The viscosity of immiscible polymer blends: influences of the interphase and deformability

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The viscosity of immiscible polymer blends has been studied via application of certain aspects of rheology. A symmetric mixture rule was derived, and the deviations from the 'additivity rule' have been associated, essentially, with the properties of the interphase, with its influence on the effective volumes of the two polymers constituting the blend and with the deformability of both the interphase and the disperse phase. The rule predicts a positive deviation for a mixture with a disperse-phase viscosity (η_d) greater than that (η_m) of the continuous medium, and a much higher-viscosity interphase, i.e. $\eta_i \gg \eta_d \geqslant \eta_m$. Negative deviation is to be expected when the interphase has a much lower viscosity than those of the two pure polymers (η_d, $\eta_m \gg \eta_i$) in the blend. The viscosity and strength of the interphase depend mostly on the specific thermodynamic interactions that led to its creation.

(Keywords: polymer blends; immiscible polymers; viscosity; interfacial phenomenon; interphase; deformability)

INTRODUCTION

Polymer blends are generally classified under miscible and immiscible blends. These two types of materials differ in the level of thermodynamic compatibility between their components and the resulting effects on physical and mechanical properties. One should then expect the resulting property value P of a blend of two polymers to be described by the following equation:

$$P = P_1 c_1 + P_2 c_2 + I_t c_1 c_2 \qquad (1)$$

where P_1 and P_2 are the property values of the individual (isolated) components and c_1 and c_2 their respective concentrations. I_t is an interaction coefficient that describes the level of synergism or thermodynamic compatibility of the components in the mixture. When I_t has a positive value ($I_t > 0$), the resulting polymer combination exhibits a better property than the weighted arithmetic average of the components' properties and is termed 'synergistic'. Additive blends result when the properties of the combination are equal to the weighted arithmetic average of the constituents' properties, i.e. $I_t = 0$. When I_t takes a negative value ($I_t < 0$), with blend properties below those predicted by the components' weighted arithmetic property average, a non-synergistic blend results. The effects of the values of I_t on the resultant polymer combination property are shown graphically in *Figure 1*, where one observes that synergism corresponds to a positive deviation from the additivity rule, while the non-synergistic behaviour corresponds to a negative deviation. The resultant polymer combination property could also show positive–negative deviation behaviour (PNDB).

In general, the flow behaviour of polymer blends is quite complex. Many publications have appeared recently on the rheology of these materials[1–8], and the subject is of continuing interest, in that, with the exception of homologous polymer blends[9–11], it is rather difficult to predict the rheological blending rules. The miscibility, morphology, non-equilibrium state of commercial polymer blends, a host of independent variables and even the flow geometry tend to complicate the description. Several reports[12–17] observed that miscible polymer blends are synergistic polymer combinations with real property advantages, derived from a high level of thermodynamic compatibility between the components (they exhibit strong intermolecular forces and form single-phase systems with unique glass transition temperatures). Nonetheless, there is mounting evidence[18–21] that synergism is not the rule for miscible polymer blends. Depending on the system and method of preparation, $\eta_0 = \eta_0(\phi)$, i.e. the viscosity–composition dependence, can be synergistic, additive or non-synergistic. Immiscible polymer blends, by comparison, have less intense thermodynamic compatibility than miscible blends. (They exhibit discrete polymer phases and multiple glass transition temperatures: this, however, is where industrial interest in these materials lies, in that the presence of the discrete phases lends to the resulting polymer blend a combination of properties of its pure constituents.) However, a compatibilizing agent may be incorporated

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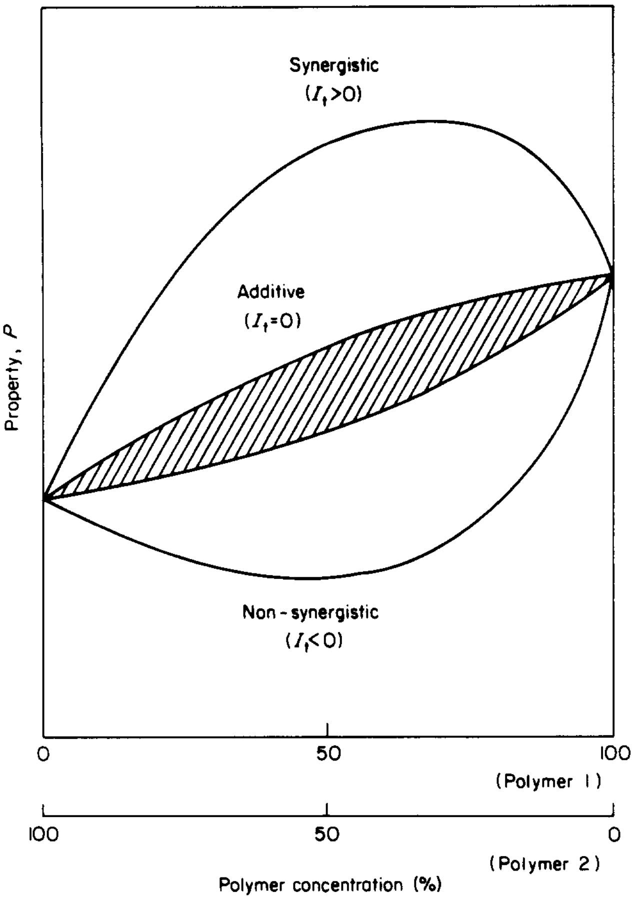

Figure 1 Property relationship of blends as a function of concentration

in these materials to enhance the physical and mechanical properties of the mixture. In these materials, also, there are reports in which synergism, additivity and non-synergism have been observed. It was, however, pointed out that the deviation from log additivity is pertinent to the flow mechanism, but not to the chemical nature of the blends.

