Concentration Profile for a Polymer–Polymer Interface. 1. Identical Chemical Composition and Molecular Weight

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ABSTRACT: The concentration profile $C(x,t)$ for a symmetric polymer–polymer interface due to reptation is derived by using the minor chain reptation model. The concentration of monomers contributed from reptation is discontinuous at the interface when the healing time, t, is less than the reptation time, T_r. The non-Fickian discontinuity decays with time at a rate that is proportional to $t^{-1/2}M^{-3/2}$ and disappears at $t = T_r$. The total number of monomers $N(t)$ crossing from one side to the other is given by $N(t) \sim t^{3/4}M^{-7/4}$. The molecular properties of the interface are derived from $C(x,t)$ and can be expressed in terms of a common scaling law $H(t) = H_\infty(t/T_r)^{r/4}$, where $r = 1, 2, 3, ..., H_\infty = H(T_r)$, and $T_r \sim M^3$. These properties are unique to the reptation model and can be investigated by experiments.

Introduction

Interdiffusion at a polymer–polymer interface is of interest because of its importance in welding, lamination of composites, polymer blends, and polymer processing. One important aspect of the interface problem is the dynamics of the polymer chains in the interface region. The reptation model, which was developed by de Gennes,[1] and later by Doi and Edwards,[2] has been used to describe the chain motion at an interface by several investigators including de Gennes,[3] Prager and Tirrell,[4] and Wool and O'Connor.[5] Kim and Wool[6] developed the minor chain reptation (MC) model based on the reptation model to analyze the healing problem for amorphous interfaces. The purpose of this paper is to use the MC model to derive the concentration profile contributed by reptation for a symmetric polymer–polymer interface. The profile is then analyzed to investigate other molecular aspects of interdiffusion at an amorphous polymer–polymer interface. The non-Fickian characteristics of the profile as predicted by the reptation model will be examined at healing times less than the reptation time T_r and larger than the Rouse time R_{ROU} and diffusion distances less than the radius of gyration. These are the times and distances over which a symmetric interface can gain its strength. The derivation of the profile is also important for comparison with concentration profiling experiments currently being conducted at this laboratory.

Derivation of the Concentration Profile

When two pieces, A and B, of the same amorphous polymer contact above the glass transition temperature to form a symmetric polymer–polymer interface, interdiffusion of chains near the interface occurs. This motion of chains can be described by the minor chain reptation model on the time scale $T_{ROU} < t < T_r$, as shown in Figure 1. According to this model a chain, confined by its surroundings into a tubelike region, moves back and forth along the initial tube. When the chain moves "forward" the "head" of the chain chooses its direction randomly, and when it moves "backward" the "tail" chooses its direction randomly. As a result, the end portions of the chain can "escape" from the initial tube, forming the "minor chains" as shown in Figure 1a. The minor chains can take the conformation of a Gaussian (random) coil and move freely across the interface.

As time goes by, the minor chains emerging from the ends of the initial tubes become longer. By a one-dimensional span analysis it has been found that the average minor chain length, $l(t)$, increases as[6]

$$l(t) = (16Dt/\pi)^{1/2} \tag{1}$$

where D is the one-dimensional curvilinear diffusion coefficient and is inversely proportional to molecular weight, M, of the polymer.[1]

In the interface problem, brownian motion attempts to relax the nonequilibrium chain conformations at the interface. It has been shown that when the equilibrium state is reached, the distribution of end segments is uniform. In this paper we evaluate the concentration profile with the reasonable assumption that the initial chain-end and chain-segment distribution function is flat. However, the foregoing derivation can be performed in principle with any distribution function. For chemical and polydispersity reasons, a chain-end rich, or depletion layer, could develop near the surface which would affect the development of the initial stages of the concentration profile.

Let Φ denote the uniform mass density of a bulk polymer in the melt state; then the number of chain ends per unit volume, N_v, is given by

$$N_v = 2\Phi N_a/M \tag{2}$$

where N_a is Avogadro's number. If n is the number of monomers in a minor chain at healing time, t, then

$$n = l(t)/a \tag{3}$$

where a is the length of a monomer.

