \int_V [f(\phi) + \frac{\kappa}{2}(\nabla\phi)^2] dV \quad (1)$$

where, ϕ is volume fraction of polymer A, $f(\phi)$ is homogeneous part of free energy, and κ is concentration gradient coefficient. The non-linear Cahn-Hilliard expresses the component diffusion mass balance during phase separation process by the following equation:

$$\frac{\partial\phi}{\partial t} = M\nabla^2 \left(\frac{\partial f(\phi)}{\partial\phi} - \kappa\nabla^2\phi \right) \quad (2)$$

where, M the mobility of species which is assumed to be constant. For polymer blends, the gradient energy coefficient is concentration dependent, but for a symmetrical blend, this coefficient may be reasonably assumed to be constant. The homogeneous part of the free energy for a blend of two polymers can be successfully expressed by Flory-Huggins lattice model of free energy as follows:

$$f(\phi) = \frac{k_B T}{v} \left[\frac{\phi}{N_A} \ln\phi + \frac{1-\phi}{N_B} \ln(1-\phi) + \chi\phi(1-\phi) \right] \quad (3)$$

where, k_B is Boltzmann constant, v is cell volume, N_A and N_B are the chain lengths of the polymers A and B, and χ is the interaction parameter between segments of A and B, respectively. The interaction parameter may be a function of both temperature and con-

centration to fit the experimental data of the polymer blend phase equilibrium. Using the following scaling terms:

$$\tau = \frac{k_B T / \nu}{L^2 / M} \quad (4a)$$

$$\bar{\nabla} = L \nabla \quad (4b)$$

Eqn (2) can be represented in dimensionless format as presented in eqn (5):

$$\frac{\partial \phi}{\partial \tau} = \nabla^2 [A(\phi) - \varepsilon^2 \nabla^2 \phi] \quad (5)$$

where,

$$\varepsilon^2 = \frac{\kappa / L^2}{k_B T / \nu} \quad (6)$$

The ε term in eqn (6) is the capillary number and it is the ratio of interface energy to homogeneous free energy and controls the microstructure of the separated phases. The $A(\phi)$ is the first derivative of free energy function as given:

$$A(\phi) = \frac{1}{N_A} \ln \phi - \frac{1}{N_B} \ln(1 - \phi) + \frac{1}{N_A} - \frac{1}{N_B} + \chi(1 - 2\phi) \quad (7)$$

The solution of eqn (5) with appropriate boundary and initial conditions provides the concentration field which describes the microstructure. The conventional boundary condition for phase separating system is zero mass flux as: $\nabla \phi = 0$, and $\nabla^3 \phi = 0$, which is suitable in the study of specified simulation box in a phase separating domain. The initial condition is mathematically expressed in form of concentration fluctuations around the initial concentration.

Solution Method

Eqn (5) is a fourth order dynamic PDE whose solution provides the concentration field changes with time. The finite differences methods are fast and feasible but suffer from instability in time, while finite element methods provide stable convergent solution but require computational facilities. A very robust numerical procedure to provide accurate reliable

numerical information is always demanding.

Eyre [19] and Stuart [20] proposed an efficient theory for solving initial value problems based on the spectral method which ensures the convergence and stability of time explicit methods on the dynamic term and uses a discrete cosine transform (DCT) algorithm. The DCT maps the discrete concentration field to a discrete wave domain similar to Fourier transform. A two-dimensional discrete cosine transformation of a concentration $\phi(n_1, n_2)$ in a two-dimensional field may be mapped to a point $\Phi(k_1, k_2)$ of wave domain according to:

$$\Phi(k_1, k_2) = \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \phi(n_1, n_2) \times \cos\left[\frac{\pi k_1 (2n_1 + 1)}{2N_1}\right] \times \cos\left[\frac{\pi k_2 (2n_2 + 1)}{2N_2}\right] \quad (8)$$

where, N_1 and N_2 are the number of points in each direction in wave domain. We used a time explicit finite difference scheme by applying the discrete cosine transform on eqn (5). The DCT projected PDE has been converted to a set of algebraic equations, and then the results are projected to the concentration field by applying the inverse DCT method.

