Polymer–Polymer Mutual Diffusion via Rheology of Coextruded Multilayers

Rui Zhao and Christopher W. Macosko
Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

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The mutual diffusion coefficient of a pair of polyethylenes using coextruded multilayers has been measured. Two polyethylenes with different molecular weight were coextruded in 32 alternating layers in about 45 s of contact time. When the multilayer sample was remelted in a parallel plate rheometer, its apparent viscosity increased due to interdiffusion. By following the kinetics of the apparent viscosity increase, the mutual diffusion coefficient was measured. The theory of Kramer et al. (Polymer. 1984; 25:473-480) was used to describe the mutual diffusion coefficient as a function of the chain mobility parameter, molecular weight, and concentration. The finite element method was used to solve the nonlinear interdiffusion problem to give a concentration profile in these multilayers. By fitting the apparent viscosity of the sample vs. time, the chain mobility parameter was found to be 4.5×10^{11} m/N s, and the range of the mutual diffusion coefficient for these two PE's was 10^{-12}–10^{-14} m^2/s at 200°C (depending on concentration). This is an easy and rapid method to measure the mutual diffusion coefficient for miscible polymers with different melt viscosities.

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Introduction

Polymer–polymer mutual diffusion has been an important topic in industrial technology development and in academic research on polymer chain dynamics. For example, in the polyolefin industry, polyethylenes with different molecular weight or different chain structures (i.e., linear or branched) are often mixed together to tailor the end-use properties and proccessibility.[1–6] If they are totally miscible, the homogeneity of the mixture is controlled by mutual diffusion. The molecular dynamics of mutual diffusion is often treated using the reptation model (each polymer chain crawls within a tube formed by the topological constraints of all the other polymer chains).[7,8] This theory predicts the self-diffusion coefficient, D, of a chain of degree of polymerization N should decrease as N^{-2}.[7–10] However, this result is only valid for self diffusion. Most diffusion problems of practical interest involve concentrated diffusion couples, and the mutual diffusion coefficient shows large deviation from the N^{-2} dependence.[11,12] Brochard et al. demonstrated that this deviation is due to the enthalpy of mixing in concentrated polymer solutions.[13] They assumed the fluxes of the two diffusing species are equal and opposite. This assumption was later challenged by Kramer et al.[14] who assumed the gradient of the chemical potential field of vacancies is zero. Zero gradient of vacancies ensures the incompressibility condition of most polymer melts, and is supported by their experimental results and subsequent work.[14–21]

Many techniques have been developed to measure the diffusion coefficients of small or large molecules in polymer melts or solutions. For example, pulsed field gradient-nuclear magnetic resonance (PFG-NMR) spectroscopy,[22] X-ray microanalysis in scanning electron microscopy,[23] neutron scattering,[24,25] neutron reflection,[26] neutron spin echo,[27] for-

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Current address of Rui Zhao: ExxonMobil Chemical Company, 5200 Bayway Dr, Baytown, TX 77520.
Correspondence concerning this article should be addressed to C. W. Macosko at macosko@umn.edu.

ward recoil spectrometry,[28] Fourier transform infrared spectroscopy,[29] and transmission electron microscopy[30] have been used. All these techniques require the samples to be either chemically labeled or spectroscopically differentiated. They are often unable to accurately map the concentration profile in real time due to the wide concentration range and high concentration gradient in mutual diffusion couples.

We have developed a technique to determine mutual diffusion coefficients using rheological measurements on coextruded multilayers. Coextruded multilayers of a pair of miscible polymers are sheared by small amplitude oscillation between parallel plates. The apparent viscosity of the multilayers increases when the two polymers diffuse into each other. By following the kinetics of the viscosity change, the mutual diffusion coefficient can be measured. This rheological technique was first used by Bousmina and coworkers,[31] to study the mutual diffusion between polymethyl methacrylate (PMMA) and polystyrene acrylonitrile (SAN). Their rheology samples consisted of a pair of layers of these two polymers. They documented a concentration-dependent mutual diffusion coefficient; however, to simplify data analysis, they assumed an interphase region between the diffusion layers where the concentration gradient was zero. This is a good approximation at the very beginning of the mutual diffusion, but it fails when the mutual diffusion propagates into each layer. In their experiment, since the number of layers in the sample was only two, the interfacial area through which the mutual diffusion took place was very limited, and the accuracy of their experimental data are questionable. Baer and coworkers studied the mutual diffusion between high density and linear low density polyethylene (HDPE/LLDPE) using coextruded multilayers.[32,33] The melting temperatures of these two PE's were different. When the two polymers diffused into each other, the two melting temperatures converged into one temperature. By following the convergence of the two melting temperatures, they calculated the mutual diffusion coefficient. However, in their data analysis, a simple symmetric Fickean diffusion model is used with a concentration-independent mutual diffusion coefficient, and the dependence of the mutual diffusion coefficient was assumed to decrease with molecular weight as N^{-2}.

