

Polymer-Polymer Interdiffusion During Coextrusion

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Polymer-polymer interdiffusion during coextrusion is considered theoretically from the point of view of interdiffusion between two melt streams flowing side by side in a film or sheet coextrusion die. It has been found that three factors, namely, molecular weight, the interaction parameter, and polydispersity have a profound influence on the interfacial layer thickness and adhesive bond strength of coextruded films and sheets. It is pointed out that when interdiffusion between two chemically dissimilar polymers takes place in stratified two-phase flow, the chain orientation in the flow channel greatly influences the rate of interdiffusion, and consequently the interfacial layer thickness and adhesive bond strength. Orientation factors for macromolecular chains in a steady shear flow field are expressed in terms of shear stress at the interface and the plateau modulus of each of the respective polymers being coextruded. As an illustration, we have used information on the self-diffusion coefficients for poly(vinylidene fluoride) and poly(methyl methacrylate) in the molten state, to estimate the interfacial layer thickness and adhesive bond strength of coextruded two-layer sheets, as affected by processing variables.

INTRODUCTION

In recent years the subject of polymer-polymer interdiffusion (or mutual diffusion) in *compatible* polymer systems has extensively been discussed in the literature, both experimentally (1–8) and theoretically (9–15). Using the reptation concept of polymer chain dynamics (16, 17), some researchers considered the polymer-polymer interdiffusion process occurring in welding and crack healing problems (18–22). It should be mentioned that all of these studies dealt with polymer-polymer interdiffusion under *static* conditions. However, in the coextrusion process (23–27), where two chemically dissimilar polymers are coextruded through a die, a better understanding of polymer-polymer interdiffusion in a *shear flow field* is needed. In the absence of chemical reactions between the two melt streams, the coextruded products would have no interfacial adhesion, unless, upon contact, interdiffusion were to take place between the two melt streams across the initial interface. Thus, information on the rate of interdiffusion and the interfacial layer thickness is very important to predict the adhesive bond strength of coextruded products.

It is not difficult to speculate that the rate of interdiffusion across the initially sharp interface between two chemically dissimilar polymers would be different in a shear flow field from that under static con-

ditions, since the orientation of polymer chains in a shear flow field may profoundly influence the rate of interdiffusion. This problem has received little attention from researchers. In this paper we will present results of predictions of the interfacial layer thickness and adhesive bond strength of coextruded films or sheets in terms of processing variables, based on information on the self-diffusion coefficients of the constituent components under static conditions.

THEORETICAL CONSIDERATIONS

Let us consider the stratified two-phase flow in a sheet-forming coextrusion die (i.e., flow between two parallel planes with semi-infinite width), as shown schematically in *Fig. 1a*. When the two polymers have different viscosities, they develop velocity profiles in the flow channel, as shown schematically in *Fig. 1b*. When the two polymers are *compatible*, polymer chains will diffuse across the original interface, forming a diffuse interface. It can be surmised that under a shear field, the polymer chains will have average orientation angles in the respective phases, which are greater than 45 degrees, as shown schematically in *Fig. 1b*. Note that when there is no flow (i.e., in random distribution), the polymer chains can be assumed to have an average orientation angle of 45 degrees. Our primary objective here is to obtain expressions which will enable us to determine the interfacial layer thickness and consequently the adhesive bond strength of coextruded sheets (or films).

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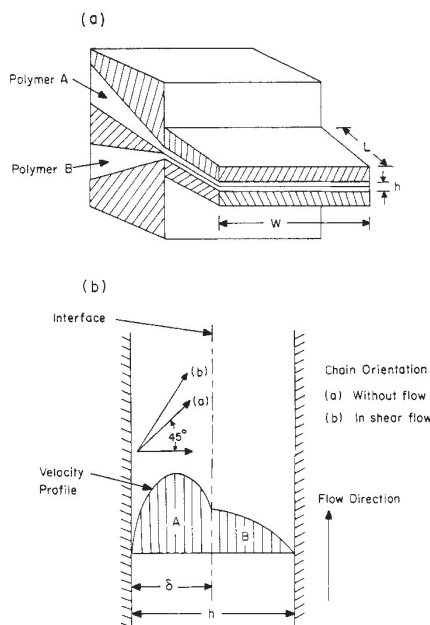


Fig. 1. (a) Schematic of a two-component sheet-forming coextrusion die; (b) Schematic depicting the velocity profiles and average orientation of macromolecules in stratified two-component flow in a sheet-forming coextrusion die.

If we postulate that a diffuse interface (i.e., an interphase) is developed by the interdiffusion of two molten polymers across the original interface during coextrusion, then the rate of formation of a diffuse interface (thus the interfacial layer thickness) would depend on the orientation of polymer chains.

Polymer-Polymer Interdiffusion Under Static Conditions

Let us first consider the interdiffusion between two polymers across an initially flat interface under static conditions. The general Fick's equation for one-dimensional diffusion can be written as

$$\frac{\partial \phi_A}{\partial t} = \frac{\partial}{\partial x} \left(D(\phi_A) \frac{\partial \phi_A}{\partial x} \right) \quad (1)$$

where $D(\phi_A)$ is the concentration-dependent interdiffusion (mutual diffusion) coefficient. There are two theories that have been proposed to relate the interdiffusion coefficient to the tracer-diffusion coefficients, namely,

(i) Fast-mode theory (14, 15):

$$D(\phi_A) = (1 - \phi_A)D_A + \phi_A D_B \quad (2)$$

(ii) Slow-mode theory (9–13):

$$1/D(\phi_A) = (1 - \phi_A)/D_A + \phi_A/D_B \quad (3)$$

where ϕ_i is the volume fraction of component i ($i = A, B$) and D_A and D_B are the intrinsic diffusion

coefficients defined by

$$D_A = N_A D_A^* \left[\frac{1 - \phi_A}{N_A} + \frac{\phi_A}{N_B} + 2|\chi| \phi_A (1 - \phi_A) \right] \quad (4a)$$

and

$$D_B = N_B D_B^* \left[\frac{1 - \phi_A}{N_A} + \frac{\phi_A}{N_B} + 2|\chi| \phi_A (1 - \phi_A) \right] \quad (4b)$$

respectively, in which D_A^* and D_B^* are the tracer-diffusion coefficients of components A and B, respectively, N_A and N_B are the degrees of polymerization of components A and B, respectively, and χ is the Flory-Huggins interaction parameter. Note that D_A^* and D_B^* appearing in Eq 4 are related to molecular weights M_A and M_B , by

$$D_A^* \propto M_A^{-2}; \quad D_B^* \propto M_B^{-2} \quad (5)$$

in the reptation model and

$$D_A^* \propto M_A^{-1}; \quad D_B^* \propto M_B^{-1} \quad (6)$$

in the Rouse model (16, 17).