Several model systems have been proposed for polymer blends. Two systems can be used as models for miscible polymer blends: (i) a mixture of low-molecular-weight liquids, i.e. a solution[22–26], and (ii) a mixture of polymer fractions or homologous polymer blends[27–29]. The systems (iii) suspension[30–34], (iv) emulsion[4,35–42] and (v) block copolymers[43,44] can serve as models for immiscible polymer blends: suspensions for blends with low concentration of the more viscous polymer, emulsions as a general model of blends with dispersed morphology, and block copolymers for well compatibilized blends and for polymer blends with co-continuous morphology. On the basis of the model systems, several mechanisms can lead to positive deviation behaviour (PDB). In miscible blends dilation on blending was the only one that can explain negative deviation behaviour (NDB). In immiscible blends, if dilation occurs, it must do so at the interfaces, i.e. it may be expected in systems that show strong antagonistic tendencies towards each other. The dilation at the interface may result in an interlayer slip, i.e. a discontinuity of velocity and stress at the interface. Lin[45], assuming interlayer slip in the telescopic flow of polymer blends through a tube, derived the following dependence:

$$\begin{aligned}1/\eta &= \beta_1(w_1/\eta_1 + w_2/\eta_2)\\ \beta_1 &= 1-(\beta_{12}/\sigma_{12})(\Pi w_1 w_2)^{1/2}\end{aligned} \qquad (2)$$

where β_1 is the interlayer slip factor, w_i is the weight fraction of polymer $i = 1, 2$ and $\beta_{12} \leqslant 0$ is the characteristic slip factor. This equation formally allows prediction of NDB. Note that for $\beta_{12} \to 0$, the fluidity–additivity rule is recovered[46,47].

It is, however, amazing that, of the several mechanisms that could lead to PDB, NDB and PNDB behaviour, and particularly in the case of immiscible polymer blends, which is where our interest lies at the moment, the interphase was neglected and the domain boundaries were considered as sharp interfaces. It is important to point out that an interfacial phenomenon[48,49] in immiscible polymer blends suggests that, in the melt, the interface should not be considered as a mathematical plane separating two phases, but as a region of interdiffusion of the two types of macromolecules. It is therefore reasonable to consider the interfacial region as an 'interphase', a third phase in the immiscible blend with its own characteristic properties.

In this study, unlike in the model systems, our approach, in contributing towards the understanding of the melt rheology of polymer blends, in particular their rheological blending rule (synergistic and non-synergistic behaviours), will be essentially based on the presence of the interphase and its influence, since it is universally known that performance properties of polymer blends also derive from the nature of the interphase. However, as these materials (polymer blends) behave as though their performance properties were more dependent on their morphology (flow-induced) than on the chemical properties of the constituents, for example, a number of polymer blends can be made, all of which are suitable for a practical purpose, but each of which differs substantially in chemical composition. We believe, and are convinced, that the most useful approach in studying such a system is to regard it as a mechanical 'construct'.

MECHANICAL APPROACH/ANALYSIS

The difficulties encountered in accounting for the deformation of the dispersed phase in a polymer matrix led most theoretical work[22–44] to be based on small deformations (as well as low concentrations of the dispersed phase), where the equilibrium shape and size of the dispersed phase is almost maintained constant. The few works on large deformations, like those of Heitmiller[47] and Doppert and Overdiep[50], on the other hand, did not include the influence of the deformation on the rheological behaviour of the blends.

Besides the interphase, we also intend, in our analysis, to include the influence of deformability on the rheological behaviour of the blends. This we shall do through a simple approach. We shall assume a flow similar to that of coextrusion with only three layers (the continuous medium, the interphase for adhesion, and the dispersed phase). These layers are considered to be concentric tubes; moreover, we assume that the tubular layers of the components corresponding to the interphase and the dispersed phase in this model system have thicknesses and volume fractions of the same order of magnitude as those of the interphase and the dispersed phase in the real mixture (no particular morphology is considered).

During flow, we assume deformation of the interphase and of the dispersed phase (without break-up). This deformation would lead to the reduction of their layer thicknesses, and consequently to the generation of extra

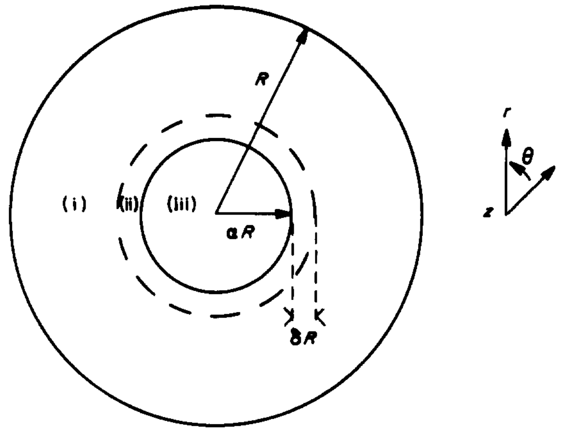

Figure 2 Schematic representation of coextruded flow with three layers, the two immiscible polymers and the interphase (considered as a third phase)

contact surface area between the phases. This would be the case if the volume fractions of the phases remain constant, i.e. in the absence of shear-induced miscibility. Then, the difference between the corresponding energies dissipated at the surfaces, after and before deformation, would be considered as the energy dispensed in deforming the interphase, the dispersed phase and probably the continuous medium. This deformation is what is being resisted at low stresses but easily accomplished at high stresses owing to the extra input of energy. Note, however, that the level of resistance would vary from one material to another, say, dependent on the elasticity of the domains present in the material under consideration.

