

COALESCENCE INDUCED GRADIENT MORPHOLOGY NEAR A WALL IN PHASE SEPARATED POLYMER BLENDS DURING QUIESCENT ANNEALING*

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Abstract A fast coalescence mechanism is proposed to account for the wall effect on the formation of gradient morphology in phase separated polymer blends during quiescent annealing. The existence of solid wall with high polarity is believed to change the potential field around the dispersed particles near the wall. This additional potential interaction between the solid wall and the dispersed particles causes faster coalescence of the dispersed particles near the wall than in the bulk. The gradient phase morphology thus formed can be predicted by combining the wall-particle interaction and the touch-coalescence mechanism. The effect of interfacial tension on the gradient morphology is also discussed.

Key words Gradient morphology, Wall effect, Coalescence, Polymer blends, Interfacial tension

INTRODUCTION

The morphology of polymer blends depends not only on their rheological properties, but also on processing technology. Annealing is known to be able to coarsen the morphology of dispersed phase and thus the desired morphology can be achieved. Many theoretical^[1–9] and experimental^[8–12] studies have been done to probe the mechanism of coarsening behavior. The generally accepted mechanisms, such as Oswald ripening mechanism^[1–4], “collision-coalescence” mechanism^[5], Fortelný coalescence mechanism^[6, 7] and “touch-coalescence” mechanism^[8, 9], aim to describe the coarsening behavior of blends with spatially uniformly distributed morphology. However, little effort has been invested in the study of the mechanism of formation of gradient morphology near a solid wall.

Recently, Xie *et al.*^[13–16] investigated the gradient morphology in polymer blends, polypropylene/ethylene vinyl acetate (PP/EVAc) and polyethylene/ethylene vinyl acetate (PE/EVAc), formed near a solid wall (glass or polyimide). It was found that a solid wall has a dramatic effect on the morphology of polymer blends. The mean particle radius of dispersed droplets decreases gradually as the distance from the wall increase, forming the gradient morphology. Troian and her co-workers^[17–19] proposed a model to explain the accelerated growth of domains next to a wall. However, their model is of spinodal decomposition explicating the fast coarsening of the domain of a nonwetting phase near a wall coated with wetting phase. As for the fully phase separated binary polymer blends, the model is no longer applicable.

In order to explain the formation of gradient phase morphology in phase separated polymer blends near a solid wall, we will propose a wall-induced fast coalescence mechanism in this paper. This mechanism is based on

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our previous research work on the “touch-coalescence” mechanism^[8, 9] of phase separated polymer blends. Concerning the system Xie *et al.*^[13–15] used, we may expect the formation of gradient morphology as a reflection of the polar interaction between the solid wall with polar properties and the dispersed particles (EVAc). For example, glass surface has two-layer structure^[20]: the inner chemisorbed water layer and outer physisorbed water layer (Fig. 1). This two-layer structure of the absorbed water film can form a polarized zone on the glass surface. The depth of this polarized zone depends on the type of glass and the method of surface treatment. The polar zone can interact with the polar component in polymer blends, such as EVAc in Xie *et al.*’s experiments^[13–16]. In other words, the existence of polar solid wall makes the polar dispersed particles (EVAc here) in an additional potential field besides the original potential field produced by nearby particles. Comparatively, this original potential field arising from the interaction between particles exerts little effect because the overall interaction of surrounding particles on a specific particle is cancelled out by the random distribution of particles.

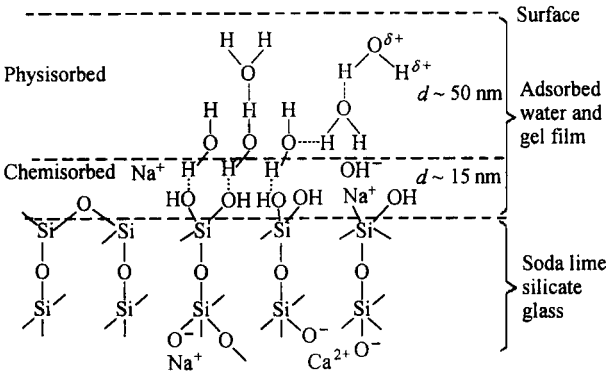


Fig. 1 Structure of glass surface

In this paper, by integrating the wall induced polar interaction with the “touch-coalescence” mechanism^[8], we can predict the formation of the gradient phase morphology, and the influence of interfacial tension on the gradient morphology.