Some researchers (7, 8, 28, 29) have reported experimental results that support Eq 2, while others (4, 6, 30) have reported experimental results that support Eq 3. It can be shown that the values of $D(\phi_A)$ predicted by Eq 3 will always be lower than those predicted by Eq 2. Note that for $D_A^* \gg D_B^*$, Eq 2 gives $D \sim D_A^*$ (dominated by the fast component) and Eq 3 gives $D \sim D_B^*$ (dominated by the slow component). Note that in the most general situations both D_A^* and D_B^* depend on the composition of the system. The fundamental difference between the derivations of Eqs 2 and 3 is that, vacancy fluxes across the interface were included in the derivation of Eq 2, whereas they were neglected in the derivation of Eq 3. However, very recently, Hess and Akcasu (31) and Kehr, *et al.* (32), concluded that neither Eq 2 nor Eq 3 gives satisfactory description of the interdiffusion of a pair of chemically dissimilar polymers in the long time limit. Specifically, based on numerical simulations Kehr, *et al.* (32), argued that the tracer diffusion, where the motion of labeled chains is monitored, contains additional off-diagonal Onsager coefficients and thus such a simple relationship, as that given by Eq 2 or Eq 3, between the interdiffusion coefficient and the tracer-diffusion coefficients may not be satisfactory.

Let us now consider the case where two compatible polymers A and B of semi-infinite dimensions are brought together at a temperature greater than their respective glass transition temperatures and that an inert marker is placed at the original interface at time zero, $t = 0$. One would then expect mass transfer to occur, under static conditions, across the interface due to the interdiffusion of long-chain macromolecules across the interface, forming a diffuse layer of finite thickness which increases with time. The

equation of continuity for component A is given by:

$$\frac{\partial(\rho w_A)}{\partial t} + \nabla \cdot W_A = 0 \quad (7)$$

where ρ is the density of the mixture, w_A is the weight fraction of component A, ∇ is the gradient operator, and W_A is the total mass flux defined by

$$W_A = j_A - (v_A j_A - v_B j_B) \rho w_A \quad (8)$$

in which v_A and v_B are the partial specific volumes of components A and B, respectively, and j_A and j_B are the mass fluxes of components A and B, respectively.

For one-component mass transfer in the x -direction, j_A and j_B are given by

$$j_A = -\rho D_A \frac{\partial w_A}{\partial x}; \quad j_B = -\rho D_B \frac{\partial w_B}{\partial x} \quad (9)$$

When a polymer mixture is considered to have zero excess volume of mixing, its specific volume v is given by

$$v = w_A v_A + (1 - w_A) v_B \quad (10)$$

Note that the specific volume v of the mixture is related to the density ρ of the mixture by $v = 1/\rho$. In the general case under consideration here, the density ρ varies with both time t and distance x , and thus we have

$$\frac{\partial \rho}{\partial t} = -(v_A - v_B) \rho^2 \frac{\partial w_A}{\partial t}; \quad \frac{\partial \rho}{\partial x} = -(v_A - v_B) \rho^2 \frac{\partial w_A}{\partial x} \quad (11)$$

Substituting Eqs 8 through 11 into Eq 7 and after rearranging, one obtains

$$\begin{aligned} & \rho v_B \frac{\partial w_A}{\partial t} \\ &= [D_A - \rho w_A (v_A D_A - v_B D_B)] \frac{\partial^2 w_A}{\partial x^2} - \rho [(v_A - v_B) D_A \\ & \quad - 2\rho (v_A - v_B) w_A (v_A D_A - v_B D_B) \\ & \quad + (v_A D_A - v_B D_B)] \left(\frac{\partial w_A}{\partial x} \right)^2 \\ & \quad + \left[\frac{\partial D_A}{\partial x} - \rho w_A \frac{\partial}{\partial x} (v_A D_A - v_B D_B) \right] \frac{\partial w_A}{\partial x} \end{aligned} \quad (12)$$

Substituting Eq 4 into Eq 12, we obtain

$$\frac{\partial w_A}{\partial \tau} = g_1 \frac{\partial^2 w_A}{\partial \xi^2} + g_2 \left(\frac{\partial w_A}{\partial \xi} \right)^2 \quad (13)$$

where

$$\begin{aligned} g_1 &= \left[(1 - w_A) + w_A \frac{D_B^* N_B}{D_A^* N_A} \right] \\ & \quad \cdot \left[(1 - \phi_A) + \phi_A \frac{N_A}{N_B} + 2\phi_A (1 - \phi_A) |\chi| N_A \right] \end{aligned} \quad (14)$$

and

$$\begin{aligned} g_2 &= \left[(1 - 2v_A \rho) + (2v_A \rho - 1) \frac{D_B^* N_B}{D_A^* N_A} \right] \\ & \quad \cdot \left[(1 - \phi_A) + \phi_A \frac{N_A}{N_B} + 2\phi_A (1 - \phi_A) |\chi| N_A \right] \\ & \quad + v_A \rho \left[(1 - v_A \rho w_A) + v_B \rho w_A \frac{D_B^* N_B}{D_A^* N_A} \right] \\ & \quad \cdot \left[-1 + \frac{N_A}{N_B} + 2(1 - 2\phi_A) |\chi| N_A \right. \\ & \quad \left. + 2\phi_A (1 - \phi_A) N_A \frac{\partial |\chi|}{\partial \phi_A} \right] \end{aligned} \quad (15)$$

In Eq 13, τ and ξ are dimensionless variables defined as

$$\tau = (D_A^*/L^2)t; \quad \xi = x/L \quad (16)$$

where L is a characteristic length.

When $v_A D_A = v_B D_B$, $v_A = v_B = v = 1/\rho$, and D_A is independent of x (hence, independent of position), Eq 12 reduces to the well-known expression:

$$\frac{\partial w_A}{\partial t} = D_A \frac{\partial^2 w_A}{\partial x^2} \quad (17)$$

When $\rho_A = \rho_B = \rho$ and $v_A = v_B$, the volume fraction ϕ_A becomes identical to the weight fraction w_A and thus Eq 12 reduces to

$$\frac{\partial \phi_A}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \phi_A}{\partial x} \right) \quad (18)$$

where D is defined by Eq 2. When D_A and D_B are assumed to be constants which certainly are not supported by Eq 4, g_1 and g_2 appearing in Eq 13 are given by

$$g_1 = \left[(1 - w_A) + w_A \frac{D_B}{D_A} \right] \quad (19)$$

and

$$g_2 = \left[(1 - 2v_A \rho) + (2v_A \rho - 1) \frac{D_B}{D_A} \right] \quad (20)$$

respectively. Note that Wu, Chuang, and Han (2), hereafter abbreviated as WCH, solved Eq 13, using Eqs 19 and 20.

The mean-square interfacial layer thickness d^2 can be calculated with the expression (2):

$$d^2 = 4 \int_{-\infty}^{\infty} \frac{\partial w_B}{\partial x} (x - x_0)^2 dx \bigg/ \int_{-\infty}^{\infty} \frac{\partial w_B}{\partial x} dx \quad (21)$$

where x_0 is the initial interfacial position.

Polymer-Polymer Interdiffusion in Steady Shear Flow

The interfacial layer thickness formed during coextrusion can be predicted with Eq 21 when the effect of shear flow on the interdiffusion coefficient is

properly taken into account in solving Eq 12. For this, we propose the use of *apparent* intrinsic diffusion coefficients, $\tilde{D}_A$ and $\tilde{D}_B$, defined by

$$\tilde{D}_A = \alpha_A D_A; \quad \tilde{D}_B = \alpha_B D_B \quad (22)$$

where D_A and D_B are defined by Eq 4, and α_A and α_B are orientation factors in steady shear flow for polymers A and B, respectively, which are defined by (33):

$$\alpha_i = \frac{\cos\{(\pi/4) + [\tan^{-1}(J_{eb,i}^o/\sigma_{\text{int}})]/2\}}{\cos(\pi/4)} \quad (i = A, B) \quad (23)$$

where σ_{int} is the shear stress at the interface and $J_{eb,t}^o$ is the steady-state shear compliance for component i in a polydisperse polymer.