Further assumptions include: (i) the two immiscible polymers adhere perfectly to the interphase; (ii) flow is at steady state, without inertial, concentration (irrespective of the model system) or wall slip effects.

The model

Figure 2 presents our model system of coextruded flow with three layers, (i) the continuous medium, (ii) the interphase and (iii) the dispersed phase, whose viscosities are, respectively, η_m, η_i and η_d, in a capillary tube of length L and radius R. αR and δR, respectively, represent the layer thicknesses of the dispersed phase and the interphase. Flow is in the z direction with a pressure drop of ΔP maintained across the capillary tube. For such a flow, and without slip effects, one deduces respectively for the velocity, shear stress and pressure that:

$$u=0 \qquad v=0 \qquad w=w(r) \qquad \tau=\sigma_{rz}(r) \qquad p=p(z)$$

Dynamic equilibrium of forces gives:

$$\frac{d\sigma_{rz}}{dr}+\frac{\sigma_{rz}}{r}=\frac{dp}{dz}=-\frac{\Delta P}{L} \tag{3}$$

where dp/dz is the pressure gradient along z. Resolution of this differential equation, and writing the continuity of stress on the z axis and at the interfaces, one obtains for each layer, the shear stress:

$$\sigma_{rz}(r)=-\frac{\Delta Pr}{2L} \tag{4}$$

Newtonian fluids

For Newtonian fluids, one writes:

$$\sigma_{rz}=\eta_j\frac{dw_j}{dr} \tag{5}$$

and deduces the velocity profile in each layer as:

$$w_j(r)=\frac{-\Delta Pr^2}{4\eta_j L}+C_j \tag{6}$$

with $j=\mathrm{m,i,d}$, meaning respectively the continuous medium, the interphase and the dispersed phase. C_j is determined by iterations, starting from the outermost layer where there is the non-slip condition at the wall, and then applying the continuity of the velocities at the interfaces.

In the course of flow, there would be viscous dissipation of energy by the three phases present in our system. This dissipation is due essentially to the internal friction of their respective macromolecular chains. In comparison, the energy dissipated by an equivalent flowing Newtonian fluid, assuming conservation of the total pressure drop, ΔP, across the capillary and the boundary conditions of non-slip at the wall and at the interfaces, could be expressed as:

$$\begin{aligned}\dot{W}&=\Delta PQ\\&=2\pi L\left(\int_{(\alpha+\delta)R}^{R}\eta_m\dot{\gamma}_m^2 r\,dr+\int_0^{\alpha R}\eta_d\dot{\gamma}_d^2 r\,dr\right.\\&\qquad\left.+\int_{\alpha R}^{(\alpha+\delta)R}\eta_i\dot{\gamma}_i^2 r\,dr\right)\end{aligned} \tag{7}$$

where

$$Q=\frac{\pi\Delta PR^4}{8\eta L}$$

represents the volumetric flow rate. Then one deduces:

$$\frac{1}{\eta}=\frac{1-(\alpha+\delta)^4}{\eta_m}+\frac{\alpha^4}{\eta_d}+\frac{(\alpha+\delta)^4-\alpha^4}{\eta_i} \tag{8}$$

a relationship between the viscosity η of the system, and those of its constituents, η_m, η_d and η_i. Note that the above relation is valid for a flow without deformation of the domains, i.e. the interphase and the dispersed phase, and for this reason we purposely ignored the energy dissipated at the interfaces, $E=\int\sigma w\,ds$ (continuous medium–interphase–dispersed phase), which is proportional to the frictional forces exerted by the medium on the interphase and the interphase on the dispersed phase and vice versa. This energy, however, as we shall see later, would be accounted for. Furthermore, one observes that the relation above is non-symmetric, as is evidenced by the absence of the volume fractions ($\phi_m=1-(\alpha+\delta)^2$, $\phi_d=\alpha^2$, $\phi_i=(\alpha+\delta)^2-\alpha^2$) of the phases present in the system.

Should deformation occur in the course of flow, and always assuming the volume fractions of the phases to be constant and in the absence of break-up, then the minimum layer thickness of the interphase and the dispersed phase, one could imagine, could be estimated through a flow geometry of the type shown in *Figure 3*, with $1-(\alpha'+\delta')^2=\alpha^2$, $\alpha'^2=1-(\alpha+\delta)^2$. Incidentally, this geometry corresponds to the inversed image of the preceding one (*Figure 2*), but with the layer thicknesses of the interphase and the dispersed phase smaller. One