We use a similar pair of fully miscible polyethylenes coextruded into multilayers and study them via rheological measurement. The theory of Kramer et al.[14] is used to describe the mutual diffusion coefficient as a function of concentration. The concentration profile in the multilayers is solved numerically using the Galerkin Finite Element Method (FEM). By fitting the experimental data, a unique chain mobility parameter is found with which the mutual diffusion coefficient is expressed explicitly as a function of concentration.

Theory of Polymer–Polymer Mutual Diffusion

In the framework of Brochard-Wyart et al.[13] and Kramer et al.,[14] a one dimensional mutual diffusion between homopolymer A with degree of polymerization N_A and homopolymer B with degree of polymerization N_B is considered. Assuming diffusion is along the x direction, the A and B fluxes are:

$$\begin{aligned} J_A &= -\Lambda_A \frac{\partial}{\partial x}(\mu_A + U) \\ J_B &= -\Lambda_B \frac{\partial}{\partial x}(\mu_B + U) \end{aligned} \tag{1}$$

where Λ_A and Λ_B are the Onsager coefficients. U is a potential ensuring the incompressibility condition for polymer melts. This potential was considered by Kramer et al.[14] as the chemical potential of vacancies, μ_v, which are required for chains to diffuse by reptation. These vacancies are just lattice sites that are not occupied by polymer chains. Since the amount of lattice sites is conserved, i.e. incompressible, the fluxes of A, B, and the vacancies should be balanced. Thus, Eq. 1 can be rewritten as:

$$\begin{aligned} J_A &= -\Lambda_A \frac{\partial}{\partial x}(\mu_A - \mu_v) \\ J_B &= -\Lambda_B \frac{\partial}{\partial x}(\mu_B - \mu_v) \\ J_v &= \Lambda_A \frac{\partial}{\partial x}(\mu_A - \mu_v) + \Lambda_B \frac{\partial}{\partial x}(\mu_B - \mu_v) \end{aligned} \tag{2}$$

Any finite gradient of vacancy potential implies the existence of an osmotic pressure gradient, which should relax rapidly in a polymer melt relative to chain diffusion, so Kramer et al.[14] proposed:

$$\nabla \mu_v = 0 \tag{3}$$

which leads to:

$$\begin{aligned} J_A &= -\Lambda_A \frac{\partial \mu_A}{\partial x} \\ J_B &= -\Lambda_B \frac{\partial \mu_B}{\partial x} \\ J_v &= \Lambda_A \frac{\partial \mu_A}{\partial x} + \Lambda_B \frac{\partial \mu_B}{\partial x} \end{aligned} \tag{4}$$

Thus, the total flux J_A^T of polymer A along the x direction is

$$J_A^T = -(1-\phi)\Lambda_A \frac{\partial \mu_A}{\partial x} + \phi \Lambda_A \frac{\partial \mu_B}{\partial x} \tag{5}$$

where ϕ is the volume fraction of sites occupied by A. Conservation of the volume of lattice sites means

$$\frac{1}{\bar{v}} \frac{\partial \phi}{\partial t} = \frac{\partial}{\partial t}(-J_A^T) \tag{6}$$

where $\bar{v}$ is the volume of one lattice site. Inserting Eq. 5 into Eq. 6 and using the Flory–Huggins equation[34] for the chemical potentials gives

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x}\left\{ \bar{v} k_B T \left(\frac{1-\phi}{\phi}\Lambda_A + \frac{\phi}{1-\phi}\Lambda_B \right) \times \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \frac{\partial \phi}{\partial x} \right\} \tag{7}$$

where k_B is Boltzman's constant, T is temperature, and χ is the Flory–Huggins interaction parameter. Therefore, the mutual diffusion coefficient D_{AB} is just:

$$D_{AB} = \bar{v} k_B T \left(\frac{1-\phi}{\phi} \Lambda_A + \frac{\phi}{1-\phi} \Lambda_B \right) \times \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \tag{8}$$

Obviously, the mutual diffusion coefficient is a strong function of concentration. It scales as N^{-1}. This is different from the self-diffusion coefficient, which scales as N^{-2} for entangled polymer chains.

The Onsager coefficients for highly entangled A and B, i.e., $N_A \gg N_e$ and $N_B \gg N_e$, can be related to the polymer chain segment mobility[13]:

$$\begin{aligned} \Lambda_A &= \Lambda_{oA} \frac{N_{eA}}{N_A} \frac{\phi}{\bar{v}} \\ \Lambda_A &= \Lambda_{oB} \frac{N_{eB}}{N_B} \frac{1-\phi}{\bar{v}} \end{aligned} \tag{9}$$

where Λ_{oA} and Λ_{oB} are the Rouse mobilities of the A and B segments.

