External potential dynamics simulation of the compatibility of T-shaped graft copolymer compatibilizing two immiscible homopolymers

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Abstract: The compatibilizing effect of T-shaped graft copolymers between two incompatible homopolymers A and B was studied by using the external potential dynamics (EPD) method based on dynamic self-consistent field theory. We specifically focus on the role of the concentration and the junction position of the graft copolymer on the compatibility. The blend containing compatibilizers exhibits slow dynamics during the phase separation. We observed that the compatibilizers are particularly efficient when the graft point is close to the free end of the backbone chain.

Introduction

It is well known that blending two or more homopolymers can markedly improve the mechanical properties of polymeric materials, such as their stiffness and toughness [1]. Unfortunately, in most cases, homopolymers are normally immiscible and the blends of them will separate into macroscopic domains because of the small mixing entropy [2, 3]. Incompatible blends with these macroscopic phase-separated regions often exhibit poor mechanical properties. Considerable attention has been focused on the block copolymer as compatibilizers to increase the miscibility and to control the dispersion within the past decades [4-11]. However, block copolymers are relatively expensive to be synthesized, which limits the practical application of block copolymers as compatibilizer in a large amount. Comparing with block copolymers, graft copolymers can be used as effective compatibilizers with low costs of the synthesis [1].

It is demonstrated that graft copolymer as compatibilizer can localize at the interface between immiscible homopolymers, acting as a surfactant, reduce the interfacial tension and disperse the incompatible polymers into smaller domains effectively [12-23]. Oomen et al. studied the morphology and properties of heterogeneous poly(methyl methacrylate)/natural rubber blends by the addition of a graft copolymer of natural rubber and poly(methyl methacrylate) (NR-g-PMMA). A sharp decrease in the dispersed domain size and an increase of interfacial adhesion were observed by the addition of a few percent of the copolymer [12]. Feng et al. investigated the compatibilizing effect of polyethylene-g-polystyrene (LLDPE-g-PS) on immiscible LLDPE/PS blends. Their results indicated that LLDPE-g-PS is an effective compatibilizer for LLDPE/PS blends, and the compatibilizing effect of LLDPE-g-PS on LLDPE/PS blends depends on the PS grafting yield and molecular structure of the
compatibilizers and also on the composition of the blends [13]. Moreover, some research groups used PE-g-SBH, where the SBH is a semiflexible copolyester synthesized by the melt polycondensation of sebacic acid (S), 4,4’-dihydroxybiphenyl (B), and 4-acetoxybenzoic acid (H), to compatibilize the immiscible PE/SBH blends [14-16]. Chuayjuljit et al. chose the polystyrene grafted natural rubber copolymers (NR-g-PS) as the compatibilizer to compatibilize the natural rubber/polystyrene(NR/PS) blend [21]. Lucia et al. suggested that the compatibility of PP/PS blends with PP-g-PS copolymer as compatibilizer is improved with increasing either the PP sequences length or the PS side chains length or the number of the side chains [23].

Theoretically, Monte Carlo (MC) simulation method has been used to study polymer blends with graft copolymers [24-26]. Zhu et al. employed the Monte Carlo method to study the compatibility of incompatible A/B blends by introducing graft copolymer(A-g-B or B-g-A) and found that A-g-B copolymer was more effective than B-g-A copolymer to compatibilize the blend if homopolymer A formed dispersed phase. Another powerful technique for characterizing polymeric blends is self-consistent field theory (SCFT) [27-33]. Anna C. Balazs et al. investigated the compatibilizing activity of linear block copolymers, branched copolymers and copolymer mixtures using the SCFT and an analytical theory [3, 31-33]. Although SCFT is suitable for exploring equilibrium morphologies, it is limited for studying the dynamic process of phase separation of blends. In this paper, external potential dynamics (EPD) [34-38] which can give a realistic dynamical process of phase separation was applied to study the compatibility of graft copolymers. The purpose is to shed light on the effect of the concentration and junction position of the simple T-shaped graft copolymer.