RESULTS AND DISCUSSION

A 2D square 256×256 grid domain has been selected to solve the Cahn-Hilliard equation. To examine the capability of the model, the properties of an industrially relevant polymer blend system have been used. The blends of polystyrene (PS) and polyvinylmethylether (PVME) have been extensively studied experimentally to investigate the different characteristics of polymer blends [21-26]. The parameters used in the model and sample polymer blend are presented in Table 1 for polystyrene and polyvinylmethylether blend [26].

Figure 1 shows the temperature-concentration phase diagram of the PS/PVME blend using the parameters shown in Table 1. The phase diagram shows a one homogeneous phase, stable below the critical temperature which separates into two

Table 1. Parameters and properties of the PS/PVME blend [26].

Point	1	2	3
ϕ_0	0.1	0.2	0.4
T_0 (°C)	130	120	140
χ	0.0026	0.0021	0.0024
ϕ_a	0.018	0.011	0.007
ϕ_b	0.700	0.760	0.799
ϕ_c	0.20		
T_c (°C)	86.26		
M_{ps}	200 (kg/mol)		
M_{pvme}	51,5 (kg/mol)		
ε	0.005		

ϕ_a and ϕ_b , are lower and upper binodal concentrations, ϕ_c and T_c are critical concentration and temperature, M_{ps} and M_{pvme} are molecular weights of polystyrene and polyvinylmethylether, ϕ_0 and T_0 are the initial concentration and temperature of the phase separated system, and χ is the Flory-Huggins interaction parameter.

equilibrium phases upon temperature increase. The LCST behaviour is very common in the majority of polymer blends. The phase diagram of Figure 1 has been drawn by using classical standard method for determination of the phase diagram, where, the chemical potentials of both polymers A and B must be equal in two equilibrium phases [4,21,25].

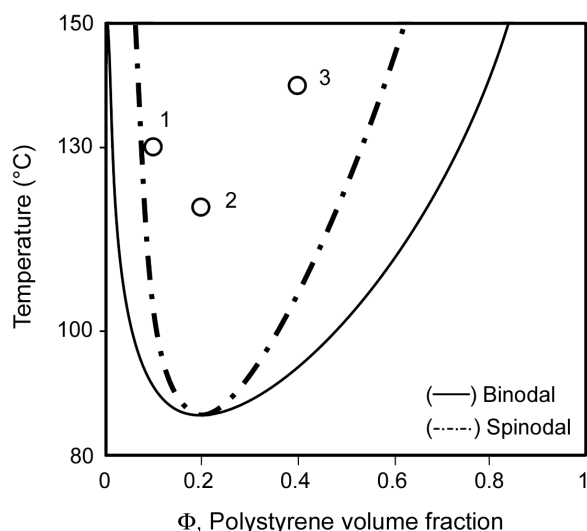


Figure 1. The phase diagram of PS/PVME blend system, three points 1, 2, and 3 are in unstable region.

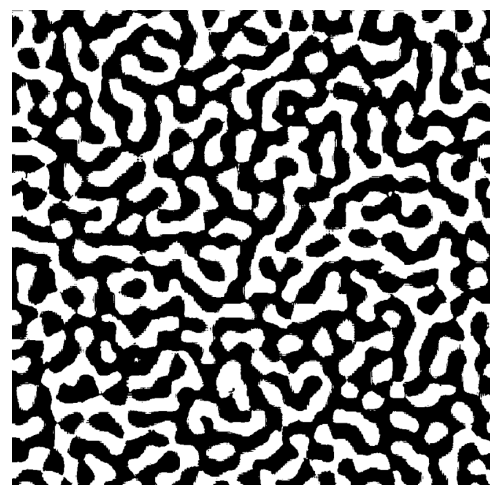
As it is clearly shown, the diagram of the phases is unsymmetrical and skewed towards a lean polystyrene phase. We studied the kinetics of phases separation of PS/PVME blend at three different temperatures and concentration points (namely 1, 2, and 3) where 1 and 3 were off-critical and 2 was the on-critical points. All temperature-concentration points are specified in the spinodal unstable region. In each phase separation process, at specified temperature, the polymer blend separates into two equilibrium phases at the same temperature to reach the binodal concentrations.