Mutual Diffusion in HDPE/LLDPE Multilayers

The mutual diffusion between 32 alternating layers of high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) is studied in this work. The mutual diffusion in HDPE/LLDPE multilayers can be considered one-dimensional, as shown in Figure 1. Thus for $t > 0$,

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x}\left(D_{AB} \frac{\partial \phi}{\partial x}\right) \tag{10}$$

where ϕ is the volume fraction of HDPE. Initially, there is no mixing between the polymers, so $\phi = 1$ in the HDPE layers and $\phi = 0$ in the LLDPE layers. This implies periodic initial conditions:

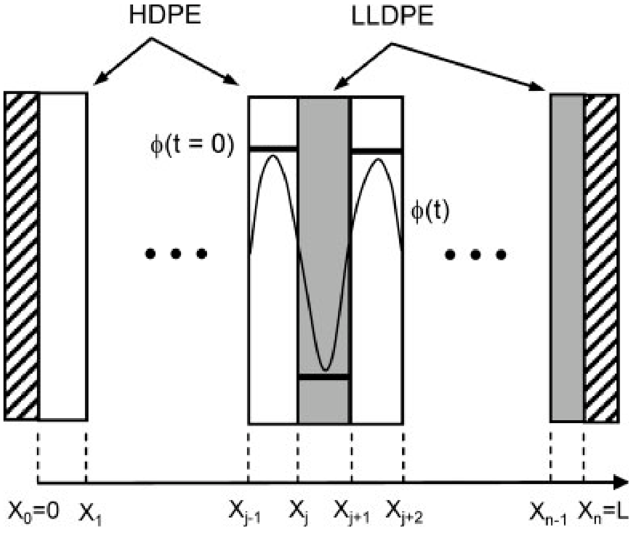

Figure 1. One-dimensional mutual diffusion between alternatively combined HDPE and LLDPE layers.

$$\begin{cases} \phi(t=0,x) = 1 & \text{within HDPE layers where } x_{j-1} \le x \le x_j,\ j = 1,3,5,\ldots,n-1 \\ \phi(t=0,x) = 0 & \text{within LLDPE layers where } x_j \le x \le x_{j+1},\ j = 1,3,5,\ldots,n-1 \end{cases} \tag{11}$$

where n is the total number of layers.

The multilayer sample is confined between two solid walls, and there is no diffusion of polymers into the wall, so the boundary conditions are:

$$\begin{cases} \dfrac{\partial \phi(t,x)}{\partial x} = 0 & \text{for } x = x_o = 0 \\ \dfrac{\partial \phi(t,x)}{\partial x} = 0 & \text{for } x = x_n = 1 \end{cases} \tag{12}$$

x is normalized by the total thickness of the multilayer sample, i.e., the gap between the two parallel plates.

Once the concentration profile is solved, the multilayer sample is subdivided into N elements along the x coordinate. N is chosen to be large enough, i.e. greater than 1000, such that the maximum concentration difference within each element is $<1\%$. Under this condition LLDPE/HDPE can be considered completely mixed within each element. For completely mixed LLDPE/HDPE blends, the apparent viscosity, η_{app}, as a function of volume concentration, ϕ, is fit with a power law mixing rule[35,36]:

$$\eta_{app}^s = \phi \eta_a^s + (1-\phi)\eta_b^s \tag{13}$$

where η_a and η_b are the viscosity of HDPE and LLDPE, respectively. On the other hand, the apparent viscosity of a multilayer sample is

$$\frac{1}{\eta_{app}} = \frac{\sum_i h_{a,i}/H}{\eta_a} + \frac{\sum_j h_{b,j}/H}{\eta_b} \tag{14}$$

where $h_{a,i}$ and $h_{b,j}$ are the thicknesses of HDPE and LLDPE layers, and H is the total layer thickness (which is equal to the gap between the two parallel plates). Combining Eqs. 13 and 14, the apparent viscosity of the multilayer sample at time t is

$$\frac{1}{\eta_{app}(t)} = \sum_{i=1}^{N} \frac{1/N}{\left[\phi(t,x_i)\eta_a^s + (1-\phi(t,x_i))\eta_b^s\right]^{1/s}} \tag{15}$$

As discussed before, D_{AB} is a strong function of the concentrations of the two PE's. This makes Eqs. 10, 11, and 12 nonlinear partial differential equations. They cannot be solved analytically. We first treat D_{AB} as a constant and give an analytical solution. Then, we treat D_{AB} as a function of concentrations and solve it numerically.

Constant diffusion coefficient

Neglecting the dependence of the diffusion coefficient D_{AB} on concentration, Eq. 10 can be rewritten as

$$\frac{\partial \phi}{\partial t} = D_{AB} \frac{\partial^2 \phi}{\partial x^2} \tag{16}$$

with same initial and boundary conditions as in Eqs. 11 and 12. The analytical solution of these linear PDE's is expressed as a Fourier series:

$$\phi(t,x) = \sum_{j=1}^{n-1}(x_{j+1} - x_j) + \sum_{k=1}^{\infty}\cos(k\pi x)e^{-(k\pi)^2 D_{\mathrm{AB}} t} \times \left\{ \sum_{j=1}^{n-1} \frac{2}{k\pi}\left[\sin(k\pi x_{j+1}) - \sin(k\pi x_j)\right] \right\} \tag{17}$$

where j has only odd values. Inserting this solution into Eq. 15, $\eta_{\mathrm{app}}(t)$ of the multilayer sample can be calculated and D_{AB} can be found by fitting the experimentally measured $\eta_{\mathrm{app}}(t)$.