**Model and theory**

We consider a system with volume \( V \), containing T-shaped graft copolymers, homopolymers A and homopolymers B. The schematic picture of the graft copolymer molecule is presented in Fig. 1. The length of the graft copolymer and homopolymer is \( N \) and \( N_H \), respectively. The volume fraction of segments A in the copolymer is \( f \).

The degree of polymerization of A chains \( N_A = N_{A1} + N_{A2} = fN \). The graft point is determined by \( \tau \) given by \( \tau = N_H / N_A \). If \( \tau = 0 \), the graft point is at the end of the linear chain, whereas the graft point is at the middle of the linear chain if \( \tau = 0.5 \). We scale distances by the Gaussian radius of gyration of the graft copolymer, \( R_g = a(N/6)^{1/2} \).

The monomer statistical Kuhn length \( a \) and the bulk monomer density \( \rho_0 \) are assumed to be the same for all chemical species.

![Fig. 1. Molecular architecture of a T-shaped graft copolymer. Black and gray lines represent backbone chain A and side chain B, respectively.](image-url)
The free energy (in the units of $K_B T$) of the blend is given by:

$$F = - \sum_{k,a,C,HA,HB} f_k \ln \frac{Q_k}{f_k V} - \frac{1}{V} \int \! dt \left[ \chi_{AB} N \phi_A(r) \phi_B(r) - \sum_{\alpha=A,B} \omega_{\alpha}(r) \phi_{\alpha}(r) + \frac{K_H}{2} [\phi_A(r) + \phi_B(r) - 1]^2 \right] \tag{1}$$

where $K = C, HA, HB$ represents graft copolymer, homopolymer A and homopolymer B in the blend. $f_k$ is the polymer concentration in the system, $\phi_{\alpha}$ is the monomer density field of species $\alpha$, where $\alpha = A, B$. The Flory-Huggins interaction parameter $\chi_{AB}$ is responsible for repulsion between unlike species, and $K_H$ is the coefficient of compression energy. $\omega_{\alpha}(r)$ is the self-consistent field that conjugates to the density field $\phi_{\alpha}(r)$, and $Q_k = \int dr q(r) N_k$ is the partition function of a single chain in the effective field $\omega_{\alpha}(r)$. The end-segment distribution function $q(r,s)$ gives the probability of finding segment $s$ at position $r$, which satisfies a modified diffusion equation:

$$\frac{\partial q_{ka}(r,s)}{\partial s} = \nabla^2 q_{ka}(r,s) - \omega q_{ka}(r,s) \tag{2}$$

where $\omega$ is $\omega_A$ when $s$ belongs to A, $\omega_B$ when belongs to B. The boundary conditions are periodic and the detailed initial condition is $q_{ka}(r,0) = 1$.

Expressed in terms of $q_k(r,s)$, the density fields can be written:

$$\phi_{ka}(r) = \frac{f_k V}{Q_k} \int_0^{N_{ka}} q_{ka}(r,s) q_{ka}(r,N_{ka} - s) \tag{3}$$

$$\phi_k(r) = \sum_{\alpha=A,B} \phi_{ka}(r) \tag{4}$$

$$\phi_{\alpha}(r) = \sum_{K=C,HA,HB} \phi_{ka}(r) \tag{5}$$

The dynamic equation for density field is:

$$\frac{\partial \phi_{\alpha}(r,t)}{\partial t} = -\sum_{\beta} \int \! dr' M_{\alpha\beta}(r,r') \mu_{\beta}(r') dt' \tag{6}$$

where $M$ is the mobility matrix, and $\mu$ is the intrinsic chemical potential, which is defined by the functional derivatives of free energy: $\mu_{\alpha}(r') \equiv \frac{\delta F}{\delta \phi_{\alpha}(r')}$. Using the Rouse approximation, Eq. (6) can be rewritten:

$$\frac{\partial \phi_{\alpha}(r,t)}{\partial t} = D_{\alpha} \sum_{\beta} \nabla r \cdot \int \! dr' P_{\alpha\beta}(r,r') \nabla r' \mu_{\beta}(r') dt' \tag{7}$$