Figure 2 shows a 2D presentation of the dynamic phase separation as microstructural evolution of a PS/PVME blend at the initial concentration of 0.2 (dimensionless) and at temperature of 120°C namely an on-critical quench. The phase separation is represented by sudden appearance of individual microdomains of two phases followed by growth due to coalescence of merging domains until late stages of phase separation. As it is shown, at first the size of the droplets are very small but as the phase separation proceeds, the size of macrodomains or droplets increases until the concentration of phases reach the binodal values. The results of Figure 2 shows qualitative agreement with experimental observations for the PS/PVME blend [21,24-27].

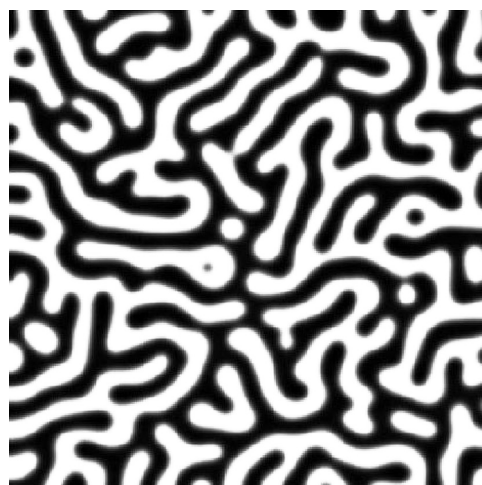
To follow the progress of phase separation with time qualitatively, the extent of phase separation may be defined as:

$$\lambda = \left\langle \frac{\phi_{ij} - \phi_0}{\phi_e - \phi_0} \right\rangle \tag{9}$$

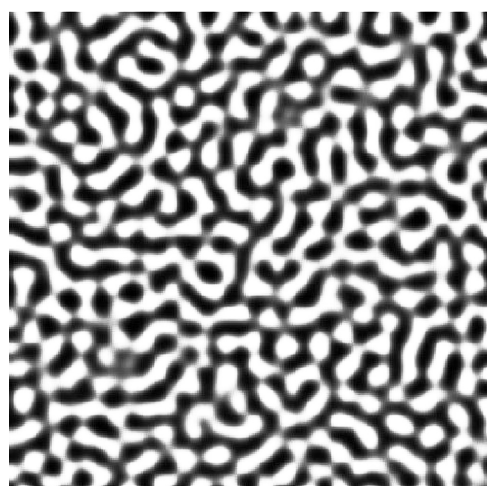
where, λ is the extent of phase separation, and ϕ_{ij} , ϕ_0 , and ϕ_e are concentrations of polystyrene (PS) at point (i,j) in the 2D domain, initial concentration, and binodal concentration of the either phases, respectively. The value of the extent of phase separation theoretically starts from zero (where all points have initial concentration ϕ_0) and reaches the value of unit at the final stages of phase separation when each point has the binodal concentration value. However, due to the presence of smooth diffusive interface between two equilibrium phases, the extent of phase separation never reaches the unit value.



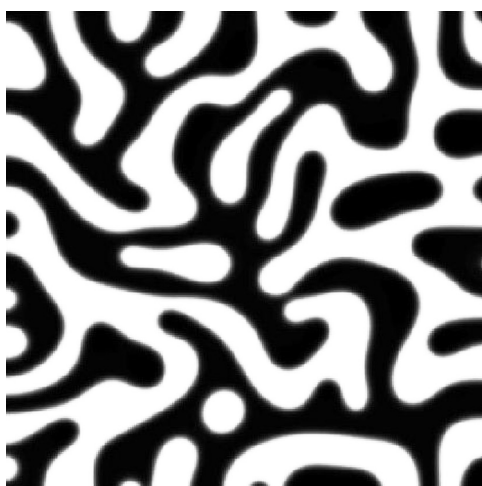
(a)



(d)