We now calculate the monomer concentration profile at the interface for the time scale of the order of the reptation time, T_r. Consider a minor chain of length $l(t)$ that emerged from its tube end at $x = -x_0$ as shown in Figure 2. The origin of the coordinates is chosen so that the interface plane is at $x = 0$ and a piece A is located on the region where $x < 0$. Since the conformation of the minor chain is random, the probability $p(s,x/x_0)$ that the sth monomer in the minor chain occurs at interval distance $(x,x+dx)$ from the interface, as shown in Figure 2a, is given by

$$p(s,x/x_0) = 1/(2\pi sa^2)^{1/2} \exp[-(x + x_0)^2/2sa^2]\, dx \tag{4}$$

Equation 4 also gives the probability that each monomer contained in the interval $(s,s+ds)$ of the minor chain occurs in the interval distance $(x,x+dx)$, as shown in Figure 2b, since ds is assumed to be very small compared with s. Thus, the probability that the ds monomers of the minor chain occur in the interval distance $(x,x+dx)$, as shown in Figure 2c, is the same as $p(s,x/x_0)$. Therefore, the number of monomers $f(x,n)$ of the minor chain occurring at the interval distance $(x,x+dx)$ from the interface at time t is determined as

$$f(x,n) = \int_0^n [1/2\pi sa^2]^{1/2} \exp[-(x + x_0)^2/2sa^2]\, dx\, ds \tag{5}$$

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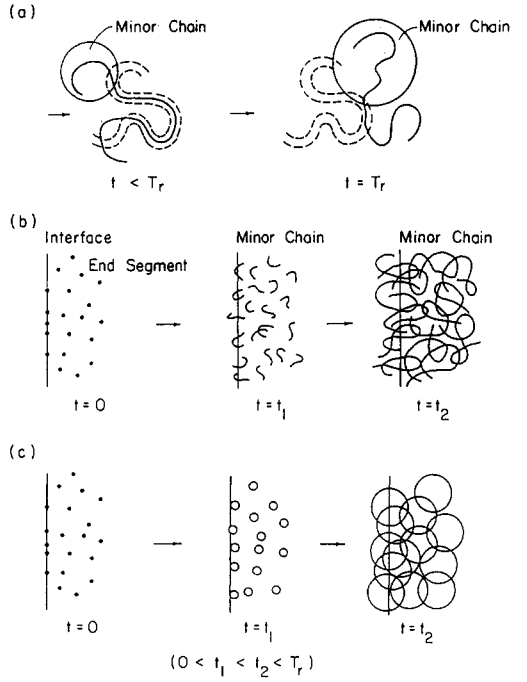

Figure 1. Minor chain reptation model. (a) Disentanglement of a minor chain from its initial tube. (b) Growth of the minor chains that have emerged from one side of the interface. (c) Growth of the spherical envelopes of minor chains that have emerged from one side of the interface.

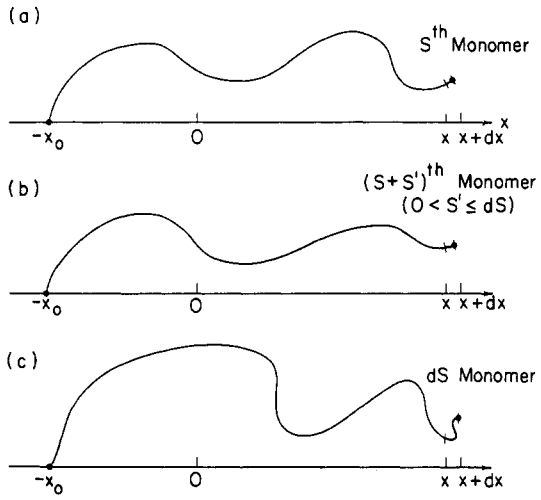

Figure 2. (a) Minor chain with s monomers. The last monomer (i.e., the sth monomer) occurs in the distance interval $(x, x+dx)$. (b) Minor chain with $(s + s')$ monomers, where $0 < s' < ds$. The monomer $(s + s')$ occurs in the interval $(x,x+dx)$. (c) Minor chain with $(s + ds)$ monomers, where ds monomers occur in the interval $(x,x+dx)$.