There are several different ways of relating the steady-state shear compliance for *polydisperse* polymers J_{eb}^o to the steady-state shear compliance for *monodisperse* polymers J_e^o , as suggested in the literature (34–36). In the present study we have chosen the following relationship (35):

$$J_{eb,l}^o = J_{el}^o (\bar{M}_w / \bar{M}_n)^3 \quad (24)$$

Note that J_e^o for monodisperse polymers can be determined from information on the plateau modulus G_N^o , by using the following relationship (34):

$$J_e^o G_N^o \approx 3.0 \quad (25)$$

From Eqs 23 through 25, we obtain

$$\alpha_i = \frac{\cos\{(\pi/4) + [\tan^{-1}(3\sigma_{\text{int}}(\bar{M}_{wt}/\bar{M}_{nt})^3/G_{Nt}^\circ)]/2\}}{\cos(\pi/4)} \quad (26)$$

It can be seen in Eq 26 that α_i ($i = A, B$) depend on the shear stress at the interface σ_{int} , the plateau moduli G_{Ni}^0 , and polydispersity $\bar{M}_w/\bar{M}_n$. Note in Eq 26 that α_i ($i = A, B$) will become unity when there is no flow and will decrease steadily from unity as σ_{int} and polydispersity increase.

In reference to the schematic given in *Fig. 1*, the shear stress at the interface, σ_{int} , can be calculated by solving the equation of motion in rectangular coordinates (x, y, z):

$$-\frac{\partial p}{\partial z} + \frac{\partial \sigma_{yz}}{\partial y} = 0 \quad (27)$$

for phases A and B , respectively, subject to the boundary conditions:

$$(\sigma_{yz})_A = (\sigma_{yz})_B = \sigma_{\text{int}} \quad \text{at} \quad y = \delta \quad (28a)$$

$$(v_z)_A = 0 \quad \text{at } y = 0 \quad (28b)$$

$$(v_z)_B = 0 \quad \text{at } y = h \quad (28c)$$

where σ_{yz} is the shear stress, and $(v_z)_A$ and $(v_z)_B$ are the velocities for phases A and B, respectively. In order to solve Eq 27, we use the truncated power law,

$$\sigma_{yz} = \begin{cases} \eta_o \dot{\gamma} & \text{for } \dot{\gamma} \leq \dot{\gamma}_o \\ \eta_o (\dot{\gamma}/\dot{\gamma}_o)^{n-1} \dot{\gamma} & \text{for } \dot{\gamma} > \dot{\gamma}_o \end{cases} \quad (29)$$

where η_0 is the zero-shear viscosity, $\dot{\gamma}$ is shear rate, dv_z/dy , and $\dot{\gamma}_0$ is the critical shear rate at which the

viscosity η starts to deviate from η_o . Substituting Eq 29 into Eq 27 and then solving the resulting expression, subject to the boundary conditions given by Eq 28, we can obtain the velocity profiles and values of σ_{int} for given processing conditions. Note that the above analysis can easily be extended to multilayers consisting of more than two chemically dissimilar polymers.

It should be pointed out that for a given pair of polymers and extrusion temperature, the value of σ_{int} depends on both the total flow rate and the position of the interface. Thus, the interfacial layer thickness and thus adhesive bond strength should depend on the total volumetric flow rate and also the position of the interface (i.e., the layer thickness ratio of the two polymers).

RESULTS AND DISCUSSION

Recently we coextruded poly(methyl methacrylate) (PMMA) with poly(vinylidene fluoride) (PVDF) using a two-layer, sheet-forming coextrusion die and found that the layers of coextruded PVDF/PMMA sheets had very strong adhesion (37). Note that mixtures of PVDF and PMMA are known to be compatible on a molecular level (38–41).

In order to determine the mean-square interfacial thickness d^2 under *static* conditions as defined by Eq 21, we had to solve Eqs 13 through 15 for the interdiffusion between PMMA and PVDF across an initially flat interface, subject to the following boundary and initial conditions:

$$w_A(-\infty, t) = 0 \quad \text{for } t \geq 0 \quad (30a)$$

$$w_A(+\infty, t) = 1 \quad \text{for } t \geq 0 \quad (30b)$$

$$w_A(\xi, 0) = 0 \quad \text{for} \quad -\infty < \xi \leq 0 \quad (30c)$$

$$w_A(\xi, 0) = 1 \quad \text{for } 0 < \xi < \infty \quad (30d)$$

For this, we needed information on tracer-diffusion coefficients, namely, D_A^* for PMMA and D_B^* for PVDF. Since there was no experimental data available for the tracer-diffusion coefficients for PMMA and PVDF, we calculated the self-diffusion coefficient for PMMA, D_A^0 , having the weight-average molecular weight of 1.075×10^5 , using the following expression [42]:

$$D_i^o = \frac{G_N^o}{135} \left(\frac{\rho RT}{G_N^o} \right)^2 \left(\frac{R_o^2}{M} \right) \frac{M_c}{M^2 \eta_o(M_c)} \quad (i = A, B) \quad (31)$$

where G_N^o is the plateau modulus, ρ is the density, R is the universal gas constant, T is the absolute temperature, R_o^2 is the unperturbed mean-square end-to-end distance, M is the molecular weight, M_c is the critical molecular weight for viscosity, and $\eta_o(M_c)$ is the zero-shear viscosity for the molecular weight M_c . Since the numerical value for $\eta_o(M_c)$ was not available, we used the following relationship:

$$\frac{\eta_o(M_c)}{\eta_o(M)} = \left(\frac{M_c}{M}\right)^{3.4} \quad (32)$$

in Eq 31.

In order to determine the value of D_A^0 for PMMA from Eq 31, values of G_N^0 , $\eta_0(M_c)$, and M_c must be known. Using the numerical values of various parameters, except for G_N^0 , given in Table II of WCH (2) we determined the value of D_A^0 for PMMA at 230°C to be 1.05×10^{-12} cm²/s. Note that M_c was determined from the relationship, $M_c = 2M_e = 2\rho RT/G_N^0$, and that the value of $G_N^0 = 6 \times 10^5$ Pa for PMMA was used (43). The value of D_B^0 for PVDF having the weight-average molecular weight of 1.45×10^5 and the G_N^0 of 4×10^5 Pa was then calculated using the following expression:

$$\frac{D_A^0}{D_B^0} = \frac{(G_{NA}^0/\eta_{0A})(R_{0A}^2)}{(G_{NB}^0/\eta_{0B})(R_{0B}^2)} \left(\frac{M_A/M_B}{M_{cA}/M_{cB}} \right)^{0.4} \quad (33)$$

where G_{NA}^0 and G_{NB}^0 are the plateau moduli of components A and B, respectively, η_{0A} and η_{0B} are the zero-shear viscosities of components A and B, respectively, R_{0A}^2 and R_{0B}^2 are the mean-square end-to-end distances of components A and B, respectively, M_A and M_B are the molecular weights of components A and B, respectively, and M_{cA} and M_{cB} are the critical molecular weights of components A and B, respectively. We have determined the value of D_A^0/D_B^0 to be 0.5 and consequently the value of D_B^0 for PVDF at 230°C to be 2.11×10^{-12} cm²/s.