Concentration dependent diffusion coefficient

Since HDPE and LLDPE have the same chemistry and similar chain structure (but different molecular weights) to a good approximation, we can set

$$\Lambda_{\mathrm{oA}} = \Lambda_{\mathrm{oB}} = \Lambda_{\mathrm{o}} \text{ and } N_{\mathrm{eA}} = N_{\mathrm{eB}} = N_{\mathrm{e}} \tag{18}$$

Alamo et al.[37] studied the miscibility of HDPE and LLDPE using small angle neutron scattering and found they are fully miscible when the branch content of LLDPE is <4 branches per 1000 —C—. Under such condition, we can set $\chi = 0$. Combining Eqs. 8, 9, and 18, D_{AB} can be simplified to

$$D_{\mathrm{AB}} = \Lambda_{\mathrm{o}} N_{\mathrm{e}} k_{\mathrm{B}} T \left(\frac{1-\phi}{N_{\mathrm{A}}} + \frac{\phi}{N_{\mathrm{B}}} \right)^2 \tag{19}$$

Thus Eq. 10 can be rewritten as:

$$\frac{\partial \phi}{\partial t} = \Lambda_{\mathrm{o}} N_{\mathrm{e}} k_{\mathrm{B}} T \frac{\partial}{\partial x}\left[\left(\frac{1-\phi}{N_{\mathrm{A}}} + \frac{\phi}{N_{\mathrm{B}}} \right)^2 \frac{\partial \phi}{\partial x} \right] \tag{20}$$

with same initial and boundary conditions as in Eqs. 11 and 12. The Galerkin FEM is used here to give a numerical solution.

First, the diffusion domain $0 \leqslant x \leqslant 1$ is discretized into N elements. The original interfaces between each HDPE and LLDPE layer are set as nodes, and more nodes are inserted to make up N elements. The number of nodes inserted into each layer is determined such that the element density distribution is uniform in the whole diffusion domain. Let $\psi(x)$ be the basis function, then $\phi(t,x)$ is approximated as:

$$\phi(t,x) = \sum_{i}^{N+1} \alpha_i(t)\psi^i(x) \tag{21}$$

Applying the Galerkin FEM,[38]

$$R = \int_0^1 \sum_{j=1}^{N+1} \left\{ \frac{\partial \phi(x,t)}{\partial t} - \frac{\partial}{\partial x}\left(D_{\mathrm{AB}} \frac{\partial \phi}{\partial x} \right) \right\} dx \tag{22}$$

then Eq. 20 can be reduced to:

$$\underline{\underline{\mathbf{M}}} \frac{d\underline{\alpha}(t)}{dt} = -\underline{\underline{\mathbf{A}}}\,\underline{\alpha}(t) \tag{23}$$

where

$$\mathbf{M}_{ij} = \int_0^1 \psi^i \psi^j dx \tag{24}$$

and

$$-\mathbf{A}_{ij} = \int_0^1 D_{\mathrm{AB}} \frac{d\psi^i}{dx}\frac{d\psi^j}{dx} dx \tag{25}$$

and

$$\underline{\alpha}(t) = \left\{ \alpha_1(t), \alpha_2(t), \ldots, \alpha_{N+1}(t) \right\} \tag{26}$$

Equation 23 is a set of ordinary differential equations. The 4th order Runge–Kutta method is used to solve them. After $\phi(t,x)$ is solved, first the concentration difference in each element is checked to make sure it is <5%, otherwise the total number of elements N is increased. Then Eq. 15 is used to calculate $\eta_{\mathrm{app}}(t)$ except that the viscosity of a HDPE/LLDPE homogenous mixture with concentration $\phi(t,x)$ is found using a 3rd order spline interpolation method (as explained later in the *Experimental section*). By fitting the experimental values of $\eta_{\mathrm{app}}(t)$, the constant Λ_0 can be found. Thus, using Eq. 19, D_{AB} can be calculated at any concentration.

Experimental

The two polyethylenes used in this study were HDPE (Dowlex 4452, Dow Chemical Company) with $M_{\mathrm{w}} = 40$ kg/mol and $M_{\mathrm{w}}/M_{\mathrm{n}} = 3.1$ and LLDPE (Exceed 305-D60, ExxonMobil Chemical Company) with $M_{\mathrm{w}} = 160$ kg/mol and $M_{\mathrm{w}}/M_{\mathrm{n}} = 2.5$. The viscosity of these two PE's at 200°C was measured in a parallel plate rheometer (DSR, Rheometric Scientific Inc.), and plotted in Figure 2.

