Rheology and dynamics of immiscible polymer blends

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Synopsis

The fundamental problems in two immiscible polymer blends, such as deformation, break-up, and coalescence of the dispersed phase, were considered. Instead of formulating a single droplet problem, it was assumed that there is a kind of structure of the interfaces, in which the interfacial area (Q) and its anisotropy (\( q_{ij} \)) are equilibrated due to the competition between flow and interfacial tension. Relaxation mechanisms of the interfaces in heterogeneous systems were phenomenologically considered so that a more general constitutive equation was proposed, which can be used not only for arbitrary volume fractions but also for arbitrary flow fields. Also, the effect of simple shear flow on the morphology of polystyrene (PS)/linear low-density polyethylene (LLDPE) blends was experimentally investigated. Whereas most works along these lines have been done visually in a flow cell, our samples were quenched after steady shear and their resulting structures were analyzed by scanning electron microscopy. In order to achieve a better understanding of morphological effects on polymer blending processes, the semiphenomenological expressions describing the interface contributions of immiscible polymer blends were formulated and compared with dynamic shear experiments of PS/LLDPE blends.

I. INTRODUCTION

The theoretical problem of predicting macroscopic properties of blends in terms of their component properties is difficult because of the difficulties of characterizing the blends' microstructure and relating this complex morphology to macroscopic phenomena. Multiphase chemical reactions, emulsification, liquid-liquid extraction, emulsion polymerization, and polymer processing are some processes in which two or more immiscible fluids and their interfaces play an important role in determining the global process. There has been much work reported since Taylor (1934) performed a pioneering analysis of a viscous drop deformed by external flow. Many theoretical and experimental studies of deformation and break-up focused on a single droplet and neglected any interactions and complications between droplets. It is certainly necessary to have a theory good for concentrated droplets in the arbitrary flow for real applications.

For two-phase polyblends, Han (1981) illustrated that the morphology will exert far-reaching influences on the rheological behavior of multiphase systems. It is of great interest to establish the rheological property-morphology relationship when the two-phase dispersed polymer blends are subjected to the shearing forces in a given flow field. Melt blend rheology is a special class of emulsion rheology, and it is more difficult due

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to the presence of viscoelastic and nonlinear effects within both phases. Recently, several studies [Scholz et al. (1989); Graebling et al. (1989, 1990)] on the rheological properties of some immiscible blends and their comparison to the predictions of the emulsion models developed by Oldroyd (1953) and Choi and Schowalter (1975) have been performed. The most important feature of their models was the pronounced appearance of elasticity from interfacial tension at low frequency. According to their results, it seemed that elastic properties were more sensitive to the state of dispersion (morphology) than to the viscous properties of the immiscible blends. However, strictly speaking, such models were restricted to the case of Newtonian phases and had no inclusion of contributions to morphological effects, especially for concentrated systems. A refined treatment of the linear viscoelastic modulus at arbitrary concentration was given by Palierne (1990) for polydispersity of spherical inclusions with the most general behavior of the interface. He used a frequency-dependent surface dilatation modulus and a surface shear modulus to describe the viscoelastic phenomena observed with immiscible polymer blends. However, these models were not obvious to obtain experimentally and their expressions were of practical use only for the oscillatory flow.

In a purely formal sense, the rheological properties of the heterophase system can be written as \( \eta = \eta (\eta_m, \eta_i, \phi, \alpha, S) \), where \( \phi \) is volume fraction, \( \alpha \) interfacial tension, \( S \) a structure parameter, and subscripts \( m \) and \( i \) identify the matrix and inclusion phase, respectively. The present study was launched in an effort to refine and verify this point. Our aim is to attempt a new theoretical approach to consider the influence of morphology in determining the rheological properties for a given flow field, so that we will verify the formation of our model and blending law by comparing the predicted results with the experimental ones of polystyrene/linear low-density polyethylene (PS/LLDPE) blends in the oscillatory shear flow. Additionally it will be experimentally shown that polymer/polymer interfaces exhibit a high degree of mobility at high concentrations, evoking complex morphologies. Comparison between theory and experiment will be focused on dynamic shear data.