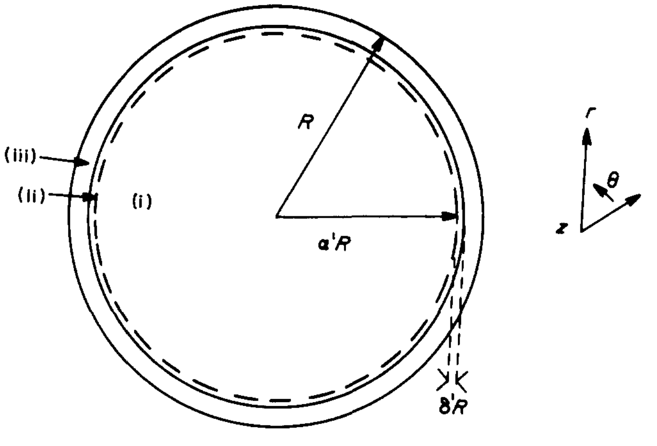

Figure 3 Inversed image of *Figure 3* and at constant volume fraction of the three layers (phases)

observes a global increase in the interfacial contact area, and correspondingly more energy would be dissipated at these interfaces, when compared to that dissipated in the preceding geometry, under the same conditions. Note that this way of looking at the problem is only for the purpose of simplification and is not supposed to imply migration of the dispersed phase towards the wall. Like in the preceding case, and also in the absence of the deformation, the relationship between η and η_m, η_d and η_i for this flow geometry could be expressed as:

$$\frac{1}{\eta}=\frac{[1-(\alpha+\delta)^2]^2}{\eta_m}+\frac{1-(1-\alpha^2)^2}{\eta_d}+\frac{(1-\alpha^2)^2-[1-(\alpha+\delta)^2]^2}{\eta_i} \tag{9}$$

a relationship that is also non-symmetric. However, a combination of both geometries, which is equivalent to combining equations (8) and (9), would lead to a symmetric solution, but such a combination would then require taking into account the energy of deformation or the energy necessary for the change in configuration. In this situation, an equivalent flowing Newtonian fluid would dissipate a total energy per unit time per unit volume that could be expressed in the form:

$$\dot{W}=c_m\dot{w}_m+c_d\dot{w}_d+c_i\dot{w}_i+\Delta E_{def} \tag{10}$$

where c_m, c_d and c_i correspond respectively to the volume fractions of the continuous medium, the dispersed phase and the interphase, and $\dot{w}_m$, $\dot{w}_d$ and $\dot{w}_i$ are their respective average individual viscous dissipations. ΔE_{def} represents the energy dissipated in deforming the interphase and consequently the dispersed phase. From a combination of equations (8) and (9) in the form of relation (10), which combines flow and deformation (change in configuration), one deduces:

$$\frac{1}{\eta_{blend}}=\frac{\phi'_m}{\eta_m}+\frac{\phi'_d}{\eta_d}+\frac{\phi'_i}{\eta_i}-\left[\left(\frac{1}{\eta_m}-\frac{1}{\eta_d}\right)\phi'_m\phi'_d+\left(\frac{\phi'_m}{\eta_m}-\frac{\phi'_d}{\eta_d}\right)\phi'_i+\frac{\phi'_i}{\eta_i}(\phi'_d-\phi'_m)\right] \tag{11}$$

with the volume fraction of the interphase, the dispersed phase and the continuous medium in the blend, respectively, defined as:

$$\phi'_i=\phi_i+x_m\phi_m+x_d\phi_d \qquad \phi'_d=(1-x_d)\phi_d$$
$$\phi'_m=(1-x_m)\phi_m$$

where x_m and x_d represent, respectively, the percentages of the initial volume fractions ϕ_m and ϕ_d of the continuous medium and the dispersed phase before blending that eventually went into the creation of the interphase with the compatibilizing agent of volume fraction ϕ_i. This means that interfacial properties may change the effective volumes of the dispersed phase and the continuous medium. Note, however, that the relation above, which we could now call a 'mixture or blending rule', is symmetric, and that the obtention of synergism, additivity or non-synergism depends essentially on ϕ'_i, η_i and also on the bracketed term on the right-hand side of the equation. The latter accounts for the influence of the deformability of the domains (dispersed phase, interphase and continuous medium).

In a more general form, the above 'mixture rule' could be written as:

$$\frac{1}{\eta_{blend}}=\frac{\phi'_m}{\eta_m}+\frac{\phi'_d}{\eta_d}+\frac{\phi'_i}{\eta_i}-\lambda\left[\left(\frac{1}{\eta_m}-\frac{1}{\eta_d}\right)\phi'_m\phi'_d+\left(\frac{\phi'_m}{\eta_m}-\frac{\phi'_d}{\eta_d}\right)\phi'_i+\frac{\phi'_i}{\eta_i}(\phi'_d-\phi'_m)\right] \tag{12}$$

where λ is an adjustable parameter (which could vary from one material to another, as the energy required to achieve the level of deformation as depicted in the model, from *Figures 2* to *3*, would depend on material morphology and properties of the domains present) that takes into account the fact that there is a resistance to deformation (of the domains) gradient in going from low stresses to high stresses. The higher this resistance to deformation, the more energy will be required to maintain the velocity gradient constant. In our model, and for the sake of simplicity, we shall permit this parameter to take two extreme values, 0 and 1, the former at high stresses and the latter at low stresses. At high stresses, ΔE_{def} is negligible when compared to viscous dissipation (deformation of the domains having been achieved at the early stages of flow, and the dispersed phase drawn into long streaks; in this situation, measurement will only give information concerning viscous dissipation), and the Newtonian mixture rule (equation (12)) obtained for steady-state flow without slip (good adhesion) reduces to:

$$\frac{1}{\eta_{blend}}=\frac{\phi'_m}{\eta_m}+\frac{\phi'_d}{\eta_d}+\frac{\phi'_i}{\eta_i} \tag{13}$$