For an interface with cross-sectional area S, there are $[2\Phi N_a S\, dx_0/M]$ minor chain ends in the volume element $S\, dx$ between the interval distance $(-x_0,-x_0-dx_0)$. Among them there are $(2\Phi N_a S\, dx_0/M)f(x,n)$ monomers that occur in the interval distance $(x,x+dx)$. The total number of the monomers $f_t(x,t)$ occurring in the interval distance $(x,x+dx)$ is given by

$$f_t(x,t) = \int_{x_0=0}^{x_0=\infty} (2\Phi N_a S\, dx/M)\, dx_0 \int_{s=0}^{s=n} (1/2\pi s a^2)^{1/2} \exp[-(x + x_0)^2/2sa^2]\, ds \quad (6)$$

Therefore, the number of moles of monomers per unit volume at x (>0) coming from the polymer piece A, i.e.,

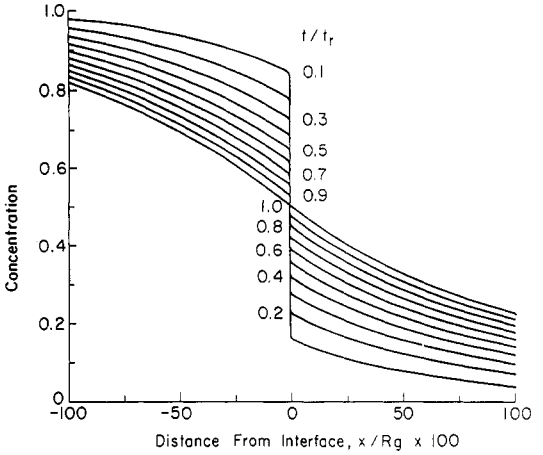

Figure 3. Normalized concentration profile $[C(x,t)/(\Phi/M_0)]$ at an amorphous polymer–polymer interface. R_g is the radius of gyration, and T_r is the reptation time.

the monomer concentration profile, $C_A(x,t)$, occurring at the interval distance $(x,x+dx)$ at time t is given by

$$C_A(x,t) = (2\Phi/M) \int_{x_0=0}^{x_0=\infty} dx_0 \times \int_{s=0}^{s=n} (1/2\pi s a^2)^{1/2} \exp[-(x + x_0)^2/2sa^2]\, ds \quad (7)$$

Exchanging the order of the integration and evaluating the integral with respect to x_0 yield

$$C_A(x,t) = (\Phi/M) \int_{s=0}^{s=n} \text{erfc}\, \{x/[a(2s)^{1/2}]\}\, ds \quad (8)$$

where for $y = x/[a(2s)^{1/2}]$, the complementary error function is

$$\text{erfc}\ (y) \equiv (2/\pi^{1/2}) \int_y^\infty \exp(-z^2)\, dz$$

Integrating eq 8 by parts gives

$$C_A(x,t) = (\Phi/M)\Big[n\ \text{erfc}\, \{x/[a(2n)^{1/2}]\} - [x/(a2^{1/2})] \int_{s=0}^{s=n} (1/s^{1/2}) \exp[-x^2/(2sa^2)]\, ds\Big] \quad (9)$$

Evaluating the integral in eq 9, the monomer concentration profile for the symmetric polymer–polymer interface is finally given as

$$C(x,t) = (\Phi/M_0)\{(l(t)/L + x^2/aL)\ \text{erfc}\, \{x/[a(2n)^{1/2}]\} - (2n/\pi)^{1/2}(x/L) \exp[-x^2/(2na^2)]\} \quad (10)$$

where M_0 is the monomer molecular weight, $l(t)$ is given by eq 1, n is given by eq 3, and L is the contour length of the chain of N monomers. Noting the symmetry of the interface under consideration, the expression is identical for the number of monomers per unit volume at $-x$ (<0) coming from the polymer piece B, $C_B(-x,t)$.