Sheets of HDPE/LLDPE with 32 alternating layers were prepared using a multilayer coextrusion line. Details of this multilayer coextrusion setup are given elsewhere.[39] The multilayer sheets were about 1.0 mm thick and 40.0 mm wide. The volume concentration of the HDPE was 30% or 50%. Colored polyethylene pellets were used to measure the residence time and found to be about 45 s. Upon exiting the

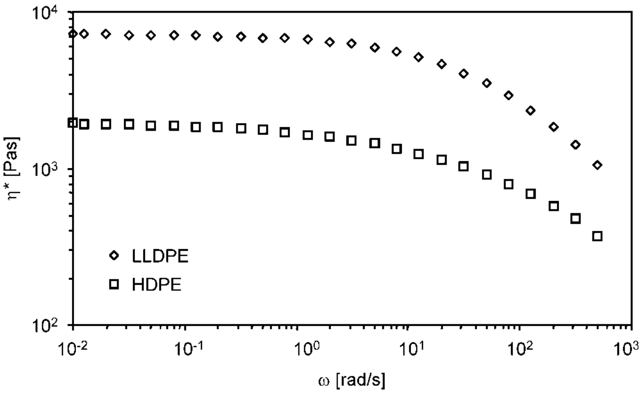

Figure 2. Complex viscosity of LLDPE and HDPE at 200°C.

coextrusion die, the multilayer melt was quenched between two water chilled rolls, which stopped the diffusion.

The multilayer sheets were cut into 25 mm disks. The disks were loaded into the parallel plate rheometer which was preheated at 200°C. To preserve the layer structure, the gap between the two plates was adjusted while the multilayer sample was being melted so no material was squeezed out from between the plates. To minimize thermal degradation or crosslinking, the test cell was blanked with flowing nitrogen. The complex viscosity of the multilayer samples was measured at a frequency of $\omega = 1.0$ rad/s every 30 s for about 1 h.

The multilayer sheets were microtomed immediately after coextrusion to obtain cross sections. The layer structure was examined via light microscopy (Nikon Optiphot-Pol) using polarized light. Figure 3a shows a cross section view. The layer structure is clear, and the interfaces are sharp. This confirms that the diffusion between the two PE's in the short residence time (45 s) during coextrusion is negligible. After the multilayer sheets were tested for about 2 h, a cross section of the sample was also examined, as shown in Figure 3b. The layer structure completely disappeared due to mutual diffusion.

Melt blends of these two PEs were also made in a HAAKE mixer at 180°C and 60 rpm for 10 min. To prevent thermal degradation or crosslinking during the blending, 1.0 wt% of irganox 1010 was added. Five blends were prepared with HDPE volume concentration as 0, 30, 50, 70, and 100%. The complex viscosities of these blends were measured in the parallel plates at 200°C. The viscosities of these blends at $\omega = 1.0$ rad/s are plotted in Figure 4. The solid line is the fit using Eq. 13 with $s = 1/2.3$. The fit is good except at low HDPE concentration, where the measured value is much higher than the calculation. This type of deviation has been reported by many others, as reviewed by Utracki.[36] Generally, an emulsion model with negative heat of mixing can fit the data. However, we did not find a model that could fit the whole concentration range with enough accuracy. Therefore, in this study the experimental data were used as a master curve and a 3rd order spline interpolation method was used to find the viscosity of the blends at any concentration.

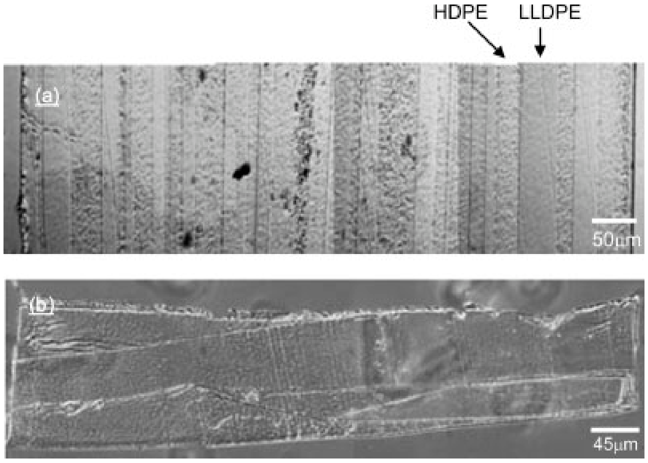

Figure 3. (a) Micrograph of a HDPE/LLDPE 32 layer sample; (b) micrograph of a HDPE/LLDPE multilayer sample after annealing at 200°C for 2 h.