This could be termed an 'additivity rule' for ternary polymer blends. On the other hand, at low stresses, where ΔE_{def} is no longer negligible, in the absence of the interphase $\phi'_i=0$ (say, in mechanically mixed polymer blends without any chemical reaction occurring during melt blending), then the same mixture rule (equation (12)) reduces to:

$$\frac{1}{\eta_{blend}}=\frac{\phi_m}{\eta_m}+\frac{\phi_d}{\eta_d}-\lambda\left(\frac{1}{\eta_m}-\frac{1}{\eta_d}\right)\phi_m\phi_d \tag{14}$$

and PDB or NDB behaviour should depend on the ratio η_d/η_m of the viscosities and also on the value of λ. Normally, however, one should expect synergism when $\eta_d>\eta_m$, i.e. when the dispersed phase resists deformation.

Note, then, that, at high stresses (ΔE_{def} negligible), the known 'additivity rule' for immiscible polymer blends[46,47] should be anticipated.

In conclusion, when one compares equation (14) to equation (12), one observes that the presence of the interphase effectively modifies the mixture rule, and, as such, the interphase should not be neglected in the course of melt rheological data interpretation of polymer blends, in particular immiscible ones.

Non-Newtonian fluids

In the case of non-Newtonian fluids, a complication arises from the shear dependence of the viscosity of the fluids, which in general is not the same. This makes the elimination of the pressure gradient $\Delta P/L$ from the mixture rule difficult, except, of course, the comparison is intended at constant shear stress. For Newtonian systems, as we have seen, this is of no consequence. If, however, the flow behaviour of these power-law fluids obeys Ostwald's power law, then the shear dependence of the viscosity may be represented as[51]:

$$\sigma_{\mathrm{rz}}=K|\dot{\gamma}|^{\mathrm{n}-1}\dot{\gamma} \tag{15}$$

The mixture rule, derived for Poiseuille flow, becomes:

$$\begin{aligned}
&\frac{n}{3n+1}\frac{1}{\eta_{\mathrm{blend}}}\\
&=\sum_{a=\mathrm{m,d}}\left(\frac{n_a}{3n_a+1}\left(\frac{1-(1-\phi'_a)^{(1/n_a+3)/2}+\phi'^{(1/n_a+3)/2}_a}{2\eta_a}\right)\right)\\
&\quad+\frac{n_{\mathrm{i}}}{3n_{\mathrm{i}}+1}\sum_{a=\mathrm{m,d}}\left(\frac{(\phi'_{\mathrm{i}}+\phi'_a)^{(1/n_{\mathrm{i}}+3)/2}-\phi'^{(1/n_{\mathrm{i}}+3)/2}_a}{2\eta_{\mathrm{i}}}\right)\\
&\quad-\frac{\lambda}{2}\left\{\left(\frac{n_{\mathrm{m}}}{3n_{\mathrm{m}}+1}\frac{1}{\eta_{\mathrm{m}}}-\frac{n_{\mathrm{d}}}{3n_{\mathrm{d}}+1}\frac{1}{\eta_{\mathrm{d}}}\right)\right.\\
&\quad+\left[\left(\frac{n_{\mathrm{d}}}{3n_{\mathrm{d}}+1}\frac{\phi'^{(1/n_{\mathrm{d}}+3)/2}_{\mathrm{d}}+(\phi'_{\mathrm{i}}+\phi'_{\mathrm{m}})^{(1/n_{\mathrm{d}}+3)/2}}{\eta_{\mathrm{d}}}\right)\right.\\
&\quad\left.-\left(\frac{n_{\mathrm{m}}}{3n_{\mathrm{m}}+1}\frac{\phi'^{(1/n_{\mathrm{m}}+3)/2}_{\mathrm{m}}+(\phi'_{\mathrm{i}}+\phi'_{\mathrm{d}})^{(1/n_{\mathrm{m}}+3)/2}}{\eta_{\mathrm{m}}}\right)\right]\\
&\quad+\frac{n_{\mathrm{i}}}{3n_{\mathrm{i}}+1}\frac{1}{\eta_{\mathrm{i}}}\left(\phi'^{(1/n_{\mathrm{i}}+3)/2}_{\mathrm{m}}-\phi'^{(1/n_{\mathrm{i}}+3)/2}_{\mathrm{d}}\right.\\
&\quad\left.\left.+(\phi'_{\mathrm{i}}+\phi'_{\mathrm{d}})^{(1/n_{\mathrm{i}}+3)/2}-(\phi'_{\mathrm{i}}+\phi'_{\mathrm{m}})^{(1/n_{\mathrm{i}}+3)/2}\right)\right\}
\end{aligned} \tag{16}$$

where η_{m}, η_{d}, η_{i} and η_{blend} are the viscosities evaluated at the same shear stress and n_{m}, n_{d}, n_{i} and n are the respective power-law exponents for the fluids. In this case, besides the influence of the interphase and deformability, synergistic, additive and/or non-synergistic behaviour would also depend on the power-law exponents.