When $t = T_r$, $l(t) = L/2$, and $n = N/2$, then

$$C(x,T_r) = (\Phi/M_0)\{(0.5 + x^2/\langle r^2\rangle)\ \text{erfc}\, [x/(2^{1/2}\langle r^2\rangle^{1/2})] - (2/\pi)^{1/2}(x/\langle r^2\rangle^{1/2}) \exp[-(x^2)/(2\langle r^2\rangle)]\} \quad (11)$$

where $\langle r^2\rangle$ is the mean-square end-to-end distance of the Gaussian chains.

Computed curves are shown in Figures 3 and 4, in which the time is reduced with respect to T_r, the distance is reduced with respect to the radius of gyration for a Gaussian chain with N segments, and the concentration is reduced with respect to the bulk density, Φ/M_0 (moles of monomers per unit volume). Figure 3 clearly indicates

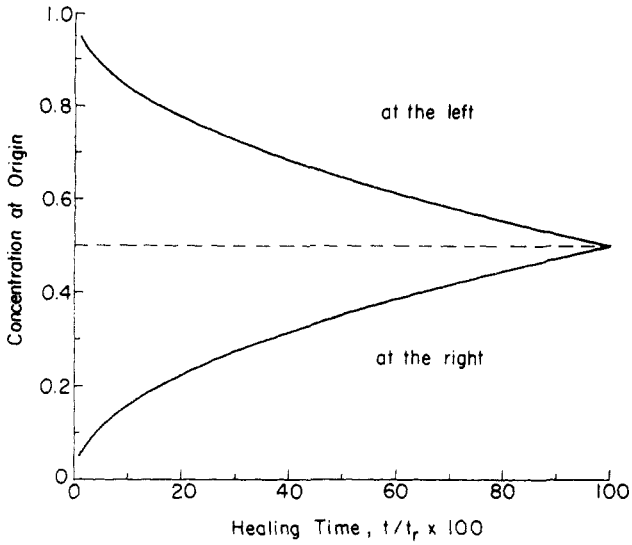

Figure 4. Discontinuity of the concentration profile at $x = 0$ as a function of time.

that the concentration at the initially joined surface ($x = 0$) is discontinuous when the healing time is shorter than the reptation time. This gap does not disappear until the reptation time as shown in Figure 4, where the reduced concentration at ($x = 0$) is plotted vs the healing time.

Application of the Concentration Profile

The concentration profile given above in eq 10 can be used to calculate molecular quantities of interest such as the average interpenetration depth, the number of bridges intersecting the interface, and the number of monomers crossing the interface and to examine the discontinuity at the interface plane, $x = 0$.

Discontinuity at the Interface Plane. Let $C_{12}(x,t)$ represent the reduced concentration of those monomers that are located on side 1 at time $t = 0$ and on side 2 at time t. For the symmetric interface, from eq 10, we have

$$C_{12}(x,t) = C_{21}(-x,t), \quad x > 0$$
$$= C_A(x,t)/(\Phi/M_0) \tag{12}$$

$$C_{12}(x,t) + C_{22}(x,t) = C_{21}(-x,t) + C_{22}(-x,t) = 1, \quad x > 0 \tag{13}$$