II. THEORETICAL BACKGROUND OF OUR MODEL

A. Deformation in dilute system

In considering a drop (radius = \( a \)) of fluid of viscosity \( \eta_i \) dispersed in a fluid of viscosity \( \eta_m \) undergoing a shear flow of magnitude \( \dot{\gamma} \), a theory has been given for the shape of the fluid drop in steady and unsteady flow by making an expansion in terms of small deformation of the drop. The Reynolds number of the motion is assumed small enough for inertial effects to be negligible. Then, as shown by Rallison (1980), the equation for the surface shape of the drop in a system of axes moving with the center of the drop can be represented by

\[
r = a(1 + \epsilon f),
\]

with

\[
f = \gamma^3 F_{ij} \frac{\delta(1/r)}{\delta x_i \delta x_j} + \epsilon \left[ \frac{6}{5} F_{ij} F_{ij} + \gamma^5 H_{ijkl} \frac{\delta(1/r)}{\delta x_i \delta x_j \delta x_k \delta x_l} \right]
\]

where the shape tensors \( F_{ij} \) and \( H_{ijkl} \) are chosen to be symmetric with respect to any permutation of their indices and traceless. In the case of a drop kept nearly spherical on account of its large interfacial tension, with viscosity ratio \( \beta = \eta_i / \eta_m \) being \( O(1) \), the small parameter \( \epsilon \) which indicates the drop deviation from sphericity, is as \( \epsilon = O(Ca) \),
where capillary number $Ca = (\gamma a \eta_i / \alpha)$ and $\alpha$ is the interfacial tension. Under these conditions the shape evolution equation may be written in the form

$$\frac{\partial F_{ij}}{\partial t} = a_0 D_{ij} + a_1 F_{ij} + O(\epsilon),$$

(2)

where the rate of strain tensor $D_{ij}$ denotes the symmetric part of the velocity gradient tensor and the coefficients $a_0$ and $a_1$ are known rational functions of $\beta$. It is an extended version of the Taylor theory corresponding the case of a drop for which interfacial tension effects were dominant over viscous effects. Here it should be noted that the deformation of the drop depends not only upon the external flow but also upon the interfacial tension through two dimensionless parameters, $\beta$ and $Ca$. On the other hand, if the viscosity of the drop $\eta_i$ is very high, then the $O(1)$ version of the shape equation is simply given by

$$\frac{\partial F_{ij}}{\partial t} = \frac{5}{6} D_{ij}$$

(3)

in which $\frac{\partial}{\partial t}$ is a Jaumann derivative rotating with the vorticity. Thus, if the dispersed phase is more viscous than the continuous one, then the basic deformation mechanism is totally dependent on the external flow only. But if the fluid viscosities are comparable then interfacial tension should be considered in the first place.

B. Complex interfaces

When two immiscible fluids are mixed, complex interfaces are formed due to deformation, break-up, and coalescence of droplets caused by shear and interfacial tension. Recently Doi and Ohta (1991) suggested an interesting model concerning the equal volumes of two fluids from a different point of view. Instead of formulating a droplet problem, the interface between two phases was considered and a semiphenomenological kinetic equation was derived which can describe the time evolution of interfacial area.
(\(Q\)) per unit volume and its anisotropy \((q_{ij})\) in a given flow field. As shown by Fig. 1, the interfacial area and its anisotropy are defined as follows:

\[
Q = \frac{1}{V} \int dS,
\]

\[
q_{ij} = \frac{1}{V} \int dS(n_i n_j - \frac{1}{3}\delta_{ij}),
\]

where \(n_i\) denotes the unit normal vector to the interfaces, \(V\) the total system volume, and \(dS\) an interface element. The time evolutions of \(Q\) and \(q_{ij}\) are affected by two factors: one is the external flow, which orients the interface to an anisotropic state so that the interfacial area becomes larger, and the other is the interfacial tension which has opposite influences:

\[
\frac{d}{dt} Q = \left. \frac{d}{dt} Q \right|_{\text{flow}} + \left. \frac{d}{dt} Q \right|_{\text{interfacial tension}},
\]

\[
\frac{d}{dt} q_{ij} = \left. \frac{d}{dt} q_{ij} \right|_{\text{flow}} + \left. \frac{d}{dt} q_{ij} \right|_{\text{interfacial tension}}.
\]