Here, $P_{\alpha\beta}(r,r')$ are the two-body correlators. Calculating the correlators at every time step is a heavy computational burden. To cure this problem, Fraaije’s group developed a feasible numerical model that incorporates all the important physical features, called the External Potential Dynamics model (EPD) [34]. The kernel of the EPD method is deriving an equation of motion for the auxiliary field $\omega$ from the
dynamics of the density field. It can reduce the computational cost and possesses all the essential physical features of nonlocal kinetic coupling, without calculating $P_{ab}(r,r')$. The two important properties of the density functional theory are as follows:

1) The density functional $\phi_\alpha$ is bijective.

2) The derivative of the density functional with respect to the external potential is the two-body correlator $P_{ab}$:

$$\frac{\delta \phi_\alpha(r)}{\delta \omega_\beta(r')} = -P_{ab}(r,r') \tag{8}$$

From Eq.(8) we have

$$\frac{\partial \phi_\alpha(r,t)}{\partial t} = \sum_\beta \int \frac{\delta \phi_\alpha(r,t)}{\delta \omega_\beta(r',t)} \delta \omega_\beta(r',t) \, dr'$$

$$= -\sum_\beta \int P_{ab}(r,r') \frac{\partial \omega_\beta(r',t)}{\partial t} \, dr' \tag{9}$$

With this result and Eq.(7), the following equation could be obtained.

$$\sum_\beta \int P_{ab}(r,r') \frac{\partial \omega_\beta(r',t)}{\partial t} \, dr' = -D_{\alpha} \sum_\beta \nabla_r \cdot \left( \int P_{ab}(r,r') \nabla_r \mu_\beta(r') \, dr' \right) \tag{10}$$

With assumption that the gradients of the two coordinates in the two-body correlators are opposite, one can obtain the final EPD equation:

$$\frac{\partial \omega_\alpha}{\partial t} = -D_{\alpha} \nabla^2 \mu_\alpha = -D_{\alpha} \nabla^2 \left( \frac{\delta F}{\delta \phi_\alpha} \right) \tag{11}$$

where $D_{\alpha}$ is a constant diffusion coefficient. The functional derivative $\delta F/\delta \phi_\alpha$ can be calculated from Eq. (1), giving

$$\frac{\delta F}{\delta \phi_A} = \chi_{AB} \phi_B + \kappa_H (\phi_A + \phi_B - 1) - \omega_A \tag{12}$$

$$\frac{\delta F}{\delta \phi_B} = \chi'_{AB} \phi_A + \kappa_H (\phi_A + \phi_B - 1) - \omega_B \tag{13}$$

Then, the set of equations 2, 3, and 11 can be conveniently solved by a simple time iteration method.

**Results and discussion**

The phase behavior of blends containing A/B homopolymers and A-g-B graft copolymers is controlled by a large number of parameters, such as the molecular weights of the polymers, the composition of the blend and the interaction parameters between different species. We simplified the parameter space for focusing on the compatibility of the graft copolymer as follows: the chain length of graft copolymer was $N = 180$, the average volume fraction of species A was $f = 0.5$. Here, we
specified the length of homopolymers, $N_H$, which was set to 60 for both the A and B chains. The concentration ratio of homopolymers A to homopolymers B was 1:3, thus homopolymers A formed the dispersed phase while homopolymers B formed the matrix. The Flory-Huggins interaction parameter $\chi_{AB}$ was 0.05, and the diffusion coefficients were $D_A = D_B = 0.3$. The compressibility coefficient was chosen to be $\kappa_H = 12.0$. Our simulations were carried out in two dimensional lattice (160×160) with periodic condition. The space grid size is $\Delta x = 0.25$, and time step is $\Delta t = 0.1$.