NUMERICAL APPLICATION/DISCUSSION (NEWTONIAN SYSTEMS)

To illustrate the ongoing analysis, i.e. the importance of the interphase, as well as the role of resistance to deformation, we shall consider a 50/50 polymer blend using equations (12) (presence of interphase, $\phi'_{\mathrm{i}}\neq 0$) and (14) (absence of interphase, $\phi'_{\mathrm{i}}=0$), both at low ($\lambda=1$, greater resistance to deformation) and at high stresses ($\lambda=0$). Cases that will be considered include:

(i) $\eta_{\mathrm{d}}/\eta_{\mathrm{m}}=0.5$; $\eta_{\mathrm{i}}=\eta_{\mathrm{m}}/8$, $(\eta_{\mathrm{d}}+\eta_{\mathrm{m}})/2$, $8\eta_{\mathrm{m}}$; $\phi'_i=40\%$

(ii) $\eta_{\mathrm{d}}/\eta_{\mathrm{m}}=1.0$; $\eta_{\mathrm{i}}=\eta_{\mathrm{m}}/8$, $(\eta_{\mathrm{d}}+\eta_{\mathrm{m}})/2$, $8\eta_{\mathrm{m}}$; $\phi'_i=40\%$

(iii) $\eta_{\mathrm{d}}/\eta_{\mathrm{m}}=2.0$; $\eta_{\mathrm{i}}=\eta_{\mathrm{m}}/8$, $(\eta_{\mathrm{d}}+\eta_{\mathrm{m}})/2$, $8\eta_{\mathrm{m}}$; $\phi'_i=40\%$

In equation (12) we assume, for the sake of simplicity, that $\phi'_{\mathrm{m}}=\phi'_{\mathrm{d}}=30\%$ and in equation (14) that $\phi_{\mathrm{m}}=\phi_{\mathrm{d}}=50\%$. Note that the values given here to ϕ'_{i}, ϕ'_{m} and ϕ'_{d} are arbitrary; the aim is to insist that interfacial properties may change the effective volumes of the dispersed phase and the continuous medium. *Tables 1* and *2* contain the results obtained for these cases.

From *Tables 1* and *2* one observes that synergism (PDB) is essentially related to the viscoelastic properties of the interphase and to its volume fraction ϕ'_{i} in the blend. Resistance to deformation of the domains, particularly at low stresses, also plays a role. When the viscosity η_{i} of the interphase is much lower than that of the less viscous component of the blend, a negative deviation behaviour (NDB) should be anticipated. When η_i is about the weighted arithmetic average of the viscosities η_{d} and η_{m} respectively of the dispersed phase and the continuous medium, the blend should present an additive viscosity behaviour. For $\eta_{\mathrm{i}}\gg\eta_{\mathrm{d}}>\eta_{\mathrm{m}}$, a synergistic behaviour (PDB) should be expected. In the absence of the interphase ($\phi_{\mathrm{i}}=0$), irrespective of the ratio $\eta_{\mathrm{d}}/\eta_{\mathrm{m}}$ and role of resistance to deformation, an additive behaviour is predicted. Generally, at high stresses, where viscous dissipation is more predominant compared to domain deformation (already accomplished at the early stages of flow), an additive behaviour is also predicted.

Table 1 Blend viscosity η_{blend} using equation (12) (with $\phi'_{\mathrm{m}}=\phi'_{\mathrm{d}}$, $\phi'_{\mathrm{i}}=40\%$) as a function of the viscosities η_{d}, η_{m} and η_{i} of the dispersed phase, continuous medium and the interphase respectively, at low ($\lambda=1$) and high ($\lambda=0$) stresses. NDB ≡ negative deviation, AB ≡ additive, PDB ≡ positive deviation behaviours

		η_{blend} (equation (12), $\phi'_{\mathrm{m}}=\phi'_{\mathrm{d}}$, $\phi'_{\mathrm{i}}=40\%$)	
$\eta_{\mathrm{d}}/\eta_{\mathrm{m}}$	η_{i}	Low stresses	High stresses
0.5	$\eta_{\mathrm{m}}/8$	$\eta=0.23\eta_{\mathrm{m}}$ (NDB)	$\eta=0.24\eta_{\mathrm{m}}$ (NDB)
	$(\eta_{\mathrm{m}}+\eta_{\mathrm{d}})/2$	$\eta=0.58\eta_{\mathrm{m}}$ (AB)	$\eta=0.7\eta_{\mathrm{m}}$ (AB)
	$8\eta_{\mathrm{m}}$	$\eta=0.8\eta_{\mathrm{m}}$ (AB)	$\eta=1.05\eta_{\mathrm{m}}$ (AB)
1.0	$\eta_{\mathrm{m}}/8$	$\eta=0.26\eta_{\mathrm{m}}$ (NDB)	$\eta=0.26\eta_{\mathrm{m}}$ (NDB)
	$(\eta_{\mathrm{m}}+\eta_{\mathrm{d}})/2$	$\eta=\eta_{\mathrm{m}}$ (AB)	$\eta=\eta_{\mathrm{m}}$ (AB)
	$8\eta_{\mathrm{m}}$	$\eta=1.5\eta_{\mathrm{m}}$ (PDB)	$\eta=1.5\eta_{\mathrm{m}}$ (PDB)
2.0	$\eta_{\mathrm{m}}/8$	$\eta=0.29\eta_{\mathrm{m}}$ (NDB)	$\eta=0.27\eta_{\mathrm{m}}$ (NDB)
	$(\eta_{\mathrm{m}}+\eta_{\mathrm{d}})/2$	$\eta=1.8\eta_{\mathrm{m}}$ (AB)	$\eta=1.4\eta_{\mathrm{m}}$ (AB)
	$8\eta_{\mathrm{m}}$	$\eta=2.9\eta_{\mathrm{m}}$ (PDB)	$\eta=2.0\eta_{\mathrm{m}}$ (AB)