THEORY

As stated above, there are interactions between polar solid wall and the polar dispersed particles. This interaction makes dispersed particles to move in an external potential field. The wall-induced potential imparts extra directional motion over the random Brownian motion. Thus, the coalescence probability along the normal direction to the wall is higher than in other directions, which results in gradient morphology. Before taking advantage of the touch-coalescence model, we should consider the polar interaction between the wall and the dispersed particles first.

WALL EFFECTS

The usual interacting potential energy between wall and particle can be expressed as^[21]:

$$\Phi_w(s_0) = -\frac{A_w}{6} \left[\frac{1}{s_0/R} + \frac{1}{s_0/R+2} + \ln \frac{s_0/R}{s_0/R+2} \right] \quad (1)$$

where A_w denotes the Hamaker constant between wall and dispersed particles, s_0 is the smallest distance between wall and spherical particle, R is the radius of spherical particle. This potential is based on the interaction between two freely rotated dipoles. As regards wall induced gradient morphology, the situation is a little different. On the one hand, the dipole molecule of the solid polar wall is almost fixed. On the other hand, the dipole moment of a macromolecule, such as EVAc, is the integration of all dipole moments of segments in a macromolecule. Because

of the high degree of entanglement between the macromolecular chains, the dipole of a macromolecule cannot rotate freely, which means it can only rotate in a limited space. Therefore, the interacting potential energy between wall and particles cannot be described by Eq. (1). Under such a constraint condition, the interacting potential energy between solid wall and dispersed particle could be written as (Appendix):

$$\Phi_w(b, R, x) = -2A_y \int_x^{x+2R} \ln\left(1 + \frac{b}{z}\right) \left[R^2 - (x + R - z)^2\right] dz \quad (2)$$

where b represents the depth of the polar zone on the wall surface; it refers to the thickness of the polyimide (PI) wall or the polarized depth of glass wall. A_y is similar to the Hamaker constant A_w , and denotes the interaction of macroscopic objects. A_y depends on the density and molecular weight of two macroscopic objects, and also on the dipole moment of two kinds of molecules, which is typically $0.1\text{--}10 \text{ J/m}^3$. In Eq. (2), x denotes the distance between the surface of particle and wall. The potential exerts a force on the dispersed particle^[22]

$$F = \frac{\partial \Phi_w(b, R, x)}{\partial x} \quad (3)$$

and gives a non-vanishing average velocity v , which in the condition of weak force, is linear in F so that

$$v = \frac{1}{6\pi \eta_m} \frac{\Phi_w(b, R, x)}{\partial x} \quad (4)$$

COALESCENCE MECHANISM

Having known interaction between the wall and the dispersed particles, we can compute the spatial distribution of phase morphology using the touch-coalescence model^[8]. We take advantage of the touch-coalescence model because this model considers various interactions, such as Van der Waals interactions, thermal motion, viscous friction and interfacial tension; and can be readily expanded to consider other interactions, such as the potential field that is encountered here. According to the model^[8], the change of particle numbers in unit volume per unit time can be described by:

$$\frac{dN(x)}{dt} = -N(x)^2 \cdot f(x) \cdot p(x) \quad (5)$$

$N(x)$ is the number of particles in unit volume at distance x from wall. $f(x)$ indicates the volume change in unit time:

$$f(x) = \frac{V(R(x))}{\tau(R(x))} \quad (6)$$

with $R(x)$ as the mean radius of dispersed particles, $V(R(x))$ the volume of dispersed particle, $\tau(R(x))$ the coalescence time of two particles with radius $R(x)$. The method for calculating the coalescence time of two particles can be found in the reference^[8]. $p(x)$ is the local touching probability, which can be calculated by integration of the nearest-neighbor distribution function. The one-dimensional nearest distribution function should be adopted instead of the 3-D nearest distribution function because of the preferably directional motion of dispersed particles in potential field. The local touching probability can be expressed as^[8]:

$$p = \int_{x_0}^{x_1} h_p(r) dr \quad (7)$$

where $h_p(r)dr$ denotes the probability that, given any sphere of radius of R at some arbitrary position in the system, there is a nearest particle surface at a distance between r and $r + dr$, which can be written as^[23]:

$$h_p(r) = \frac{2\rho}{1-\phi} \exp\left[-\frac{2\rho(r-R)}{1-\phi}\right] \quad (8)$$

where ϕ denotes the volume fraction of dispersed phase, ρ is the (one-dimensional) density. The upper and lower limit of integration in Eq. (7) can be determined as:

$$x_0 = \min\{R + h_{c,1}, R + h_{c,2}\}, \quad x_1 = \max\{R + h_{0,1} + \Delta h_1, R + h_{0,2} + \Delta h_2\} \quad (9)$$

$h_{c,l}$ denotes the critical film thickness and the subscript l denotes the film formed with adjacent particles^[8]. $h_{0,l}$ denotes the initial film thickness^[8]. Δh_i denotes the possible moving distance caused by Brownian motion and wall-induced potential field:

$$\Delta h_i = \sqrt{2D_i t} + v_i t \quad (10)$$

where D is the diffusion coefficient^[8].

When computing the spatial distributed phase morphology, we need to discretise the space into thin slices. Then, Eqs. (5)–(10) together with (2) and (4) is applied to each slice to calculate the change of particle size.

RESULTS AND DISCUSSION

Kong *et al.*^[13] investigated the wall induced gradient morphology of PP/EVAc blends and PE/EVAc blends. The results are shown in Figs. 2 and 3 as scattered dots. The model predictions are also shown in Figs. 2 and 3 as lines. It shows that the mean particle radius decreases as the distance of particles to the wall increases. The model predictions agree with the experiments for both PP/EVAc blends and PE/EVAc blends. Both experiments and model predictions show that the gradient morphology only appears in a very restricted region, whose extent is usually much less than 1 mm. This is far less than that formed under other conditions, such as temperature gradient^[24, 25]. This can be attributed to the essential microscopic polar interaction.

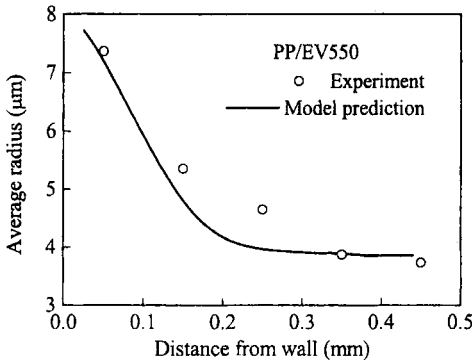


Fig. 2 The gradient morphology of PP/EVAc blend

The scattered dots are experimental data by Kong *et al.*^[13]

The solid line is our model prediction.

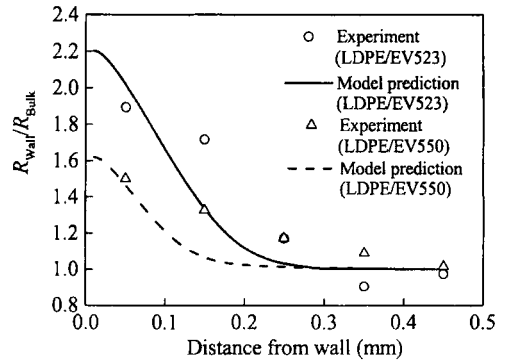


Fig. 3 The gradient morphology of LDPE/EVAc blends

The scatter dots are experimental data by Kong *et al.*^[13]

The lines are our model predictions.