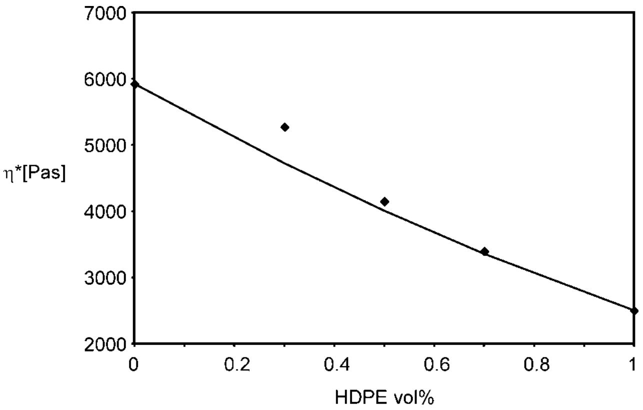

Figure 4. Complex viscosity of blends of HDPE/LLDPE measured at 200°C and 1 rad/s frequency.

The solid line is the calculated viscosity of the blends using Eq. 13 with an exponent of (1/2.3).

Results and Discussion

Miscibility of the two polyethylenes

The branch content of the LLDPE was measured using proton NMR. The areas under the methyl group —CH_3 at 0.96 ppm and the methylene group —CH_2— in the backbone at 1.37 ppm were used to determine the branch content. It was found to be <2 branches per 1000 backbone carbon. Thus, according to Alamo et al.,[37] these two PE's are fully miscible with each other. This is supported by Figure 3b, which shows that the HDPE and LLDPE layers fully diffused into each other and formed a homogenous mixture given enough time.

Rheological measurements

Figure 5a and b show the complex viscosity vs. time for the 32 layer sample with 50 and 30 vol% HDPE, respectively. The complex viscosity of both samples increased due to mutual diffusion. The whole viscosity curve can be divided into three stages. At the beginning, the viscosity increased rapidly. After about 10 min for the sample with 50% HDPE and 5 min for the sample with 30% HDPE, the rate of increase slowed and gradually transitioned to the third stage, where the viscosity of both samples approached a saturation value.

The complex viscosity of the melt blends of 50% HDPE and 30% HDPE are read from Figure 4 and plotted in Figures 5a, b as the upper bound. Using Eq. 14, the apparent viscosity of these two 32 layer samples without mutual diffusion are also calculated and plotted in Figures 5a, b as the lower limit. The measured apparent viscosities of these two samples are between the two limits. The initial values of the apparent viscosity are higher than the lower limit, indicating that a certain amount of mutual diffusion occurred during the

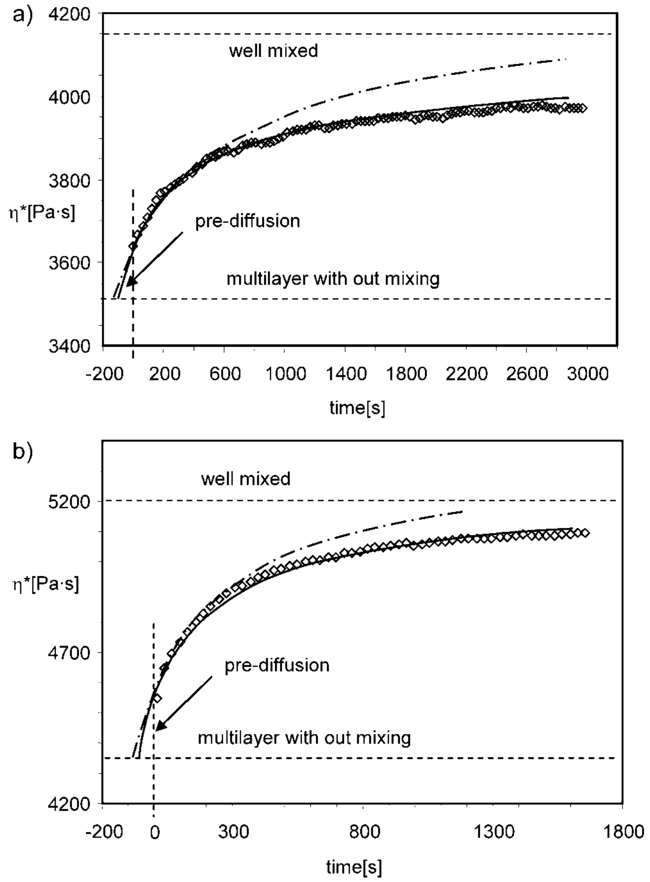

Figure 5. Complex viscosity vs time for a 32 layer HDPE/LLDPE sample with (a) 50% HDPE and (b) 30% HDPE.

The upper dashed line is the viscosity of a well mixed sample; the lower dashed line is the viscosity of a 32 layer sample calculated by Eq. 14 assuming no mutual diffusion. The broken curve is the calculated viscosity vs time for the 32 layer sample assuming constant mutual diffusion coefficient. The solid curve is the calculated viscosity vs time for the 32 layer sample assuming concentration dependent mutual diffusion coefficient. The calculated curves have been shifted left to start before zero time to account for the diffusion occurred during coextrusion and loading the rheometer.

coextrusion process. Note that it takes about 400 s for the sample with 50% HDPE to reach the half value of the final apparent viscosity, while it only takes about 150 s for the sample with 30% HDPE. This is caused by the fast diffusion of the HDPE component and agrees with the prediction by Kramer et al.[14] while Brochard-Wyart et al.[13] predict the opposite.