Table 2 Blend viscosity η_{blend} using equation (14) (with $\phi_{\mathrm{m}}=\phi_{\mathrm{d}}$, $\phi_{\mathrm{i}}=0\%$) as a function of the viscosities η_{d} and η_{m} of the dispersed phase and the continuous medium respectively, at low ($\lambda=1$) and high ($\lambda=0$) stresses. AB ≡ additive behaviour

	η_{blend} (equation (14), $\phi_{\mathrm{m}}=\phi_{\mathrm{d}}$, $\phi_{\mathrm{i}}=0\%$)	
$\eta_{\mathrm{d}}/\eta_{\mathrm{m}}$	Low stresses	High stresses
0.5	$\eta=0.6\eta_{\mathrm{m}}$ (AB)	$\eta=0.7\eta_{\mathrm{m}}$ (AB)
1.0	$\eta=\eta_{\mathrm{m}}$ (AB)	$\eta=\eta_{\mathrm{m}}$ (AB)
2.0	$\eta=1.6\eta_{\mathrm{m}}$ (AB)	$\eta=1.3\eta_{\mathrm{m}}$ (AB)
5.0	$\eta=2.5\eta_{\mathrm{m}}$ (AB)	$\eta=1.7\eta_{\mathrm{m}}$ (AB)
10.0	$\eta=3.1\eta_{\mathrm{m}}$ (AB)	$\eta=1.8\eta_{\mathrm{m}}$ (AB)

The foregoing analysis has been geared towards correlating the general morphology and the rheological blending rule in immiscible polymer blends, and emphasis has been laid particularly on the presence of the interphase, our assumed third phase in immiscible polymer blends; earlier workers ignored the interphase and associated their observations solely to the state of dispersion of the minor phase. We do not doubt that there may be a host of variables (dependent or independent) that may affect the rheology of polymer blends, but with regard to immiscible blends, we think that interfacial properties determine the state of dispersion of the minor phase and as such play a role in the rheology of these materials. The extent of this role would depend on the thickness of the interphase, which in turn depends on the level of thermodynamic interaction between the two dissimilar macromolecules, macromolecular segment size, concentration and phase conditions, these being factors that determine the properties of the layer, and for this reason neither the measurement nor the interpretation of data pertaining to this layer is straightforward.

However, we would like to point out that, in the studies by Han[52,53], Utracki[54,55] and Willis and Favis[56], aimed at correlating the morphology–rheology and properties in immiscible polymer blends, their observations are in accord with the hypothesis (presence of an interfacial layer) used in our mechanical treatment to obtain a mixture rule for immiscible polymer blends. In these works, two types of immiscible polymer blends were studied, non-compatibilized and compatibilized. The blend viscosity in the compatibilized materials showed a positive deviation behaviour from the 'additivity rule', whereas in the non-compatibilized blends, either a negative deviation or a linear viscosity–composition dependence was observed. From fractured-surface scanning electron microscopy, these authors observed that, in compatibilized blends, the dispersed particle size is small and the surfaces appear to be covered with some material (the interphase). The particle size reduction was greater than 100% when compared to particle size in non-compatibilized blends. In the latter blends, the surfaces of the particles are clean (evidence of no adhesion, $\phi_i = 0$). In the light of these observations, these authors associated the unique difference in the rheological behaviours of the two types of immiscible blends to interfacial interactions, which led to the different morphologies and appear to explain the differences in behaviour. The implication of these observations, as concerns compatibilized blends, is that the interactions across the continuous medium/dispersed phase interface promote creation of an interfacial layer, whose thickness depends on the extent of the interactions, and which assures the adhesion of the dispersed phase onto the matrix, and at the same time reduces the effective volumes of the two polymers in the blend. Globally, mechanical properties were improved in all cases of compatibilized immiscible polymer blends and these were associated with strong interfacial adhesion (adhesion increases with size of the interphase and its deformability; see Utracki[8]). A weak interphase or complete absence of it would lead to a blend with mediocre properties (possible exhibition of slip during flow).

A comparison of our model with some melt rheological experimental data obtained by Han[52,53] with two different blend systems (one non-compatibilized, the other compatibilized), composition 50/50, at the same measurement temperature (240°C) and at the same shear stresses, is shown in *Table 3*.

It is evident that the model calculations give results of the same order of magnitude as experimental data, and this lends support to the hypothesis of a third phase (the interphase), with its own characteristic properties, in immiscible polymer blends, used in this study to account for synergistic and non-synergistic blend behaviour. Note, however, that in the model calculation an arbitrary value of 40% as the volume fraction of the interphase was employed. This was just to insist that the presence of an interfacial layer reduces the effective volumes of the two immiscible polymers. This value, particularly with the compared experimental data, seems reasonable: the authors observed a dispersed particle size reduction of greater than 100% in compatibilized blends when compared to the non-compatibilized. This implies that the interphase thickness would be of the same order of magnitude. In fact, without going into details, as no particular morphology is considered, one could say to a first approximation that the reduction in the effective volume of the dispersed phase is of the same order of magnitude (ϕ_d initially 50% should be expected to be less than 25%). Also, in the example considered, one should expect a reduction in the effective volume of PA6 (nylon-6) as its amino end-groups contribute to the formation of the interphase. Furthermore, Shilov[48], in his studies of interfacial phenomena in immiscible blends, pointed out that the interphase could contain up to 60% (as determined by small-angle X-ray scattering, SAXS) of both polymers. Finally, in this context, it is only a strong interphase (strong adhesion) with a viscosity higher than that of the two components in the blend, i.e. $\eta_i \gg \eta_d$, η_m, that could explain positive deviation behaviour. In the light of these, we believe that, as concerns immiscible polymer blends, it would be erroneous to neglect the interphase, especially as we have shown, through our empirical approach, that its role is non-negligible.