Here in Fig. 3, we use the ratio between the particle radius near the wall (R_{wall}) and in the bulk (R_{bulk}) to express the extent of gradient morphology. It is clear from Fig. 3 that the gradient is more pronounced in LDPE/EV523 blends than in LDPE/EV550 blends. The reason is that the content of VAc is 14% in EV550, and 33% in EV523. High content of VAc increases the polarity of EVAc, and increases the polar interaction between the macromolecules and the solid polar wall. High polarity of dispersed phase not only increases the magnitude of the gradient morphology (R_{wall}/R_{bulk}), but also expands its range. The range of the gradient morphology usually extends to about 0.1 mm, which is much larger than the interacting distance of the usual Van der Waals forces.

This may be attributed to two points. First, the Van der Waals forces under constraint conditions extend the interacting distance between the polar solid wall and dispersed phase. Second, it was found that the rate of coarsening is accelerated by the formation of the gradient morphology^[25], thus it shows a self-accelerated formation of the gradient.

To further the understanding of the evolutionary kinetics of gradient morphology, we calculated its evolution, and the result is shown in Fig. 4. It is clear that the radius of particles far from the wall increases almost linearly with annealing time, while the particle near the wall grows at much faster speed. If the evolution of particle radius can be expressed by $R = R_0 + kt^\alpha$, where R_0 is the initial radius, k the rate constant and α the time exponent, we can utilize α to represent the increasing rate of particle size. The spatial dependence of α can be readily obtained from Fig. 4, and is shown in Fig. 5. The time exponent α far from the wall is near unity, which is the characteristic of fully phase separated polymer blends under annealing condition. The exponent increases as the distance of the particle from wall decreases. The fast increase of particle size is related to the extra polar interactions between the wall and the dispersed phase.

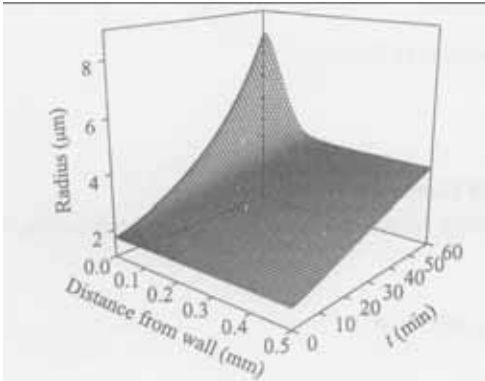


Fig. 4 The evolution of gradient morphology under quiescent annealing

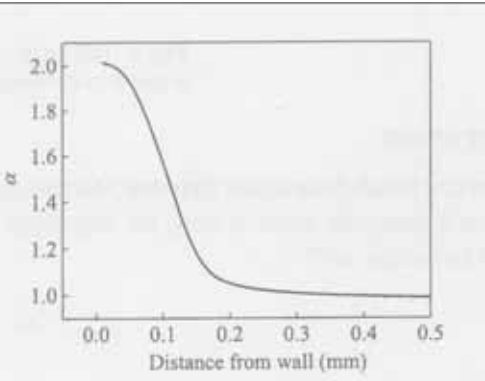


Fig. 5 The dependence of exponent α ($R = R_0 + kt^\alpha$) on the spatial position

The influence of system parameters, such as interfacial tension and viscosity of both phases, on the gradient morphology can be easily investigated by the wall induced fast coalescence mechanism. For example, according to Xie *et al.*^[16], the degree of gradient morphology greatly depends on the interfacial tension. The higher the interfacial tension, the greater is the tendency to form the gradient morphology. This trend is also revealed by our wall-induced fast coalescence model. The relation between the degree of gradient morphology and the interfacial tension is shown in Fig. 6. As we can see, the degree of gradient morphology increases with the increase of interfacial tension. In fact, the interfacial tension is only a macroscopic reflection of microscopic interaction between two materials. Higher polarity of dispersed phase means weaker interaction between the dispersed phase (EVAc) and the matrix (PP), which results in higher interfacial tension. Therefore, the influence of interfacial tension on the gradient morphology is consistent with the influence of the polarity of dispersed phase, *i.e.* Fig. 6 and Fig. 3 show same trend of the effect of polarity and interfacial tension on the gradient morphology.