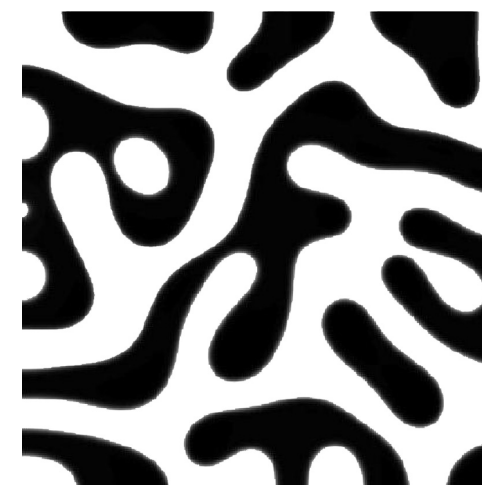
(b)



(e)



(c)



(f)

Figure 2. The dynamic morphologies of PS/PVME blend at different dimensionless times of: (a) 0.15, (b) 0.5, (c) 1, (d) 1.5, (e) 3, and (f) 7.5×10^{-3} .

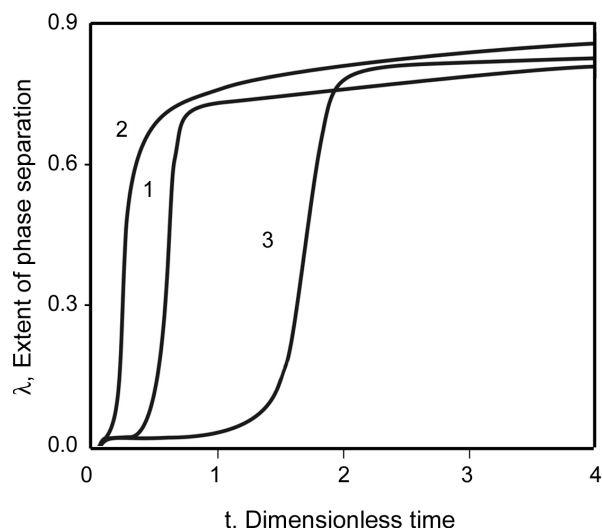
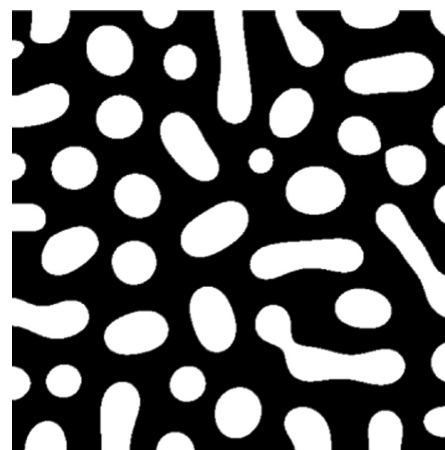


Figure 3. The extent of phase separation as a function of time for three concentration-temperature points.

Figure 3 shows the values of the extent of phase separation for three different phases separating systems at concentration points 1, 2, and 3 corresponding to Figure 1. As it is shown, the extent of phase separation suddenly increases to a very high value and experiences a constant low slope increase or a plateau until the final stage of phase separation. Figure 3 shows that the fastest phase separation happens at the critical point, while for off-critical quenches the phase separation takes longer time. Due to the skewness of the phase diagram towards lower polystyrene concentrations, the off-critical phase separation with concentration lower than the critical point happens sooner and takes less time than the phase separation with concentration higher than the critical point. This is a suitable outcome of the model and confirms that for very quick and fast temperature-induced phase separation the critical point is the most suitable concentration point.

To study the effect of initial concentration on the dynamics of phase separation, we investigate the phase separation upon temperature increase for different concentration-temperature points. Figure 4 shows the late stage morphologies of the PS/PVME blend system for initial concentration values of $\phi_0 = 0.1, 0.2,$ and 0.4 corresponding to the three points specified by 1, 2, and 3 in Figure 1. As it is shown at point 1 with the initial concentration less than the critical one, the final structure is the droplet-like



(a)



(b)



(c)

Figure 4. The final morphology of phase separated PS/PVME blend with initial concentrations of (a) 0.1, (b) 0.2, and (c) 0.4 corresponding to points 1, 2, and 3 in Figure 1.