The first term due to the flow has been derived by Doi and Ohta (1991) for a mixture of two immiscible fluids; affine deformation is assumed and the Reynolds number must be small. The fluids have the same viscosity and density and they are mixed in a volume ratio 1:1,

\[
\frac{d}{dt} Q \bigg|_{\text{flow}} = -d_{ij}q_{ij},
\]

\[
\frac{d}{dt} q_{ij} \bigg|_{\text{flow}} = -q_{ik}d_{kj} - q_{jk}d_{ki} + \frac{2}{3}\delta_{ij}d_{lm}q_{lm} - \frac{Q}{3}(d_{ij} + d_{ji}) + \left(\frac{q_{lm}d_{lm}}{Q}\right)q_{ij},
\]

where \(d_{ij} = \partial u_i / \partial x_j\) is the macroscopic velocity gradient tensor. In principle, the bulk rheological properties of many immiscible polymer blends are intimately related to the interfacial tension. On the other hand, from a phenomenological point of view, the dynamics of interfaces in this system are correlated with macroscopic rheological properties. After all, in order to determine the effects of shear-induced behavior of interfaces on the macroscopic rheological properties, one needs to be aware of their close relationship in a flowing system of deformable interfaces of any shape. For a mixture of fluids with equal viscosity, it has been known [Batchelor (1970); Onuki (1987)] that the stress tensor is given by

\[
\sigma_{ij} = \eta_m(d_{ij} + d_{ji}) - \alpha q_{ij} - P\delta_{ij},
\]

where \(\eta_m\) designates the viscosity of matrix and \(\alpha\) is the interfacial tension. Here, Eq. (10) tells us that the excess shear stress is proportional to the spatial anisotropy of the interfaces \(q_{ij}\), the steady structure of the interfaces distorted due to the competition between flow and interfacial tension.
C. Relaxation by interfacial tension

If the interfacial tension is neglected, interfaces should be predominantly affected by shear strength. For systems in which the interfacial tension is involved, we shall consider two consequences: the size relaxation effect which makes the interfacial area decrease and the shape relaxation which makes the system isotropic or $q_{ij} = 0$. This is the simplest of the relaxation mechanisms suggested by Doi and Ohta (1991). However, it is necessary to consider three different types of relaxation as shown by Fig. 2: coalescence [Fig. 2(a)], shape relaxation (deformation) [Fig. 2(b)], and break-up [Fig. 2(c)] by interfacial tension (a). Then, by dimensional analysis, it can be shown,

$$
\frac{d}{dt} \left( \frac{Q}{\eta_m} \right)_{\text{interfacial tension}} = -c_1 \frac{\alpha Q^2}{\eta_m} - c_3 \frac{\alpha}{\eta_m} q_{ij} q_{ij},
$$

(11)

$$
\frac{d}{dt} \left( \frac{q_{ij}}{Q} \right)_{\text{interfacial tension}} = -c_2 \frac{\alpha Q}{\eta_m} \left( \frac{q_{ij}}{Q} \right),
$$

(12)

where $c_1$, $c_2$, and $c_3$ are positive dimensionless numbers, which may depend on the volume fraction $\phi$. If we consider a dilute, small deformation theory like Taylor’s, it is clear that one need to have the $-c_3 (\alpha/\eta_m) q_{ij} q_{ij}$ term from the contribution of interfa-
cial tension on relaxation of the interfacial area. It will eventually provide us a nontrivial $Q$ and $q_{ij}$ at steady state even for the dilute limit. It is worth pointing out, here, that the $c_1$ term is related to the coalescence of droplets in a concentrated system, which is going to vanish at the limit of dilution. On the other hand, $c_3$ is the basic term which describes the deformation to the spherical form due to the interfacial tension and the same may be said of the $c_2$ term. Additionally, the $c_3$ term would be capable of containing some contributions from break-up of an elongated droplet.