CONCLUSION

A wall induced fast coalescence mechanism is proposed to explain the effect of polar wall on the formation of gradient morphology. The glass wall is believed to impose an additional potential field on dispersed particles. The macroscopic potential interaction between particle and wall under constraint condition is derived and integrated into the touch-coalescence model to predict the formation of gradient morphology. The model predictions agree with the experimental results. The time exponent of the evolution of radius is used to express the increasing rate, which exhibits a gradient on the direction normal to the glass surface. The high value of the time exponent near the wall reflects fast coalescence of the dispersed particles, which is the result of the influence

of wall-induced potential field. The influence of interfacial tension reveals the variation of microscopic polarity of EVAc in PP/EVAc blend. Both the interfacial tension and the polarity of dispersed phase show similar influence on the formation of gradient morphology for the blend we investigated.

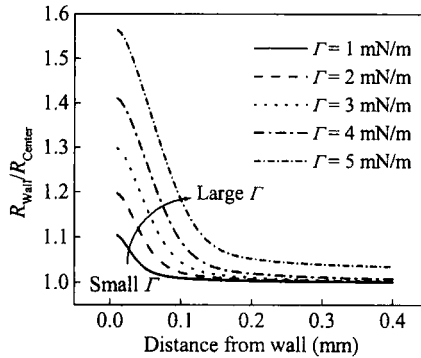


Fig. 6 Influence of interfacial tension on the formation gradient morphology

APPENDIX

Van der Waals Interaction Between Macroscopic Objects Under Constraint Condition

From a molecular point of view, the long-range electrostatic energy between two dipoles (as shown in Fig. A1) can be written as^[26]:

$$U_{\mu\mu'}(r, \theta_1, \theta_2, \phi) = \frac{-\mu\mu'}{4\pi\epsilon_0 r^3} \zeta(\theta_1, \theta_2, \phi) \quad (\text{A1})$$

where

$$\zeta(\theta_1, \theta_2, \phi) = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi \quad (\text{A2})$$

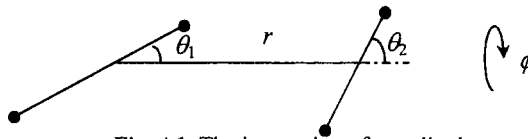


Fig. A1 The interaction of two dipoles

This dipole-dipole interaction energy describes the dependence of the energy on orientation. If the probability of observing a configuration of energy U is proportional to the Boltzmann factor $\exp(-U/kT)$, the average energy can be written as^[26]:

$$\langle U \rangle = \frac{\iint U(\omega_1, \omega_2) \exp(-U(\omega_1, \omega_2)/kT) d\omega_1 d\omega_2}{\iint \exp(-U(\omega_1, \omega_2)/kT) d\omega_1 d\omega_2} \quad (\text{A3})$$

At sufficiently high temperature, $U(\omega_1, \omega_2) \ll kT$, we may expand the exponential and integrate term-by-term to yield:

$$\langle U \rangle = (\bar{U} - \bar{U}^2 / kT + \dots)(1 + \bar{U} / kT + \dots) \quad (\text{A4})$$

where

$$\bar{U}^n = \iint U^n(\omega_1, \omega_2) d\omega_1 d\omega_2 \quad (A5)$$

The differential element is taken as $d\omega_1 = \sin\theta_1 d\theta_1 d\phi$ for a polar coordinate system. If the two molecules are free to rotate as they are in the gas phase, which means $\theta_1, \theta_2 \in [0, \pi]$, $\phi \in [0, 2\pi]$ (unconstraint). It is often that the average of the dipole-dipole energy over all possible orientations $\langle U \rangle_{\mu\mu'}$ is required. Then, at sufficiently high temperatures

$$\langle U \rangle_{\mu\mu'} = -\frac{2}{3} \frac{\mu^2 \mu'^2}{r^6 kT (4\pi \epsilon_0)^2} + \dots \quad (A6)$$