Therefore, the change in the reduced concentration from one side of the plane $x = 0$ to its other side, $J(t)$, is given by

$$J(t) = C_{11}(0^-,t) - C_{12}(0^+,t) = 1 - 2C_{12}(0^+,t) \tag{14}$$

Combining eq 1, 10, 12, and 14 gives

$$J(t) = 1 - (4(2/\pi)^{1/2})(Dt)^{1/2}/L \tag{15}$$

Since the reduced concentration is always smaller than 0.5 when $t < T_r$ and equal to 0.5 at $t = T_r$, then $J(t)$ is always positive if $t < T_r$ and zero if $t = T_r$. This means that there is a discontinuity in the profile at $x = 0$ when $t < T_r$ and it does not disappear until the reptation time. However, the discontinuity decays with time at a rate given by

$$dJ(t)/dt = -(2(2/\pi)^{1/2})D^{1/2}t^{-1/2}/L \tag{16}$$

or

$$dJ(t)/dt \propto -t^{-1/2}M^{-3/2} \tag{17}$$

Both the discontinuity and the decay rate are affected by the molecular weight. The larger the molecular weight, the more pronounced is the discontinuity and the more slowly it decays with time. Segmental motion of the monomers over a distance equal to the tube diameter is expected to reduce the discontinuity at $x = 0$.

Average Interpenetration Depth, $X(t)$. In the healing process, efforts have been made to relate structure to strength development of the interface by fracture mechanics measurements. The contour length as measured from the average interpenetration depth, $X(t)$, was suggested by Wool and O'Connor[5] to control the interface strength, K_{IC}, when disentanglement is an important mechanism in the fracture process. $X(t)$ is calculated by using the concentration profile in terms of

$$X(t) = \langle x \rangle = \int_0^\infty x C_A(x,t)\, dx / \int_0^\infty C_A(x,t)\, dx \tag{18}$$

Substituting eq 10 into eq 18 and carrying out the two integrals give

$$X(t) = (3\pi^{1/2}/128^{1/2})n^{1/2}a \tag{19}$$

Substituting eq 1 into eq 4 and then substituting the result in eq 19 yield

$$X(t) = (3\pi^{1/4}/32^{1/2})a^{1/2}(Dt)^{1/4} \sim t^{1/4}M^{-1/4} \tag{20}$$

in which $D \sim M^{-1}$ has been used.

Note that $X(t)$ calculated by using the concentration profile derived in this work has the same form as that given by Kim and Wool.[6] $X(t)$ is related to the interpenetration contour length by $X(t) \sim l^{1/2}(t)$. Equation 20 can be used to evaluate experimental profiles. When $t > T_r$, $X(t) \sim t^{1/2}M^{-1}$.

Number of Bridges Intersecting the Interface, $p(t)$. The number of bridges intersecting unit area of interface is the same as the number of monomers per unit volume occurring at the interface. Therefore, when $x = 0$, eq 10 gives

$$p(t) = C_A(0,t) = (\Phi/M_0)l(t)/L \tag{21}$$

Substituting eq 1 into eq 21 yields

$$p(t) \sim t^{1/2}M^{-3/2} \tag{22}$$

The number of bridges in the virgin or fully healed state is obtained by substituting $x = 0$ in eq 11 and is given by

$$P_\infty = p(T_r) = 1/2 \tag{23}$$

i.e.

$$p(T_r) \sim M^0$$

which indicates that the number of bridges is independent of molecular weight in the virgin state. Prager and Tirrell[4] derived a similar relation for the crossing density of segments, which is also proportional to $p(t)$, and de Gennes[3] also showed that $p(t) \sim t^{1/2}$.

Number of Monomers Crossing the Interface, $N(t)$. The number of monomers $N(t)$ having crossed the interface by time, t, is obtained by integrating the concentration profile with respect to x over the positive semiinfinite region as

$$N(t) = \int_0^\infty C_A(x,t)\, dx \tag{24}$$

Substituting eq 10 into eq 24 and evaluating the integral give the (non-Fickian) result

$$N(t) = [(16)2^{1/2}a^{1/2}/3\pi^{5/4}](Dt)^{3/4}/L \tag{25}$$

or

$$N(t) \sim t^{3/4}M^{-7/4} \tag{26}$$

This result is in agreement with previous calculations of $N(t)$ by Wool,[6] and by Tirrell et al.[8] However, the calculation of the concentration profile herein differs from that of Tirrell et al.[8] primarily in the form of the dynamic