Since there is no theoretical guideline as to how self-diffusion coefficients may be related to tracer-diffusion coefficients, in place of the tracer-diffusion coefficients D_A^* and D_B^* appearing in Eq 4, we used the values of self-diffusion coefficients D_A^0 and D_B^0 calculated above to numerically solve Eqs 13 through 15. Notice that self-diffusion can be regarded as a special case of tracer-diffusion in that, in tracer experiments the tracer-diffusion coefficient of a dilute concentration of labeled A or B chains is measured in a matrix blend of A and B chains that may differ in length and chemical species from the labeled ones, while in self-diffusion the diffusing chains and the matrix chains must be chemically identical, except for the label, and of the same degree of polymerization. Equating self-diffusion coefficient D^0 and tracer-diffusion coefficient D^* , as was done in the present study, is tantamount to equating the mobility of a labeled PVDF molecule in a PVDF matrix and that of an identically labeled PVDF molecule in a PMMA matrix. We do not believe that in the interface region during the coextrusion of PMMA and PVDF at 230°C, the mobility of a labeled PVDF molecule in the PVDF matrix is equal to the mobility of an identically labeled PVDF molecule in the PMMA matrix. Because at 230°C the labeled PVDF is only 46°C above the melting temperature T_m (ca. 174°C as reported in Table I of Ref. 44) of PVDF in the former case, whereas the labeled PVDF is 125°C above the glass transition temperature T_g (ca. 105°C) of the PMMA in the latter case. We expect that the labeled PVDF molecule will have a much lower mobility in the PVDF environment as compared to the PMMA environment.

One may be tempted to partially take into account the fact that different values of T_g for the PMMA and PVDF give rise to composition-dependent tracer-diffusion coefficients in the interface region, by applying the WLF equation to the values of D^*/T as suggested by Composto, *et al.* (7). However, the situation under consideration is much more complex, in view of the fact that the PMMA/PVDF blends exhibit crystallinity when the weight fraction w_B of PVDF in the mixture exceeds about 0.6. This indicates to us that it is not possible for us to have the same fractional free volume over the entire composition for the PMMA/PVDF blend system, and thus the tracer-diffusion coefficients for PMMA and PVDF should vary strongly with blend composition. According to a recent study by Composto, *et al.* (7), who measured tracer-diffusion coefficients for polystyrene (PS) and poly(xylene ether) (PXE), indeed the tracer-diffusion coefficients D_{PS}^* and D_{PXE}^* varied with blend composition in a very complex manner. They found that the interdiffusion coefficient in the PS/PXE blend system also varied with composition.

In view of the fact that we used composition-independent self-diffusion coefficients, in place of composition-dependent tracer-diffusion coefficients, to numerically solve Eq 13 through 15, the predicted values presented below of the interfacial thickness and orientation factors in the coextrusion of PMMA and PVDF must be regarded as approximate.

At this juncture, it is worth making a few remarks on how WCH obtained values of intrinsic diffusion coefficients, D_A and D_B (2). First, the ratio of D_A^0/D_B^0 was determined to be 1.28, using Eq 33 without the factor $[(M_A/M_B)/(M_{cA}/M_{cB})]^{0.4}$ (i.e., using the 3.0-power law for viscosity). Second, the ratio D_A/D_B was assumed to be equal to the ratio D_A^0/D_B^0 . Using this assumption, WCH determined the values of D_A and D_B by matching the experimentally measured distances between the gold marker and the crystalline boundary (see Figs. 3 and 4 in Ref. 2) with the computed values within a prescribed tolerance, by numerically solving Eq 13, 19, and 20. In other words, WCH did not determine values of self-diffusion coefficients, D_A^0 and D_B^0 . Third, D_A and D_B were assumed to be constants. Note that when the molecular weights of polymers are very large, the compositions are within a practical range (say $\phi_A > 0.01$), and the value of $|\chi| \geq 0.01$, the right-hand side of Eq 4 satisfies the following inequalities:

$$2\phi_A(1 - \phi_A)|\chi|N_A \gg (1 - \phi_A) + \phi_A N_A/N_B \quad (34a)$$

and

$$2\phi_A(1 - \phi_A)|\chi|N_B \gg (1 - \phi_A)N_B/N_A + \phi_A \quad (34b)$$

Under such circumstances, Eq 4 suggests that the following relationship is a reasonable approximation,

$$\frac{D_A}{D_B} = \frac{D_A^*}{D_B^*} \frac{N_A}{N_B} \propto (M_A/M_B)^{-1} \quad (35)$$

where Eq 5 was used. Equation 35 indicates that for polymers having very large molecular weights, the

intrinsic diffusion coefficient is inversely proportional to molecular weight. It should be remembered that according to Eq 5, the tracer-diffusion coefficient is inversely proportional to the square of molecular weight. It then becomes clear that the assumption that $D_A/D_B = D_A^0/D_B^0$ made by WCH is not valid for the PMMA and PVDF investigated.

Figure 2 gives interfacial composition profiles under static conditions plotted against the dimensionless variable, $u = x/2\sqrt{D_A^*t}$, for several values of M_A/M_B and thus of D_A^*/D_B^* . Note that the values of D_A^* and D_B^* were calculated using the procedure presented above. It is seen that the introduction of the dimensionless variable u permits us to have a single curve for a given pair of PMMA and PVDF. This indicates that the interfacial layer thickness d is proportional to the square root of diffusion time t , i.e., $d \propto t^{1/2}$. The broken straight line in Fig. 2 represents the following expression:

$$\phi_B = 1/2 - u/30.0 \quad \text{for } -15.0 \leq u \leq 15.0 \quad (36a)$$

$$\phi_B = 1.0 \quad \text{for } u \leq -15.0 \quad (36b)$$

$$\phi_B = 0.0 \quad \text{for } u \geq 15.0 \quad (36c)$$

which is the solution for a special case of Eq 13, specifically, $D_A^* = D_B^*$, $N_A = N_B$ and $\rho_A = \rho_B = \rho$. Equation 36 was obtained earlier by Brochard, *et al.* (10).

It can be seen in Fig. 2 that as the molecular weight of PVDF is decreased, the shape of the interfacial composition profile tends to become more asymmetric. This means that the distance penetrated by the PVDF phase into the PMMA phase is greater than the distance penetrated by the PMMA phase into the PVDF phase.

Figure 3 shows the dependence of the interfacial layer thickness d on the molecular weight of PVDF. It can be seen in Fig. 3 that d is proportional to $M_B^{-1/2}$ up to a certain value of M_B and then it decreases much more slowly, approaching a limiting value as the value of M_B becomes very large. This can

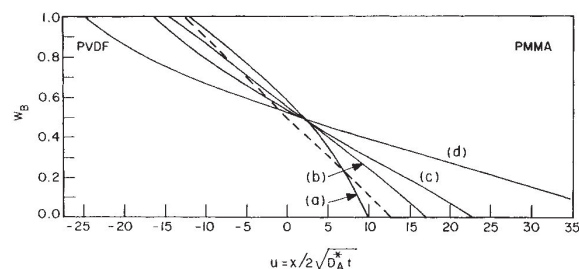


Fig. 2. Plots of interfacial composition profile versus the dimensionless variable $u = x/2\sqrt{D_A^*t}$ for $M_A = 1.075 \times 10^5$, $D_A^* = 1.05 \times 10^{-12} \text{ cm}^2/\text{s}$ and $|\chi| = 0.3$: (a) $M_A/M_B = 0.1$ and $D_A^*/D_B^* = 27.26$; (b) $M_A/M_B = 0.4$ and $D_A^*/D_B^* = 1.72$; (c) $M_A/M_B = 0.74$ and $D_A^*/D_B^* = 0.5$; and (d) $M_A/M_B = 2.7$ and $D_A^*/D_B^* = 0.038$. Broken line represents Brochard's curve (10).