From Eqs. (11) and (12), we obtain

$$\frac{d}{dt} Q_{\text{interfacial tension}} = -\lambda \mu \frac{\alpha}{\eta_m} Q^2 - \lambda \alpha \frac{\eta_m}{\eta_m} q_{ij} q_{ij},$$  \hspace{1cm} (13)

$$\frac{d}{dt} q_{ij} = -\lambda \frac{\alpha}{\eta_m} - \lambda \alpha \frac{\eta_m}{\eta_m} \frac{q_{im} q_{im}}{Q} q_{ij},$$  \hspace{1cm} (14)

where $\lambda = c_1 + c_2$, $\mu = c_1/(c_1 + c_2)$, and $\nu = c_3/(c_1 + c_2)$. The above equations have three dimensionless parameters, $\lambda$, $\mu$, and $\nu$, which represent degree of total relaxation ($\lambda$), size relaxation ($\mu$), and break-up and shape relaxation ($\nu$), which can be correlated with the volume fraction ($\phi$). In the dilute limit, no coalescence would take place to form a larger droplet, so that the relaxation of shape deformation is dominant. On the other hand, in a concentrated system where the interfaces will have complex shapes, one might expect that both size and shape relaxations mutually happen. Therefore, it is obvious that dynamic equilibrium between coalescence and break-up of droplets should be taken into account when analyzing the dependence of morphology on intensity of shearing. According to other scholars [Elmendorp and Van Der Vegt (1986); Fortenlý and Kovár (1989)], it has been known that the effect of coalescence on droplet size increases with increasing volume fraction of the dispersed phase. In a sense $\mu$ is a factor indicating the probability that coalescence of the dispersed phase will occur after mutual collisions, and will contain quadratic terms in $\phi$. The $\nu$ dependence on the volume fraction is complicated by taking into account simultaneous relaxations of shape and break-up. In an infinitely dilute system, the shape relaxation prevails over the others ($\mu \sim 0$ and $\nu \sim 1$) and in the concentrated system all the relaxations are of the same order [for $\phi \sim 0.5$, $\mu \sim 0.25$, and $\nu \sim (0.25 + 0.25)$]. With this view in mind, we shall propose the following approximative relation, although difficulties arise in taking it as a general rule:

$$\mu \sim \phi^2 \quad \text{and} \quad \nu \sim (1 - \phi),$$  \hspace{1cm} (15)

where proportionality constants are empirical parameters. The situation is quite different for oscillatory shear flow. The small amplitude dynamic experiments, carried out in the linear viscoelasticity range, allow only small deformations of the dispersed domain so that no coalescence would be expected. The shape of the droplet will oscillate with the frequency of the oscillation imposed. Hence the following can be suggested:

$$\mu \to 0 \quad \text{and} \quad \nu \sim (1 - \phi).$$  \hspace{1cm} (16)

D. Constitutive equation

Many polymer processing problems involve a broad range of viscosity ratios. If we consider the small deformation theory of dilute and very viscous droplets once more, the contribution of the $\nu$ term suggested for $Q$ is going to be small and rather approaches a value comparable with the $\mu$ contribution even for the dilute limit. Therefore, $\nu$ is a function of not only the volume fraction but also the viscosity ratio. However, in this
paper, to take a much easier approach, we disregard the dependence on viscosity ratio of \( \nu \), so that the overall effects of viscosity ratio will be taken into account separately. In general, the macroscopic stress tensor for two-phase fluid can be considered as follows:

\[
\sigma_{ij} = (\text{pressure term}) + \eta_m (d_{ij} + d_{ji}) + (\text{viscosity ratio term})
\]

\[+ (\text{morphology-dependent term}). \]  \hspace{1cm} (17)

According to Schowalter et al. (1968) and Mellema and Willemse (1983), the viscosity ratio term of almost spherical fluid particles (\( \alpha \to \infty \)) can be expressed as a function of volume fraction (\( \phi \)). Here only first order of volume fraction is considered:

\[
\text{viscosity ratio term} = \lim_{V \to \infty} \frac{1}{V} \left( \eta_i - \eta_m \right) \int_{\partial V_p} dS(u_i n_j - n_i u_j)
\]

\[= \frac{6}{5} \left( \frac{\eta_i - \eta_m}{\eta_m + \eta_i} \right) \eta_m \phi D_{ij}, \]  \hspace{1cm} (18)

where the rate of strain tensor is defined by \( D_{ij} = (1/2)(d_{ij} + d_{ji}) \) and \( \partial V_p \) is the interface of the dispersion within the total system volume \( V \). And also at the same condition, the morphology-dependent term can be expressed as

\[
\text{morphology-dependent term} = \lim_{V \to \infty} \frac{1}{V} \int_{\partial V_p} dS \left( \frac{1}{2} \delta_{ij} - n_i n_j \right)
\]

\[= \frac{16 \eta_i + 19 \eta_m}{5(\eta_m + \eta_i)} \eta_m \phi D_{ij}. \]  \hspace{1cm} (19)