Constant diffusion coefficient

Assuming the mutual diffusion coefficient is not a function of concentration, the concentration profile and apparent viscosity of the 32 layer samples with 30 or 50% HDPE can be expressed explicitly using Eqs. 15 and 17. To account for the mutual diffusion which occurred during coextrusion and sample loading the zero times were shifted. The residence time in the coextrusion was about 45 s, and the sample loading and melting time in the rheometer was about 60 s. To best fit the viscosity data, the zero time of the sample with 30% HDPE was shifted to -110 s, and the zero time of the sample with 50% HDPE was shifted to -130 s. The difference is likely due to the sample loading and melting time in the rheometer.

The calculated viscosity vs. time is plotted in Figure 5a as a dashed line. By fitting the experimental data in the initial rapid diffusion stage, the diffusion coefficient was found to be 3.5×10^{-14} m^2/s. The calculated apparent viscosity vs. time deviates from the measured data in the transition stage and is consistently higher in the final stage. This error is obviously due to the assumption of a constant mutual diffusion coefficient. In the initial stage, there is only a small amount of HDPE and LLDPE diffused into each other. The mutual diffusion is limited to the vicinity of the interface region, and the concentration profile in bulk layers remains unchanged. At this stage, the mutual diffusion is just like tracer diffusion. Thus, the mutual diffusion coefficient is determined by the molecular weight of the two PE's, which is constant. However, in the later stage, when the HDPE and LLDPE diffuse into each other, the concentration gradient starts to affect the mutual diffusion coefficient. Thus, the assumption of constant diffusion coefficient becomes invalid.

Similar results were obtained with the 32 layer sample with 30% HDPE. The calculated viscosity vs. time is plotted as the dashed line in Figure 5b. Fitting the short time data, the mutual diffusion coefficient is found to be 2.5×10^{-13} m^2/s, which is about one order of magnitude higher than that found in the 32 layer sample with 50% HDPE. This again shows the strong dependence of the mutual diffusion coefficient on concentration.

Diffusion coefficient as a function of concentration

When the mutual diffusion coefficient is considered a function of concentration, the nonlinear partial differential equations, i.e., Eqs. 11, 12, and 20, are solved numerically using FEM as derived in *Concentration dependent diffusion coefficient section*. Using the computed concentration profile in the diffusion domain, the apparent viscosity vs. time for the 32 layer sample with 50% HDPE is calculated and plotted in Figure 5a as a solid line. Again to account for the mutual diffusion which occurred during coextrusion and sample loading the zero time was shifted to -100 s. The calculations fit the experimental data well using a mobility parameter Λ_0 of 4.5×10^{11} m/N s. Since the HDPE volume concentration is a function of position and time, the mutual diffusion coefficient is also a function of position and time. Inserting the obtained mobility parameter into Eq. 19, the mutual diffusion coefficient for 32 layers sample with 50% HDPE at $x = 0.52$ (HDPE rich) and $x = 0.24$ (LLDPE rich) at different times is calculated and listed in Table 1.

Table 1. The Mutual Diffusion Coefficient (m^2/s) in the 32 Layers With 50% HDPE

	$t = 0$ s	$t = 100$ s	$t = 500$ s	$t = 3000$ s
$x = 0.52$	2.4×10^{-14}	3.2×10^{-14}	7.3×10^{-14}	8.4×10^{-14}
$x = 0.24$	2.0×10^{-12}	1.8×10^{-12}	1.2×10^{-12}	0.9×10^{-12}