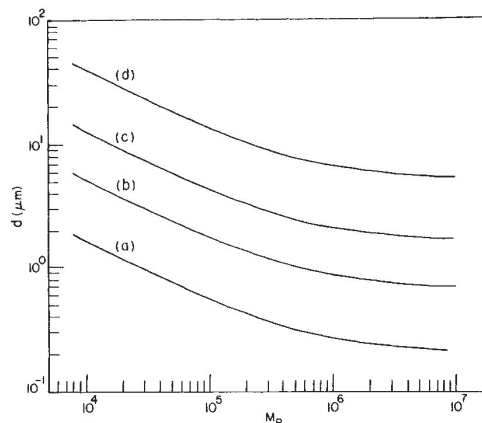


Fig. 3. Plots of interfacial layer thickness versus molecular weight of PVDF for $M_A = 1.075 \times 10^5$, $D_A^* = 1.05 \times 10^{-12} \text{ cm}^2/\text{s}$, and $|\chi| = 0.3$ at various diffusion times (s): (a) 1; (b) 10; (c) 60; (d) 600.

be explained upon examination of the following expression:

$$D(\phi_A) \approx D_A^* \left[(1 - \phi_A) + \phi_A \left(\frac{D_B^*}{D_A^*} \right) \left(\frac{N_B}{N_A} \right) \right] 2\phi_A(1 - \phi_A) |\chi| N_A \quad (37)$$

It should be mentioned that Eq 37 can be obtained from Eq 2 if the entropic term in Eq 4 is neglected for large values of N_A and N_B . Notice that as N_B increases to a sufficiently large value, making the value of $(D_B^*/D_A^*)(N_B/N_A)$ negligibly small (see Eq 5) compared to the value of $(1 - \phi_A)$, Eq 37 reduces to

$$D(\phi_A) \approx 2D_A^*\phi_A(1 - \phi_A)^2 |\chi| N_A \quad (38)$$

Equation 38 suggests that $D(\phi_A)$ can become independent of N_B for large values and thus the molecular weight of PVDF.

Figure 4 gives interfacial composition profiles under static conditions plotted against the dimensionless variable, $u = x/2\sqrt{D_A^*t}$, for different values of the interaction parameter χ , which was assumed to be independent of composition. Figure 5 gives interfacial composition profiles under static conditions plotted against the dimensionless variable, $u^* = x/2\sqrt{2D_A^*|\chi|t}$, for different values of $|\chi|$. It can be seen that the introduction of the dimensionless variable u^* yields a master curve, which is independent of $|\chi|$. This means that the interfacial layer thickness d is proportional to the square root of $|\chi|$. This observation indicates that as the degree of compatibility of a pair of polymers increases, the interfacial layer thickness increases accordingly.

In the results presented above, we assumed that both PMMA and PVDF were monodisperse. In order to demonstrate the effect of polydispersity on interdiffusion between PMMA and PVDF we considered the situation where only the PVDF is polydisperse while the PMMA is monodisperse, due to the

enormous computational time required. For this, we considered three different values of polydispersity for PVDF, using the log-normal distribution function. We could have used different forms of the distribution function (e.g., Shultz-Flory distribution function), but the choice of a different distribution function would not change the essential features of our analysis.

In solving Eqs 13 through 15 for the interdiffusion between a monodisperse PMMA and a polydisperse PVDF, the weight fraction of PVDF, w_B , was calculated using the following expression:

$$w_B = \sum_{i=1}^N \psi_{B,i} w_{B,i}(D_{B,i}^*) \quad (39)$$

where $\psi_{B,i}$ is the i th fraction of the molecular weight M_B for PVDF and $w_{B,i}$ is the interfacial composition

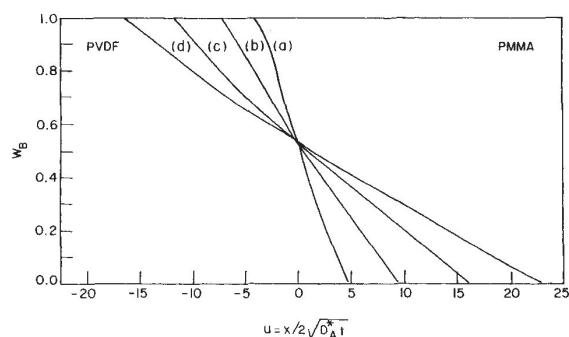


Fig. 4. Plots of interfacial composition profile versus dimensionless variable $u = x/2\sqrt{D_A^*t}$ for $M_A = 1.075 \times 10^5$, $M_A/M_B = 0.74$, $D_A^* = 1.05 \times 10^{-12} \text{ cm}^2/\text{s}$, and $D_A^*/D_B^* = 0.5$ for different values of $|\chi|$: (a) 0.01; (b) 0.05; (c) 0.15; and (d) 0.30.

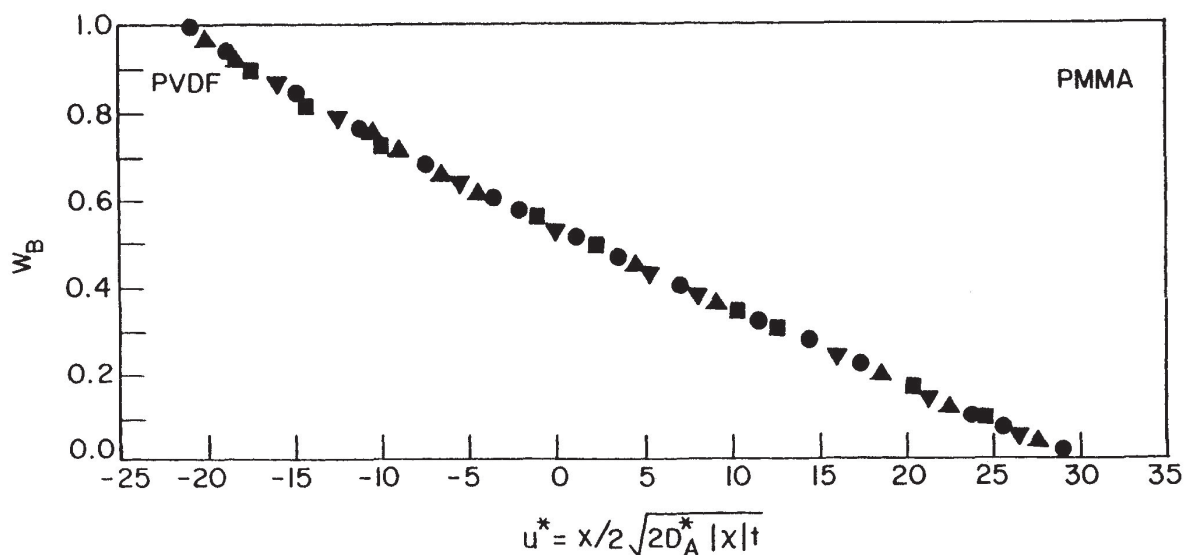


Fig. 5. Plots of interfacial composition profile versus dimensionless variable $u^* = x/2\sqrt{2D_A^*|\chi|t}$ for $M_A = 1.075 \times 10^5$, $M_A/M_B = 0.74$, $D_A^* = 1.05 \times 10^{-12} \text{ cm}^2/\text{s}$ and $D_A^*/D_B^* = 0.5$ for different values of $|\chi|$: (●) 0.3; (▼) 0.15; (▲) 0.05; and (■) 0.01.

profile, calculated numerically, for the molecular weights, M_A for PMMA and $M_{B,i}$ for PVDF. Note in Eq 39 that we had to compute the self-diffusion coefficient $D_{B,i}^*$ for each weight fraction of the PVDF having molecular weight $M_{B,i}$ before we could begin to numerically solve Eqs 13 through 15.