Eq. (A6) is the classic dipole-dipole interaction energy, which only applies to molecules that can rotate freely. If one molecule is fixed, the other can rotate only in half plane (to keep the interaction energy negative), i.e. $\theta_1 = 0$ (fixed), $\theta_2 \in [0, \pi/2]$ (limited rotation), $\phi \in [0, 2\pi]$, then Eq. (A5) can be calculated as:

$$\bar{U} = -\frac{2\pi \beta'}{r^3}, \quad \bar{U}^2 = \frac{8\pi}{3} \frac{\beta'^2}{r^6} \quad (A7)$$

where $\beta' = \frac{\mu\mu'}{4\pi \epsilon_0}$. Substituting Eq. (A7) into Eq. (A4), we can obtain:

$$\langle U \rangle \cong -\frac{2\pi \beta'}{r^3} = -\frac{\beta}{r^3}, \quad \beta = \frac{\mu\mu'}{2\epsilon_0} \quad (A8)$$

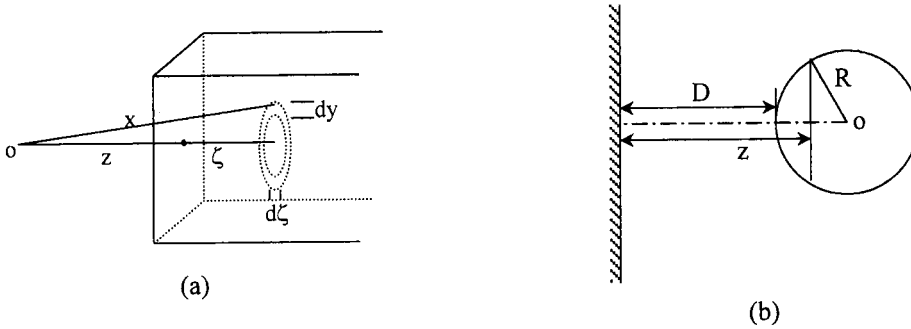


Fig. A2 The interaction between sphere and wall

To obtain the interaction energy between macro objects, we just integrate the interaction energy of all dipoles in the objects. The interaction energy between sphere and wall is schematically shown in Fig. A2. The volume of the circle block with the distance x from point o is $dV = 2\pi y dy d\zeta$. The incremental energy between the molecule and the plane caused by the circle block is: $d\Phi = -\frac{\rho N_A}{M} \beta \frac{2\pi y dy d\zeta}{x^3}$, where ρ is the density, M is the molecular weight and N_A is the Avogadro number. Using $x^2 = (z + \zeta)^2 + y^2$, we integrate twice with $0 < y < \infty$ and $0 < \zeta < b$ (b is the depth of polar zone) and obtain the interaction energy between a molecule and wall:

$$\Phi = -\frac{\rho N_A}{M} \beta 2\pi \ln\left(1 + \frac{b}{D}\right) \quad (A9)$$

In the particle, the volume element of disk with distance z from wall is $dV = \pi[R^2 - (D + R - z)^2] dz$, with $z \in [D, D + 2R]$. The interaction energy between the plane and the disk is

$-\left(\frac{\rho N_A}{M}\right)^2 \beta \cdot 2\pi^2 \ln\left(1 + \frac{b}{D}\right) [R^2 - (D + R - z)^2] dz$. Integrating z from D to $D + 2R$, we obtain:

$$\Phi = -2A_y \int_D^{D+2R} \ln\left(1 + \frac{b}{D}\right) [R^2 - (D + R - Z)^2] dz \quad (\text{A10})$$

where

$$A_y = \pi \left(\frac{\rho N_A}{M} \right)^2 \beta \quad (\text{A11})$$

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