For comparison with the blend with graft copolymer compatibilizer, we give the domains evolution of the blend without graft copolymers in Fig. 2. The phase domains are considerably large, indicating that the interfacial tension between homopolymers A and B is quite high. However, after introducing graft copolymer into the A/B polymer blends, the domain size of the dispersed phase A is evidently reduced. Fig. 3 shows snapshots of the time evolution of the domain structures with graft copolymer concentration $f_C$ from 0.025 to 0.2. The junction position was fixed at the middle of the backbone chain, i.e. $r = 0.5$. It shows that the graft copolymers locate at the interfaces between the two incompatible homopolymers. By comparing the snapshots of the mixture with varied graft copolymer concentration at a given time, we found that the average domain size is smaller for the mixture with higher graft copolymer concentration. We can thus conclude qualitatively that the domain growth is slower for the blends with higher graft copolymer concentration.

![Fig. 2. Snapshots of the domain structures formed during the phase separation process for the mixture without copolymer. (a) $t = 5\times10^3 \Delta t$; (b) $t = 1\times10^4 \Delta t$; (c) $t = 2\times10^4 \Delta t$; (d) $t = 4\times10^4 \Delta t$. The black and gray areas represent homopolymers A rich region and homopolymers B rich region, respectively.](image1)

For measuring the average domain size of the mixture quantitatively and systematically, we use the definition of average domain size $R(t)$ as follows:

$$R(t) = 2\pi \sum_k S(k,t) \frac{k^2 S(k,t)}{\sum_k k S(k,t)}$$

where $S(k,t)$ is the circularly-averaged structure factor corresponding to the order parameter $\phi(r,t)$. Here, $\phi(r,t) = (\phi_{HA}(r,t) - f_{HA}) - ((\phi_{HB}(r,t) - f_{HB}) + (\phi_C(r,t) - f_C))$.

Fig. 4 shows the variation of the average domain size $R(t)$ with time for the mixture with various graft copolymer concentrations. It is seen that the compatibility efficiency of the graft copolymer can be improved by increasing the copolymer concentration up to 0.175, thereafter it remains briefly unchanged. This can be further confirmed by Fig.5 which gives the average domain size $R$ as a function of the compatibilizer.
concentration $f_c$ at the time $t = 40000\Delta t$. Similar results were found by Retsos et al. [39] for the polyisoprene/polystyrene blend with the addition of the T-shaped graft copolymer of (polyisoprene)$_2$(polystyrene)(I$_2$S). They observed that the interfacial tension decreases with the addition of small amounts of copolymer and reaches a plateau at higher copolymer concentration.

Fig. 3. Snapshots of the domain structures formed during the phase separation process for the mixture with varied graft copolymer concentration at $\tau = 0.5$, $f_c = 0.05$ (column a), 0.1 (column b), 0.15 (column c). Snapshots from top to bottom correspond to times $t = 5 \times 10^3 \Delta t$, $1 \times 10^4 \Delta t$, $2 \times 10^4 \Delta t$, $4 \times 10^4 \Delta t$. The gray, black and light gray areas represent homopolymers A rich region, graft copolymers rich region and homopolymers B rich region, respectively.