Table I
Molecular Aspects of Interdiffusion at a Polymer–Polymer Interface

molecular aspect	symbol	dynamic relation, $H(t)$	static relation, H_∞
no. of chains	$n(t)$	$t^{1/4}M^{-5/4}$	$M^{-1/2}$
no. of bridges	$p(t)$	$t^{1/2}M^{-3/2}$	M^0
monomer depth	$x(t)$	$t^{1/4}M^{-1/4}$	$M^{1/2}$
total chain depth	$x_0(t)$	$t^{1/2}M^{-3/2}$	M^0
center of mass	$x_{cm}(t)$	$t^{1/2}M^{-1}$	$M^{1/2}$
total contour length	$L_0(t)$	$t^{3/4}M^{-7/4}$	$M^{1/2}$
av length	$l(t)$	$t^{1/2}M^{-1/2}$	M
av bridge length	$l_p(t)$	$t^{1/4}M^{-1/4}$	$M^{1/2}$
no. of monomers crossing the interface	$N(t)$	$t^{3/4}M^{-7/4}$	$M^{1/2}$
total monomer depth	$B(t)$	tM^{-2}	M
general property	$H(t)$	$t^{r/4}M^{-s/4}$	$M^{(3r-s)/4}$

[a] r,s = 1, 2, 3, 4, ...

function and from that of Wool,[6] who used a scaling arguement to derive eq 26. The result is also unique to the reptation model and provides another experimental method of investigating the widely used model. At $t > T_r$, $N(t) \sim t^{1/2}$ and the crossover from $t^{3/4}$ should be observable.

Discussion and Conclusions

In this paper we derived the concentration profile, contributed by reptation, for a symmetric amorphous polymer–polymer interface with a uniform chain-end distribution using the MC model. The profile was used to examine the discontinuity of the monomer concentration at the interface and to calculate molecular quantities such as the average interpenetration depth, the number of bridges intersecting the interface, and the number of monomers having crossed the interface by time, t. From these calculations the following conclusions can be drawn:

The discontinuity at $x = 0$ exists until the reptation time and decays inversely with the square root of the healing time. The longer the chain, the more pronounced is the discontinuity and the more slowly it decays. Segmental motion between entanglements is expected to wash out the discontinuity.[9]

The average monomer interpenetration depth $X(t)$ behaves as $t^{1/4}M^{-1/4}$.

The total number of the monomers $N(t)$ crossing the interface due to reptation increases as $t^{3/4}M^{-7/4}$.

The number of the bridges $p(t)$ intersecting the interface increases as $t^{1/2}M^{-3/2}$.

Using the relationship $T_r \sim M^3$, we obtain at $t = T_r$, $X(T_r) \sim M^{1/2}$, $p(T_r) \sim M^0$, and $N(T_r) \sim M^{1/2}$. The virgin-state properties, H_∞, depend on molecular weight according to $H_\infty \sim M^{(3r-s)/4}$, where r,s = 1, 2, 3, ...

The molecular properties related to interdiffusion in the amorphous polymer–polymer interface depend on the healing time and have a similar functional form, $H(t)$, expressed as $H(t) = H_\infty(t/T_r)^{r/4}$, where r = 1, 2, 3, ... A summary of the dynamic, $H(t)$, and static molecular properties, H_∞, for healing a polymer–polymer interface is given in Table I. The dynamic scaling laws are unique to the reptation model and can be studies by experiments.[10]

Finally, we would like to point out that the concentration profile calculated in this work is contributed only by the reptation process. However, the motion of monomers described by the Rouse model also contributes to the concentration profile. Therefore, the complete concentration profile on the reptation time scale can be obtained only by superposing the two profiles contributed by reptation and Rouse motion, respectively. Rouse broadening will make the complete concentration profile continuous at the plane $x = 0$. The details of this investigation will be published later.

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