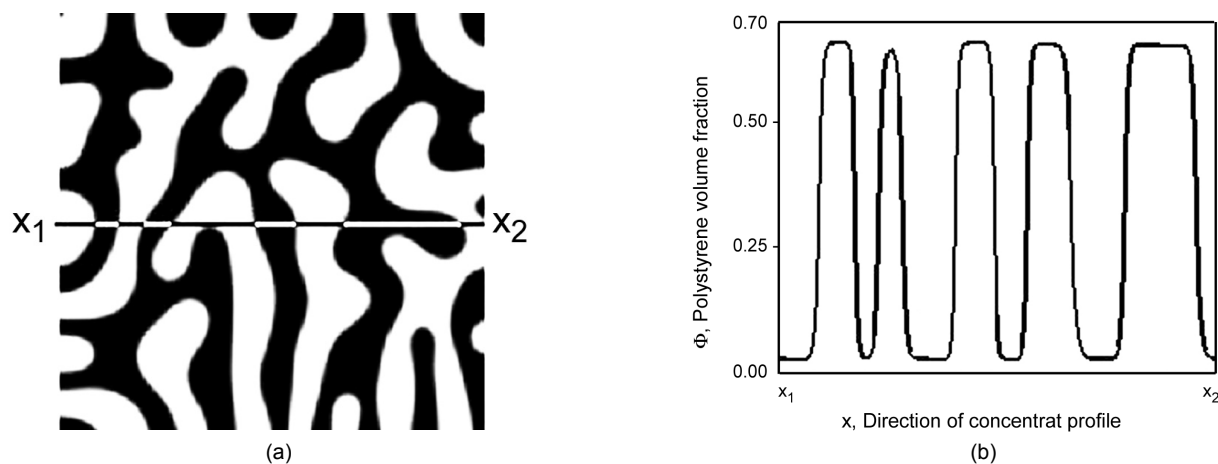


Figure 5. (a) 2D representation of phase separated PS/PVME blend system and (b) concentration profile along the line x_1x_2 in 2D representation.

morphology in which the droplets of polystyrene lean phase (light regions) are dispersed in a continuous rich polystyrene phase (dark regions).

As the initial concentration of polystyrene in blend increases, the droplets of dispersed phase merge together to form larger clusters until at the critical concentration, point 2, a bicontinuous morphology is evolved in which the large infinite clusters of two equilibrium phases are presented and entangled with each other. The bicontinuous or percolation morphology is a characteristic of the on-critical temperature-induced phase separation. As the initial concentration further increases, point 3, the late stage morphology is a droplet type again, but in this case, the droplets of the polystyrene rich phase (dark regions) are dispersed in a continuous matrix of polystyrene lean phase (light regions). The behaviour shown in Figure 4 confirms that the initial concentration of a blend is a key factor to control the final blend microstructure in achieving the desired or specified structural properties. The model is also capable of providing information on the interfacial properties between two equilibrium phases at the final stages of the phase separation.

Figure 5a shows late stage morphology of PS/PVME blend at a typical concentration. One can track the concentration profile at any desired path such as line x_1x_2 . Figure 5b shows the concentration profile along the horizontal line x_1x_2 . The concentration profile experiences alternate lower and higher binodal concentrations through the light and dark regions, or polystyrene lean and polystyrene

rich-region, respectively. The concentration profile between two equilibrium phases provides useful information on the value of the interfacial tension as a measure of the thickness of interface region.

CONCLUSION

A dynamic mathematical model for studying the kinetics of phase separation upon temperature changes in phase separation of a polymer blend of PS/PVME which has been developed and solved by using the discrete cosine transform method to predict the microstructure evolution of phase separated blend. The model provides results for the formation of different morphologies based on different values of parameters such as initial concentration of the blends. This also offers a tool to control the microstructure or to determine the morphology suitable for required structural properties and applications. The model provides additional information on the interfacial properties, e.g., interfacial tension and the thickness of the interface between the two equilibrium phases which may serve to control the structural properties of polymer blends quantitatively and qualitatively.

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