To the Editor:

In "Polymer−Polymer Mutual Diffusion via Rheology of Coextruded Multilayers," (April 2007, pp. 978–985, DOI 10.1002/aic.11136), Zhao and Macosko used the following empirical expression

$$\eta_{\mathrm{app}}^{s} = \phi\eta_{\mathrm{a}}^{s} + (1-\phi)\eta_{\mathrm{b}}^{s} \qquad (13)$$

to describe the apparent viscosity η_{app} of miscible blends of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), in which η_{a} and η_{b} are the viscosities of HDPE and LLDPE, respectively, ϕ is the volume fraction of a constituent component (HDPE in this situation), and superscripts is an empirical constant. In their article, Zhao and Macosko used Eq. 13 that was reported in an article[1] published 25 years ago (their reference 35), which in turn cited Eq. 13 from an earlier article (ref. 18 cited by ref. 35) published in 1978. Twenty nine years have passed since the first appearance of the empirical expression (Eq. 13) in a journal. Since the publication of the authors' reference 35 in 1982, considerable progress on the rheology of miscible polymer blends has been reported in the literature,[2,3,4] which has been based on sound molecular viscoelasticity considerations. Incidentally, Eq. 13 with $s = 1/3.4$, although strictly empirical, was able to correlate experimental data of zero-shear viscosity of polymer blends composed of two entangled monodisperse homopolymers having an *identical* chemical structure.[5] To my knowledge, however, during the past two decades no research group has ever demonstrated that Eq. 13 was useful to describe the apparent viscosity of polymer blends composed of two *chemically dissimilar*, entangled polymers. I maintain the view that Eq. 13 has absolutely no rheological significance to describe the apparent viscosity of miscible polymer blends composed of two entangled homopolymers with *dissimilar* chemical structures.

To calculate the concentration ϕ during the mutual diffusion in a coextruded HDPE/LLDPE sheet consisting of 32 alternating layers of HDPE and LLDPE, Zhao and Macosko wrote down the following well-known one-dimensional (1-D) diffusion equation

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

in which D_{AB} is the concentration-dependent interdiffusion (mutual diffusion) coefficient defined by

$$D_{\mathrm{AB}} = \bar{v}k_{B}T\left(\frac{1-\phi}{\phi}\Lambda_{A} + \frac{\phi}{1-\phi}\Lambda_{B}\right) \times \left[\frac{1-\phi}{\mathrm{N_A}} + \frac{\phi}{\mathrm{N_B}} + 2\phi(1-\phi)|\chi|\right] \qquad (8)$$

in which $\bar{v}$ is the volume of one lattice site, k_B is the Boltzmann constant, T is the absolute temperature, Λ_A and Λ_B are the Onsager constants of components A and B, respectively, $\mathrm{N_A}$ and $\mathrm{N_B}$ are the degrees of polymerization of components A and B, respectively, and χ is the Flory–Huggins interaction parameter. However, in numerically solving Eq. 10 with the aid of Eq. 8, Zhao and Macosko set $\chi = 0$ by stating that "HDPE and LLDPE are fully miscible."

I have great difficulty understanding the rationale behind which Zhao and Macosko considered that the setting of $\chi = 0$ was justified because "HDPE and LLDPE are fully miscible." It has long been established from polymer solution thermodynamics that the free energy of mixing must be negative, and, thus, χ must be negative for miscible polymer pairs. Apparently, Zhao and Macosko do not seem to have understood the basic concept of polymer solution thermodynamics. I maintain the view that $\chi < 0$ must be satisfied for miscible polymer blends regardless of how small the value of χ might be. Thus, I conclude that the numerical solutions of Eq. 10 on the basis of $\chi = 0$ in Eq. 8 correspond to an athermal polymer blend system, and not for a fully miscible polymer blend system. It should be pointed out that there is no reason why an athermal polymer pair (with $\chi = 0$) should interdiffuse across a flat interface in the same way as a miscible polymer pair (with $\chi < 0$) would do. Therefore, I seriously question the accuracy of Figure 6, which was obtained by a numerical solution of Eq. 10, on the basis of $\chi = 0$ in Eq. 8.

Before closing, I wish to point out that 16 years ago we published a article dealing with polymer-polymer interdiffusion during coextrusion,[6] in which we presented numerical solutions of a complete set of system equations with $\chi < 0$. Apparently, Zhao and Macosko were not aware of the publication of our article 16 years ago and tried to reinvent the wheel by using Eq. 13, that has no rheological significance, and making the unjustified assumption $\chi = 0$ for miscible polymer blends, yielding questionable results.

Literature Cited

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