If interfacial tension (\( \alpha \)) is assumed to be constant throughout the interface, one can see that the morphology-dependent term is exactly the same as the anisotropy tensor term, \(-\alpha q_{ij}\), discussed in Sec. II B. For the case of suspension of solid spherical particles (\( \eta_i \to \infty \)), adding Eqs. (18) and (19) can lead to Einstein's law.

In our case, when taking Eq. (18) as providing the effects of viscosity ratio, it is possible to obtain complete constitutive equations by combining Eqs. (8), (9), (13), (14), and (18):

\[
\frac{\partial}{\partial t} q_{ij} = -q_{ik} d_{kj} - q_{jk} d_{ki} + \frac{2}{3} \delta_{ij} d_{lm} q_{lm} - \frac{Q}{3} (d_{ij} + d_{ji}) + \left( \frac{q_{lm} d_{lm}}{Q} \right) q_{ij} - \lambda \frac{\alpha}{\eta_m} Q q_{ij}
\]

\[-\lambda \nu \frac{\alpha}{\eta_m} \left( \frac{q_{lm} d_{lm}}{Q} \right) q_{ij}, \]  \hspace{1cm} (20)

\[
\frac{\partial}{\partial t} Q = -d_{ij} q_{ij} - \lambda \mu \frac{\alpha}{\eta_m} Q^2 - \lambda \nu \frac{\alpha}{\eta_m} q_{ij} q_{ij}, \quad Q = Q_0, \quad q_{ij} = q_{ij0} \quad \text{at} \quad t = 0,
\]  \hspace{1cm} (21)

\[
\sigma_{ij} = \left[ 1 + \frac{6(\eta_i - \eta_m)}{10(\eta_m + \eta_i)} \phi \right] \eta_m (d_{ij} + d_{ji}) - \alpha q_{ij} - P \delta_{ij}. \]  \hspace{1cm} (22)

Even though some question remains about evaluating the effects of the viscosity ratio in a concentrated system, the above constitutive equations might be very meaningful in the sense that contributions of the complex interfaces can be isolated. At this juncture it may be noticed that all the relaxation terms of the above equations can be interpreted as the
capillary number of the dilute system (see Sec. II A). However, as long as the type of relaxation is different, in our model each contribution is quite different, depending on the $\lambda$, $\mu$, and $\nu$ values.

E. Dynamics of interfaces in oscillatory flow

In dynamic oscillatory flow, the Cox and Merz rule said that $\eta(\dot{\gamma})$ is equal to $|\eta^*(\omega)|$ with no shift factor, and actually the pure components fulfill this rather well. The relationship between complex shear viscosity and complex shear modulus, $G^* = i\omega\eta^*$ allows us to rewrite Eq. (22) in the following form (all complex moduli being taken at the frequency $\omega$) if we assume that Cox and Merz rule can be applied to both matrix and inclusion:

$$G_b^* = \left[ \frac{6(G_i^* - G_m^*)}{10(G_m^* + G_i^*)} \right] \phi G_m^* + G_{int}^*, \quad (23)$$

in which $G_b^*$, $G_m^*$, and $G_i^*$ denote the complex moduli of blend, matrix, and inclusion phase, respectively. The term $G_{int}^*$ is defined as a complex modulus attributed only to the interfaces. For imposing an input variable (strain) $\gamma(\omega) = \gamma_0 \sin(\omega t)$ [or strain rate $\dot{\gamma}(\omega) = d^{12}(\omega) = \gamma_0 \omega \cos(\omega t)$], the resulting stress dependent on the interface $-\alpha q_{12}(\omega)$ will also vary sinusoidally with the stress amplitude ($\sigma_{int}$), but will be out of phase ($\delta_{int}$) with the strain. One may calculate the interfacial stress amplitude $\sigma_{int}$, and its phase lag $\delta_{int}$ from Fig. 3, illustrative of their typical pattern, by solving Eqs. (20) and (21) with initial values ($Q_0$ and $q_{ij0}$) and parameters ($\lambda$, $\mu$, and $\nu$) determined. Then, interfacial moduli ($G_{int}^*$, $G_{int}'$, and $G_{int}''$) can be estimated by using the following definitions:

$$G_{int}^*(i\omega) = G_{int}'(\omega) + iG_{int}''(\omega), \quad (24)$$
TABLE I. Physical characteristics for PS and LLDPE.