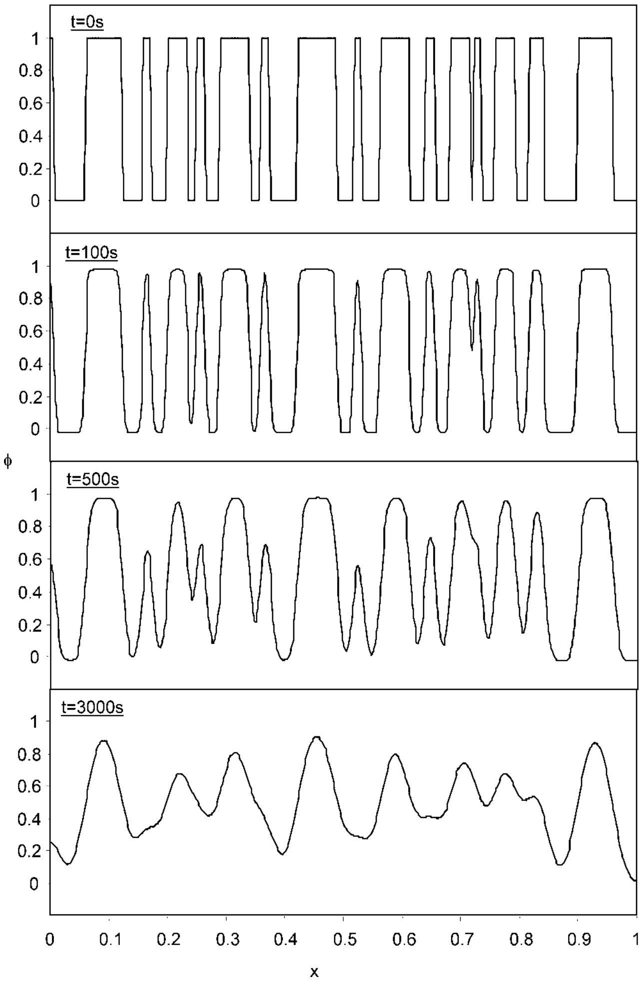

Figure 6. Calculated concentration profile in the multilayers with 50 vol % HDPE at diffusion time of 0, 100, 500, and 3000 s.

At the beginning of the mutual diffusion, there are two types of tracer diffusion in the multilayers, i.e., (1) the LLDPE tracers diffuse into the HDPE layers and (2) the HDPE tracers diffuse into the LLDPE layers. The diffusion coefficient of the first type is about two orders of magnitude lower than the second type because the molecular weight of LLDPE is about four times that of HDPE. When the mutual diffusion propagates into each layer, the mutual diffusion coefficients in HDPE-rich layers and LLDPE-rich layers converge to the same value, about 10^{-13} m^2/s (See Table 1 at 3000 s).

The concentration of HDPE in the multilayer samples varies at different locations and for different diffusing times; so does the mutual diffusion coefficient. However, the mobility parameter Λ_o remains constant. The same mobility parameter fits the measured viscosity data of the 32 layer sample with 30% HDPE, as shown in Figure 5b. The zero time was shifted to −85 s. This is in contrast to the results in *Constant Diffusion Coefficient Section*, where two different diffusion coefficients must be used to fit the measured viscosity data for the two multilayer samples.

It is interesting to examine the evolution of the concentration profile in the multilayers during the diffusion. Figure 6 shows the calculated concentration profile for 32 layers at diffusion times of 0, 100, 500, and 3000 s. The initial concentration profile is taken from a real cross sectional image like Figure 3a for 50% HDPE. When diffusion starts, the HDPE molecules quickly move into LLDPE layers, as illustrated by the rapid increase of HDPE concentration in the LLDPE layers. The diffusion front also moves into LLDPE layers, resulting an asymmetric concentration profile. This is exactly the result suggested by Kramer et al.[14] The experiment was stopped at about 1 h when there was still quite a large concentration gradient in the multilayers. However, the important features of the mutual diffusion are captured within this time frame and the mutual diffusion coefficient values in both phases are nearly equal (Table 1, 3000 s).

Conclusions

We have developed a useful technique to measure the mutual diffusion coefficient of a pair of miscible polymers via viscosity measurement of multilayer samples of these two polymers. With the large interfacial area in these coextruded layers, if the viscosity difference between the two polymers is greater than two-fold then increase of the apparent viscosity will be significant enough to allow reliable measurement. Therefore, we can extract the mutual diffusion coefficient of a miscible pair. We illustrated the technique with HDPE/LLDPE.

The theory of Brochard-Wyart et al.[13] modified later by Kramer et al.[14] is used successfully in this work to describe the physics of the mutual diffusion. The importance of a concentration dependent mutual diffusion coefficient is demonstrated in two ways here: first, two different constant mutual diffusion coefficients are needed for the same diffusion pair with different concentrations if one assumes a concentration independent mutual diffusion coefficient; second, one concentration dependent function is obtained for the mutual diffusion coefficient of the same diffusion pair with different concentrations. Using this function, the whole course of the mutual diffusion of two samples with different molecular weights can be simulated and have good agreement with the experimental data.

The mutual diffusion in this multilayer structure is described by a set of nonlinear partial differential equations. We successfully solved this problem using the Galerkin FEM. In the work of other researchers in which a multilayer structure was used, a constant mutual diffusion coefficient was assumed to simplify the problem to a set of linear differential equations. We have shown that such an assumption is only valid for the initial stage when the mutual diffusion can be approximated as tracer diffusion. However, the two components continue to diffuse into each other after the short initial stage, and the assumption of constant mutual diffusion is no longer valid.

For the mutual diffusion in multilayers, we proposed a periodic delta function for the initial conditions and zero diffusion flux at the two solid walls for the boundary conditions. Therefore, all layers are considered as one diffusion domain; thus, one unique solution is obtained. In other studies the mutual diffusion was solved on a two layer model, and the whole diffusion domain was assumed to be composed of identical replicas of these two layers. This is incorrect considering (1) the layers are generally not uniform in thickness; (2) the boundary conditions of the two layers which are in contact to the walls are different from those that are not; (3) interfaces only exist in a multilayer sheet when there is no mutual diffusion; thus, once mutual diffusion starts, there are no interfaces at all, e.g., there is one diffusion domain rather than a set of individual layers.

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