Figure 6 gives interfacial composition profiles under static conditions plotted against the dimensionless variable, $u = x/2\sqrt{D_A^*t}$, for different values of polydispersity, $\bar{M}_{wB}/\bar{M}_{nB}$, and the constant value of $|\chi| = 0.3$. It can be seen in Fig. 6 that the interfacial composition profile is smeared at large values of u as the polydispersity is increased. This means that the interfacial layer thickness increases as the polydispersity is increased, which indeed was predicted, as may be seen in Fig. 7. This prediction was made by substituting Eq 39 into Eq 21, i.e., by the following expression

$$d_{po}^2 = \frac{4 \sum_{i=1}^N \psi_{B,i} \int_{-\infty}^{\infty} (\partial w_{B,i}/\partial x)(x - x_o)^2 dx}{\sum_{i=1}^N \psi_{B,i} \int_{-\infty}^{\infty} (\partial w_{B,i}/\partial x) dx} \quad (40)$$

where d_{po} denotes the interfacial layer thickness for a polydisperse polymer. It should be remembered that, as discussed in reference to Fig. 3 for monodisperse PVDF, the interfacial layer thickness increases as the molecular weight of PVDF decreases. Therefore, we can conclude that an increase in interfacial layer thickness with increasing polydispersity, observed in Fig. 7, is attributable to the presence of the smaller macromolecules in the polydisperse PVDF.

However, Eq 40 does not give us insight as to how polydispersity influences the interfacial layer thickness d . In order to obtain an analytical expression which will enable us to describe how polydispersity

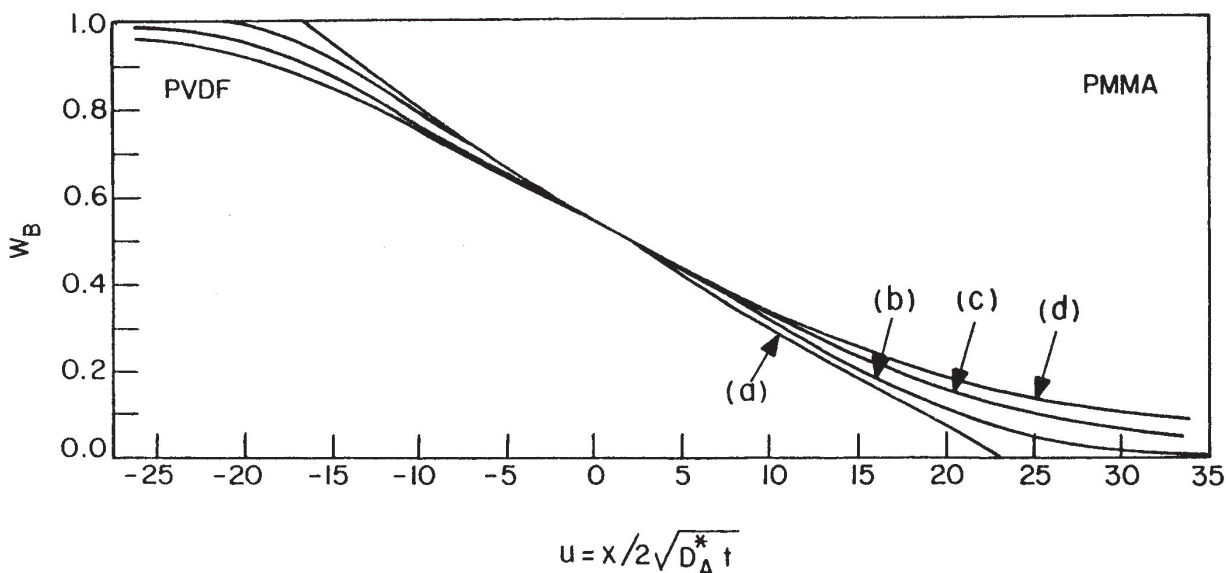


Fig. 6. Plots of interfacial composition profile versus dimensionless variable $u = x/2\sqrt{D_A^* t}$ for $M_A = 1.075 \times 10^5$, $D_A^* = 1.05 \times 10^{-12} \text{ cm}^2/\text{s}$, $|\chi| = 0.3$, $\bar{M}_{wB} = 1.45 \times 10^5$, and different values of $\bar{M}_{wB}/\bar{M}_{nB}$: (a) 1.0; (b) 1.4; (c) 2.4; and (d) 3.54.

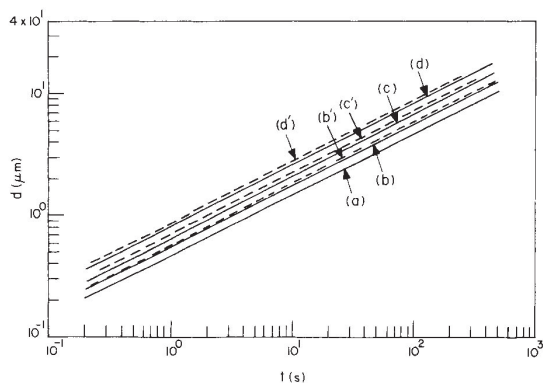


Fig. 7. Plots of interfacial layer thickness versus diffusion time for different values of $\bar{M}_{wB}/\bar{M}_{nB}$: (a) 1.0, (b) 1.4, (c) 2.4, and (d) 3.54. Other conditions are the same as in Fig. 6. Broken lines are predictions from Eq 43.

influences d , we propose the following relationship

$$d_{po}^2 = \sum_{i=1}^N \psi_{B,i} \frac{4 \int_{-\infty}^{\infty} (\partial w_{B,i} / \partial x)(x - x_o)^2 dx}{\int_{-\infty}^{\infty} (\partial w_{B,i} / \partial x) dx} \quad (41)$$

When the following relationship (see Fig. 3 for the case of molecular weight M less than a certain critical value)

$$d_i^2(M_{B,i}) = K/M_{B,i} \quad (42)$$

is used in Eq 41, one obtains

$$d_{po} = d_{mo}(\bar{M}_w/\bar{M}_n)^{1/2} \quad (43)$$

where d_{mo} is the interfacial layer thickness for a monodisperse polymer with molecular weight M_{wB} . Equation 43 clearly shows how polydispersity influ-

ences interfacial layer thickness. For comparison purposes, the predictions of interfacial layer thickness based on Eq 43 are also given in Fig. 7, as denoted by broken lines. It should be mentioned that the purpose of having derived Eq 43 is not to replace the exact expression, Eq 40, but to demonstrate in an analytical form how the interfacial layer thickness is affected by polydispersity.