<table>
<thead>
<tr>
<th>Material</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>density: 1.05 (g/cm³)</td>
</tr>
<tr>
<td></td>
<td>$M_n$: 152 000 (g/mol)</td>
</tr>
<tr>
<td></td>
<td>$M_w$: 290 000 (g/mol)</td>
</tr>
<tr>
<td></td>
<td>$T_g$: 94°C</td>
</tr>
<tr>
<td>LLDPE</td>
<td>density: 0.935 (g/cm³)</td>
</tr>
<tr>
<td></td>
<td>$M_n$: 23 000 (g/mol)</td>
</tr>
<tr>
<td></td>
<td>$M_w$: 113 000 (g/mol)</td>
</tr>
<tr>
<td></td>
<td>$T_m$: 125°C</td>
</tr>
</tbody>
</table>

\[
G'_\text{int} = \left( \frac{\sigma'_\text{int}}{\gamma_0} \right) \cos(\delta_{\text{int}}),
\]

\[
G''\text{int} = \left( \frac{\sigma''\text{int}}{\gamma_0} \right) \sin(\delta_{\text{int}}),
\]

where $\gamma_0$ is the amplitude of strain.

According to the theoretical description of Gramespacher and Meissner (1992), the complex modulus of immiscible blends consists of two contributions, i.e., (1) the viscoelastic properties of each pure component and (2) the interfacial tension between individual components. In this sense, there is a thread of connection between this model and ours. However, a simple mixing rule for the contribution of individual components was used in their model, and the nontrivial effect caused by deformability of the dispersed state was not considered.

III. EXPERIMENT

A. Materials and sample preparation

The materials used in this work were polystyrene (PS), GP-125, produced by Han-nam Chemical Co. and linear low-density polyethylene (LLDPE), 2558, by Hanyang Chemical Co., and their physical properties are listed in Table I. These polymers are thermodynamically immiscible and thus a good example of the model blend system. The materials were vacuum dried at 80°C for 5 h prior to any use. In order to examine the morphological structure induced by simple shear flow and rheological properties in dynamic oscillatory flow, the blends with seven compositions ranging from 0 to 100 wt % of PS in LLDPE were prepared in the molten state using a Brabender batch mixer at 200°C and 40 rpm for 10 min, and then compression molded at 200°C for 5 min into sheets of 1 mm thickness and cooled naturally to room temperature. The thermomechanical history of all the samples was identical. The blends will be referred to as PS10 and so forth, where the number denotes the PS weight percentage in LLDPE.

B. Methods of investigation

A cone-and-plate rheometer (RDS II) was used to measure storage ($G'$) and loss ($G''$) moduli as a function of angular frequency ($\omega$) in the oscillatory shear mode. The cone angle was 0.1 rad, and the diameter of the platen was 25 mm. Continuous nitrogen purging of the environmental chamber was necessary to avoid the oxidative degradation of PS, LLDPE, and their blends. The strain amplitude was taken as 15%, for which it has
been verified that all samples were linear viscoelastic, and all the data given below have been obtained at 200 °C, at which both components were in the molten state.