Table 3 Comparison of our model with experimental data[52,53] (see text for details). AB≡additive, PDB≡positive deviation behaviours

(a)	PA6/EVA (nylon-6/ethylene–vinyl acetate); non-compatibilized ($\phi_i = 0$)	
(i)	$\sigma = 2000\ \mathrm{N\,m^{-2}}$; $\eta_{PA6} = \eta_m$; $\eta_{EVA} = 4.8\eta_m$	
	Experiment	$\eta_{blend} = 2.6\eta_m$ (AB)
	Model (equation (14), $\phi_m = \phi_d = 50\%$, $\lambda = 1$)	$\eta_{blend} = 2.42\eta_m$ (AB)
(ii)	$\sigma = 5000\ \mathrm{N\,m^{-2}}$; $\eta_{PA6} = \eta_m$; $\eta_{EVA} = 3.1\eta_m$	
	Experiment	$\eta_{blend} = 1.8\eta_m$ (AB)
	Model (equation (14), $\phi_m = \phi_d = 50\%$, $\lambda = 1$)	$\eta_{blend} = 2.03\eta_m$ (AB)
(b)	PA6/Plexar (nylon-6/ethylene–vinyl acetate copolymer with a polyolefin onto which unsaturated carboxylic acids or anhydrides are grafted); compatibilized ($\phi_i = 0$)	
(i)	$\sigma = 2000\ \mathrm{N\,m^{-2}}$; $\eta_{PA6} = \eta_m$; $\eta_{Plexar} = 2.8\eta_m$	
	Experiment	$\eta_{blend} = 15\eta_m$ (PDB)
	Model (equation (12), $\phi'_m = \phi'_d = 30\%$, $\phi'_i = 40\%$, $\lambda = 1$, $\eta_i \gg \eta_m$)	$\eta_{blend} = 4.7\eta_m$ (PDB)
(ii)	$\sigma = 5000\ \mathrm{N\,m^{-2}}$; $\eta_{PA6} = \eta_m$; $\eta_{Plexar} = 1.6\eta_m$	
	Experiment	$\eta_{blend} = 5.6\eta_m$ (PDB)
	Model (equation (12), $\phi'_m = \phi'_d = 30\%$, $\phi'_i = 40\%$, $\lambda = 1$, $\eta_i \gg \eta_m$)	$\eta_{blend} = 2.7\eta_m$ (PDB)

Finally, one could say that the model could predict synergistic and non-synergistic blend behaviour. However, there might be contributions from other factors not included in the model, such as material morphology and the elasticity of the domains, particularly at low stresses. Our simple approach would not permit us to account fully for these, hence the introduction of λ (the adjustable parameter, which represents the resistance to deformation gradient) to this effect, though the values, particularly at low stresses, given to it in this paper might be an underestimation. For instance, in the systems PA6/EVA and PA6/Plexar, the latter presented a morphology of smaller droplets of the dispersed phase when compared to the former and as such more energy (if $F \propto 1/r$) would be required to deform these smaller droplets, i.e. λ should be higher (increased synergism) in this case than in the system (PA6/EVA) with larger droplets.

CONCLUSIONS

We have presented a symmetric mixture rule for a Poiseuille flow without slip, neither at the walls nor at the interfaces, where deviations from the 'additivity rule' are associated essentially with the viscoelastic properties of the interphase, its volume fraction and its deformability, as well as that of the dispersed phase. The rule predicts a positive deviation for a mixture with a dispersed phase of viscosity η_d greater than η_m, the viscosity of the continuous medium, and a much higher-viscosity interphase, $\eta_i \gg \eta_d > \eta_m$. Negative deviations arise when the interphase has a much lower viscosity than those of the two base polymers ($\eta_d, \eta_m \gg \eta_i$).

A dispersed phase with a viscosity higher than that of the continuous medium would tend to resist deformation in the polymer matrix, and as such more energy would be dissipated to maintain the velocity gradient constant. This should normally lead to a PDB behaviour, except, of course, there is slip within the interphase or at the interface.

In conclusion, we believe that, in the interpretation of the rheological data of immiscible polymer blends, though there might be a host of other factors (or variables) that might have an influence on their rheological behaviour, much more attention should be paid to the contribution of the interphase, particularly with respect to its viscoelastic properties and its influence on the effective volumes of the two base polymers that constitute the blend. This point is very important in that this 'phase' appears to play a major role in the performance properties of polymer blends: for example, this phase, via its properties, determines the state of dispersion in the blends and is also responsible for the adhesion of the dispersed phase to the matrix. Generally speaking, a weak interphase (i.e. weak adhesion) would lead to a negative deviation behaviour, and this represents the least desirable outcome for the formulator of the polyblend, whereas a strong interphase would give rise to a positive deviation behaviour (synergism or PDB or real property advantage).

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