Let us now consider the two-layer sheet coextrusion process, where two melt streams of PMMA and PVDF are fed separately into a die which has the following dimensions (see Fig. 1): (a) width (W) of 1 m; (b) die opening (h) of 2×10^{-3} m; and (c) die land (L) of 5×10^{-2} m. Note that the molten PMMA and PVDF streams flow side by side over the distance L (see Fig. 1a). Our objective here is to first calculate σ_{int} for PMMA and PVDF coextruded under different flow rates in the sheet-forming die and then to calculate the orientation factors, α_A and α_B , defined by Eq 26, so that the values of $\bar{D}_A$ and $\bar{D}_B$ can be estimated using Eq 22.

Figure 8 gives the velocity profiles of the PMMA/PVDF layers for the situation where the interfacial position lies along the centerline of the die, with increasing volumetric flow rate going from curve (1) to curve (3). The volumetric flow rates used to generate the velocity profiles in Fig. 8 are given in Table 1. In this numerical example, the following values of parameters were used: (1) for PMMA, $\eta_o = 1.023 \times 10^4 \text{ Pa} \cdot \text{s}$, $n = 0.44$, and $\dot{\gamma}_o = 1.7 \text{ s}^{-1}$; and (2) for PVDF, $\eta_o = 4.04 \times 10^3 \text{ Pa} \cdot \text{s}$, $n = 0.62$, and $\dot{\gamma}_o = 1.0 \text{ s}^{-1}$. Also given in Table 1 are the computed results of σ_{int} , α_A , and α_B for the nine cases (Run Nos. 1–9) considered with the following numerical values of the parameters: (a) for PMMA, $G_N^* = 6 \times 10^5 \text{ Pa}$,

$\bar{M}_w = 1.075 \times 10^5$, and $\bar{M}_w/\bar{M}_n = 2.16$; (b) for PVDF, $G_N^0 = 4 \times 10^5$ Pa, $\bar{M}_w = 1.45 \times 10^5$, $\bar{M}_w/\bar{M}_n = 2.31$. It can be seen in Table 1 that for Run Nos. 1–3, the values of α_A and α_B decrease little as the volumetric flow rates are increased; specifically, as the volumetric flow rate was increased by five-fold. This observation is attributed to the fact that the interfacial position remains almost at the centerline of the die opening, where the shear stress is the lowest in the flow channel. Note in Fig. 8 that there is a relatively

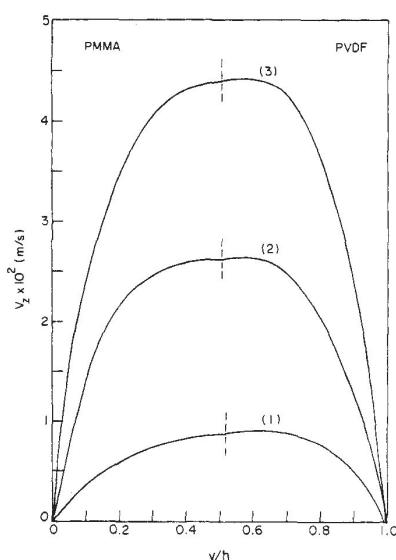


Fig. 8. Velocity profiles in the coextrusion of a PMMA/PVDF system in a sheet-forming coextrusion die. The numbers on the curves represent the run numbers given in Table 1.

small change in the curvature of the velocity profile at the interface.

When the value of η_0 of PMMA was increased from 1.023×10^4 to 3.175×10^4 Pa·s by increasing the molecular weight of PMMA from 1.075×10^5 to 1.50×10^5 , while keeping the same value of η_0 for PVDF, we observe in Fig. 9 that the velocity gradient at the interface changed very sharply; also, that the values of α_A and α_B decreased rapidly when the ratio of volumetric flow rates of PMMA and PVDF was increased while keeping the total flow rate constant, as may be seen in Table 1. Note in Fig. 9 that as the ratio of volumetric flow rates of PMMA and PVDF was increased, the interface position moved toward the PVDF phase. Furthermore, as the ratio of volumetric flow rates of PMMA and PVDF was decreased, the interface position moves toward the PMMA phase, as shown in Fig. 10. The computed values of α_A and α_B corresponding to these flow conditions (Run Nos. 10, 13 and 14) are also given in Table 1. It should be pointed out that as the values of $\bar{D}_A$ and $\bar{D}_B$ decrease due to a decrease in the values of α_A and α_B at a constant contact time, the adhesive bond strength of the coextruded product will be weaker.

We calculated the interfacial layer thickness under shear flow conditions, d_{shear} , by solving Eq 12 with $\bar{D}_A$ and $\bar{D}_B$ defined by Eq 22, in place of D_A and D_B , and the results are summarized in Table 1. Note that the values of d_{shear} given in Table 1 were obtained with $\chi = -0.3$ for the PMMA/PVDF pair. Also given in Table 1 are the values of interfacial layer thickness under static conditions, d_{static} . Based on the computed values of d_{shear} and d_{static} given in Table 1 we obtain a correlation with the following form:

$$d_{\text{shear}}/d_{\text{static}} \approx \sqrt{\alpha_{\text{avg}}} \quad (44)$$

Table 1. Orientation Factors α_A and α_B at the Interface of PMMA and PVDF in a Sheet-Forming Coextrusion Die.

Run No.	Flow rate (cm ³ /min)		Interface position ¹	$\sigma_{\text{int}} \times 10^{-4}$ (Pa)	α_A	α_B	d_{shear}^2 (nm)
	PMMA	PVDF					
(a) $\bar{M}_w(\text{PMMA}) = 1.075 \times 10^5$ and $\eta_0(\text{PMMA}) = 1.023 \times 10^4$ Pa.s at 230°C ³							
1	400	400	0.52	0.746	0.81	0.66	1080 ⁴
2	1200	1200	0.51	1.014	0.74	0.56	580 ⁵
3	2000	2000	0.51	1.109	0.72	0.53	440
4	3000	1000	0.70	2.561	0.46	0.28	325
5	3500	500	0.81	5.012	0.27	0.15	240
6	3800	200	0.89	7.134	0.19	0.11	210
7	1000	3000	0.34	4.262	0.31	0.18	265
8	500	3500	0.24	5.629	0.24	0.13	230
9	200	3800	0.16	6.498	0.21	0.12	215
(b) $\bar{M}_w(\text{PMMA}) = 1.50 \times 10^5$ and $\eta_0(\text{PMMA}) = 3.175 \times 10^4$ Pa.s at 230°C ⁶							
10	2000	2000	0.57	0.551	0.86	0.74	480
11	3500	500	0.84	4.904	0.27	0.15	230
12	3800	200	0.92	10.300	0.13	0.07	160
13	1000	3000	0.45	8.725	0.16	0.09	180
14	200	3800	0.29	9.555	0.14	0.08	165

1. The interface position is defined as δ/h (see Fig. 1b). Note that in all cases considered, $\bar{M}_w(\text{PVDF}) = 1.45 \times 10^5$ and $\eta_0(\text{PVDF}) = 0.404 \times 10^4$ Pa·s at 230°C.

2. The diffusion time (i.e., the average residence time in the die) for Run Nos. 3–14 is 1.5 seconds, whereas it is 7.5 seconds for Run No. 1 and 2.5 seconds for Run No. 2.

3. d_{static} for the diffusion time of 1.5 seconds is 580 nm.

4. d_{shear} , corresponding to the diffusion time of 1.5 seconds is 480 nm for Run No. 1.

5. d_{shear} , corresponding to the diffusion time of 1.5 seconds is 450 nm for Run No. 2.