A special shearing device with cone angle 4° and 25 mm diameter cone-and-plate fixtures was designed to carry out a constant shear rate experiment on the molten specimens and to quench them below the melting temperature of both components so as to freeze the deformed and oriented dispersed domains. This device is also connected to a liquid-nitrogen-cooled flow system, and the sample was protected by a dry nitrogen environment. The whole pool of the sample in this device was quenched in situ with liquid nitrogen, in the process of being forced by constant shear rate (\( \dot{\gamma} = 0, 1, 6.31, \) and \( 13 \text{ s}^{-1} \)). Morphologies in these solidified specimens were investigated by scanning electron microscope (SEM). The PS domains of quenched samples were extracted by using the solvent mixture of MEK (methyl ethyl ketone)/Et-OH (ethyl alcohol) (1:1). In all cases, in order to eliminate any possible interference of uncertain shear history arising from the blending and molding, the samples were allowed to relax to the equilibrium structure at 200 °C for 20 min without any shear in the experimental apparatus. We ascertained no effects of flow history on the rheological measurements (\( G' \) and \( G'' \)) by time sweep experiments.

IV. RESULTS AND DISCUSSION

A. Morphology of PS/LLDPE polymer blends

In Fig. 4 the frequency sweep results for PS and LLDPE are presented. Below \( \omega = 40 \) (rad/s), PS has a higher complex viscosity than LLDPE due to its higher molecular
FIG. 5. SEM photomicrographs of fracture surfaces of PS10, (a) for $\dot{\gamma} = 0\text{ s}^{-1}$ (magnification = 1800), (b) for $\dot{\gamma} = 1\text{ (1800)}$, (c) for $\dot{\gamma} = 6.31\text{ (1800)}$, and (d) for $\dot{\gamma} = 13\text{ (1800)}$.

weight; the former is more viscoelastic and less Newtonian-like than the latter. In general, it can be said that when the dispersed phase is less viscous than the continuous phase, the droplets may be elongated by the shear stress and form fibrils parallel to the flow direction. When the dispersed phase is more viscous, it is difficult to deform the suspended droplets except with very large stresses. The morphology of immiscible polymer blends is very complex. It depends on a number of factors: the composition, the viscoelastic properties of the components, the given flow strength, and the interfacial tension at the interface which depends on the differences in polarity between the phases.

In this work the morphology of PS/LLDPE has been analyzed for the case of the simple shear flow. As revealed by SEM, Figs. 5–9 show blend microstructures quenched by means of liquid nitrogen before starting the shear flow and that induced by various shear rates: $\dot{\gamma} = 1\text{ (s}^{-1}), 6.31, \text{ and } 13, \text{ respectively}$. In all cases, the surface of observation was perpendicular to the radial direction of the cone-and-plate geometry; that is, a constant velocity gradient $\dot{\gamma}_{12}$ was experienced on all positions.

For the PS10 in Fig. 5, the minor phase (PS) is clearly dispersed in the matrix (LLDPE) in the form of small droplets with an average radius, which can be quantified based on weight-averaged dimension of the dispersed phase. In increasing the shear rate, no variation of morphology and droplet sizes is noticed and the shape of the domains re-
mains almost spherical. For the PS30, Fig. 6 reveals a tendency toward greater irregularity in domain shapes in the larger size range, suggesting that with increasing shear rate some of the droplets were formed not only by break-up, but also by coalescence of small particles during the shearing. Significantly, as mentioned before, complex interfaces have been formed due to the coalescence, deformation, and break-up of droplets. For PS50, the fine structure is abruptly lost, cocontinuous phases are obtained, and each phase is difficult to distinguish when no flow is applied. On the other hand, if shear is applied, uniform lamellar morphology is formed at $\dot{\gamma} = 1$ (s$^{-1}$) that exhibits long treads undulated in diameter. As a general feature, the transition to the lamellar can occur as a function of temperature and shear rate. In our case the shear rate initiating this phenomena is as low as 1 (s$^{-1}$) and then a further increase in shear rate makes the microstructure more complex and interface markedly. Beginning with PS70 in Fig. 8, PS is the continuous phase and LLDPE the dispersed phase. It shows the same tendency as in Fig. 7. However, in this blend, a compositional dissymmetry of the blend morphology caused by shear rate is observed, i.e., here LLDPE dispersed in PS forms the lamellar, while at a corresponding concentration of PS in LLDPE, discrete domain structures are formed. This may be ascribed to the fact that the matrix (PS) is more viscous than the dispersed phase (LLDPE), allowing for a higher deformation of the minor phase. Finally, in the case of
the PS90 blend, the minor phase (LLDPE) is well dispersed and is almost spherical in the small size range, and because the LLDPE droplets are subjected to high stresses due to the large PS viscosity, raising the shear rate forces creates yet smaller droplets by the break-up process overcoming the interfacial energy.