To study the effect of the junction position on the compatibility, we fixed the graft copolymer concentration $f_c = 0.1$. Fig. 6 and 7 show the snapshots of the domain patterns and the time dependence of $R(t)$ for the mixture with various values of $\tau$, respectively. It is clear that the average domain size depends on the grafted position. The smaller the value of $\tau$, the smaller is the average domain size. For the purpose of clarity, we show also the average domain size $R$ as a function of $\tau$ at the
time $t = 30000\Delta t$ in Fig. 8. The results indicate that the graft copolymers with small value of $\tau$ (graft position close to the free end of the backbone chain) are more efficient than those with large value of $\tau$. To further study the effect of the graft position on the compatibility, we give a diagram showing the density distributions of various components along the diameter direction of a dispersed domain for $\tau = 0.01$ and $\tau = 0.5$ (Fig. 9). It can be found that the backbone chains of the copolymer tend to diffuse into the dispersed domains, whereas the grafted chains tend to diffuse into the matrix. Moreover, it is seen from Fig. 9 that the lower is the value of $\tau$, the higher is concentration of the copolymers located at the interface. These results indicate that the copolymer with the grafted position close to the end of the backbone chain compatibilizes the two homopolymers more effectively. This means diblock copolymers (i.e. $\tau = 0$) has more effective compatibility than the graft copolymers. Our results are in agreement with the previous studies by A. C. Balazs’s [3, 31]. Their analytical and simulation results indicated that the diblock copolymer is the most efficient compatibilizer among the copolymers with different molecular architectures. Although the diblock copolymer has great compatibilization efficiency than graft copolymer, the graft copolymers have an advantage of lower synthesis costs.

Fig. 4. Time dependence of the average domain size $R(t)$ for the mixture with various graft copolymer concentrations at $\tau = 0.5$.

Fig. 5. The average domain size $R$ as a function of the compatibilizer concentration $f_C$ at time $t = 40000\Delta t$ for the case of $\tau = 0.5$. 
Fig. 6. Snapshots of the domain structures formed during the phase separation process for the mixture with varied value of $\tau$, $\tau = 0.01$ (column a), 0.2 (column b), 0.5 (column c). The graft copolymer concentration was fixed to be 0.1. Snapshots from top to bottom correspond to times $t = 5 \times 10^3 \Delta t$, $1 \times 10^4 \Delta t$, $2 \times 10^4 \Delta t$, $4 \times 10^4 \Delta t$. The gray, black and light gray areas represent homopolymers A rich region, graft copolymers rich region and homopolymers B rich region, respectively.

Fig. 7. Time dependence of the average domain size $R(t)$ at varied value of $\tau$ for the case of $f_c = 0.1$. 

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Fig. 8. The average domain size $R$ as a function of $\tau$ at time $t = 30000\Delta t$ for the case of $f_c = 0.1$.

Fig. 9. Density distributions along the diameter direction of a dispersed domain for $\tau = 0.01$ and $\tau = 0.5$. The copolymer concentration is 0.1.

Fig. 10. Scaled structure factor $F(X)$ for the blends with various values of $\tau$ for $f_c = 0.1$ and $t = 4 \times 10^4 \Delta t$. 
Finally, we use the scaled structure factor \( F(X) = R(t)^{-2} S(k, t) \) to evaluate the dynamic process for the blend with different \( \tau \) at fixed copolymer concentration, i.e. \( f_c = 0.1 \). Here, \( X = kR(t) \) is a scaled wave vector, and \( F \) is the scaling function. It is noted that the dynamical scaling is usually observed in the systems which eventually undergo complete phase separation, and therefore the small length scales become irrelevant. We plotted the scaled structure factor \( F(X) \) for different values of \( \tau \) at the late time \( t = 4 \times 10^4 \Delta t \) in Fig. 10. It is interesting that the functions with different values of \( \tau \) overlap, indicating that \( F(X) \) is a dominating factor for the dynamic process of the present blends.

**Conclusions**

We have studied the compatibilizing effect of graft copolymers between two immiscible homopolymers A and B by using the External Potential Dynamics method. It is found that the content and the junction position of the graft copolymers play important role on the compatibility. The compatibility efficiency of the graft copolymer can be improved by increasing the copolymer concentration up to 0.175. Moreover, the compatibilizers become more effective when the graft point is close to the free end of the backbone chain. Finally, it is found that the scaled structure factor is a dominating factor for the dynamical process of the present blends.

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**References**