6. d_{static} for the diffusion time of 1.5 seconds is 560 nm.

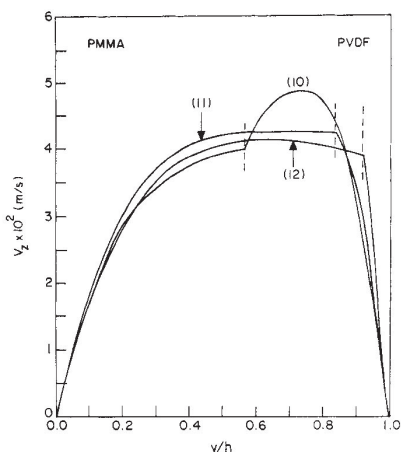


Fig. 9. Velocity profiles in the coextrusion of a PMMA/PVDF system in a sheet-forming coextrusion die. The numbers on the curves represent the run numbers given in Table 1.

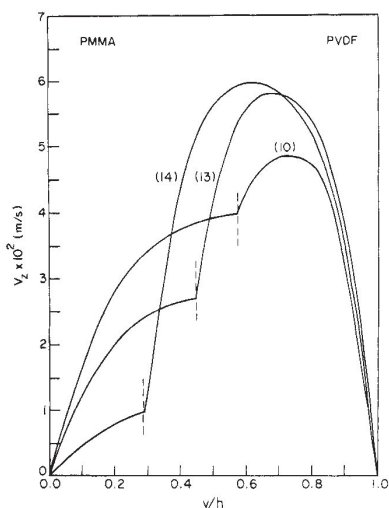


Fig. 10. Velocity profiles in the coextrusion of a PMMA/PVDF system in a sheet-forming coextrusion die. The numbers on the curves represent the run numbers given in Table 1.

where $\alpha_{\text{avg}} = \sqrt{\alpha_A \alpha_B}$. The usefulness of Eq 44, though empirical, lies in that the interfacial layer thickness under *shear flow* conditions can be estimated within the accuracy of about 10%, without necessarily solving Eq 12, using information on the interfacial layer thickness under *static* conditions and the orientation factors for components A and B, α_A and α_B .

The following observations can further be made from Table 1. (1) As the viscosity (or molecular weight) of PMMA increases, the interfacial layer thickness decreases since the diffusion coefficient decreases with increasing viscosity (or molecular weight). (2) As the interfacial position moves toward

the die wall (see Figs. 9 and 10), the interfacial layer thickness decreases rapidly. In practical terms, this observation suggests that, due to the orientation of polymer chains in a shear flow field, the interface layer thickness, and hence adhesive bond strength, will decrease as the thickness ratio of the two layers in a coextruded product deviates from 1.

In coextruding polymers with dissimilar chemical structures, one would like to be able to predict (or estimate) the adhesive bond strength of coextruded sheets or films. It is suggested in the literature (45) that in order to achieve a strong adhesive bond strength, polymer chains from each layer must diffuse to form an interfacial layer thickness of at least one entanglement mesh size. There will be *virtually* no adhesive bond strength when two polymers being coextruded are incompatible. This then suggests that adhesive bond strength would depend on the extent of compatibility (i.e., the value of the interaction parameter χ for a given polymer pair), which in turn controls the interfacial layer thickness. We have shown above that the interfacial layer thickness of coextruded sheets or films depends, among many factors, on the rate of interdiffusion and the contact (or residence) time inside the die. Using information given in Table 1 we can estimate adhesive bond strength, in terms of the number of chains within a given interphase. For example, for Run No. 12 in Table 1, we determined the interfacial layer thickness to be about 160 nm in a coextruded PMMA/PVDF sheet under the particular processing conditions. Assuming that the interphase consists of ideal Gaussian chains of PMMA and PVDF, we calculated the radius of gyration (R_g) to be about 25 nm for both PMMA and PVDF. This means that in the interphase (i.e., across the interfacial layer thickness) there is about a 6 chain length, suggesting that the residence time of 1.5 seconds for the particular PMMA/PVDF pair is sufficiently long to obtain a strong adhesive bond. This theoretical prediction is consistent with the experimental observations of Han (37), who employed a peeling test to determine the adhesive bond strength of coextruded sheets of PMMA and PVDF which were formed under various processing conditions.

According to WCH (2), the adhesive bond strength under *static* conditions, G_{static} , is proportional to the square root of the interfacial layer thickness d_{static} , i.e.,

$$G_{\text{static}} \propto \sqrt{d_{\text{static}}} \quad (45)$$

Based on the results presented above, however, the adhesive bond strength under *shear flow* conditions, G_{shear} , can be related to the diffusion time t , molecular weight M , the orientation factor α_{avg} , and the interaction parameter χ by

$$G_{\text{shear}} \propto t^{1/4} M^{-1/4} \alpha_{\text{avg}}^{1/4} |\chi|^{1/4} \quad (46)$$

The above consideration indicates that the adhesive bond strength G_{shear} of coextruded sheets (or films)

decreases with increasing extrusion rate when the ratio of the volumetric flow rates of PMMA and PVDF is kept constant since the time available for the polymer chains to diffuse will decrease with increasing extrusion rate; also, that G_{shear} decreases with an increase in the ratio of volumetric flow rates of PMMA and PVDF when the total flow rate is kept constant since the orientation factor decreases rapidly, accordingly.

CONCLUSIONS

In this paper we have shown how one can predict the effect of processing variables (e.g., extrusion rate, temperature, etc.) on the interfacial layer thickness and adhesive bond strength in coextruded sheets or coextruded films, using information on the tracer-diffusion coefficients of the polymer pair under consideration. We have shown further that the shear stress at the interface in a coextrusion die influences greatly the interfacial position and thus the interfacial layer thickness. In view of the fact that values of the shear stress at the interface depend very much on the viscosity ratio of the polymer pair under consideration, the present analysis points out that the rheological properties of the polymer pair influence greatly the interfacial layer thickness and adhesive bond strength in coextruded products. A rigorous analysis is worth pursuing to describe the chain dynamics of macromolecules in a shear flow field, where a mutual diffusion (or an interdiffusion) occurs between two chemically dissimilar polymers in the molten state.

The present study predicts that the adhesive bond strength increases as the total layer thickness of coextruded sheets (or films) increases and, also, as the thickness ratio of two adjacent layers approaches unity. The reason is that, for a given pair of polymers to be coextruded, the processing conditions that give rise to smaller values of interfacial shear stress will make the adhesive bond strength greater.

Note added in proof:

Eq 14 in Ref. 2 should read:

$$\begin{aligned} & -\left(\frac{\rho \partial w_A}{\partial t} + \frac{w_A \partial \rho}{\partial t}\right) \\ & = -\rho D_A \left(\frac{\partial^2 w_A}{\partial x^2}\right) - D_A \left(\frac{\partial w_A}{\partial x}\right) \left(\frac{\partial \rho}{\partial x}\right) \\ & \quad + \rho^2 w_A (v_A D_A - v_B D_B) \left(\frac{\partial^2 w_A}{\partial x^2}\right) \\ & \quad + \rho^2 (v_A D_A - v_B D_B) \left(\frac{\partial w_A}{\partial x}\right)^2 \\ & \quad + 2\rho w_A (v_A D_A - v_B D_B) \left(\frac{\partial w_A}{\partial x}\right) \left(\frac{\partial \rho}{\partial x}\right) \end{aligned}$$

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