According to the general features of above blends morphology, it is concluded that interfacial behaviors as produced by the controlled shear rates and volume fractions are very important and this aspect must be covered in adequate rheological models of immiscible polymer blends.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PS10%</th>
<th>PS30%</th>
<th>PS70%</th>
<th>PS90%</th>
</tr>
</thead>
<tbody>
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<td>$\lambda$</td>
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<td>0.9</td>
<td>0.8</td>
<td>1.97</td>
</tr>
<tr>
<td>$\mu$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>$R_0(\mu\text{m})$</td>
<td>3</td>
<td>4.5</td>
<td>35</td>
<td>2.5</td>
</tr>
</tbody>
</table>
FIG. 8. SEM photomicrographs of fracture surfaces of PS70, (a) for $\dot{\gamma} = 0\ s^{-1}$ (magnification = 400), (b) for $\dot{\gamma} = 1\ (500)$, (c) for $\dot{\gamma} = 6.31\ (600)$, and (d) for $\dot{\gamma} = 13\ (800)$.

B. Comparison with model predictions

The interfacial tension between PS and LLDPE varies with temperature and is 4.7 mN/m at 200 °C [Wu (1982)]. For initial conditions, $Q_0$ is calculated from the weight-averaged radius of dispersion and $q_{ij0} = 0$ is assumed, and also the proportionality constant of $\nu$ in Eq. (16) is set to unity. The complex moduli of each blend component are obtained experimentally. Thus, the predicted results will depend only on the degree of total relaxation, $\lambda$. These are summarized in Table II. According to Eqs. (20), (21), and (23), model predictions of $G''$, $G''$, and $\eta^*$ may be made, using the parameters listed in Table II, and their comparison with the experimental data for the PS10, PS30, PS70, and PS90 are presented in Fig. 10. It is obvious from these figures that there is excellent agreement between the theoretical predictions and experimental results over the whole frequency and composition ranges. Obviously, this encourages the use of this model for general blend systems with two phases. Also it can give weight to the strong point that we can calculate the moduli ($G''_\text{int}$ and $G''_\text{int}$) of the interfaces separately and gain an insight into morphological effects of such systems.
C. Relaxation times of interfaces

It is quite generally said that immiscible polymer blends show distinctive elastic properties and long relaxation time processes, given an upward tendency of the storage modulus at low frequencies, as compared to those for the individual phases. With this point in mind, it should be noted that the relaxation times of interfaces can be developed from our model. When the parameters of system and initial conditions given in Table III are adopted and the Maxwell model for each phase is assumed,

\[ G_m^*(\omega) = \frac{i\omega \eta_m}{1 + i\omega \tau_m}, \quad G_i^*(\omega) = \frac{i\omega \eta_i}{1 + i\omega \tau_i}, \quad (27) \]

where \( \eta_m, \tau_m, \eta_i, \) and \( \tau_i \) are the viscosities and relaxation times of the matrix and dispersed phase, respectively, for \( \eta_m = \eta_i = 10^5 \) (Pa s) and \( \tau_m = \tau_i = 0.1 \) (s) the theoretical curves can be calculated from Eqs. (20), (21), (23), and (27), as shown in Fig. 11. In a blend four zones of \( G_i^* \), mainly affected by the interfaces, are noticed, whereas \( G_m^* \) is almost unaffected. Apparently these results are consistent with the previous investigation [Graebing et al. (1993)]. Moreover, as previously mentioned, the moduli \( (G_i') \) and \( (G_i'') \) of interfaces normalized by moduli \( (G_b') \) and \( (G_b'') \) of blend can be obtained, designated as \( G_i'/G_b' \) and \( G_i''/G_b'' \). With increasing frequency (and correspondingly for
FIG. 10. Comparison of the predictions of our model with the experimental results for (a) PS10, (b) PS30, (c) PS70, and (d) PS90 at \( T = 200 \) °C.

<table>
<thead>
<tr>
<th>Table III. System parameters for a blend of two viscoelastic liquids.</th>
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<tbody>
<tr>
<td>Parameters</td>
</tr>
<tr>
<td>( q_{10} ) (1/m)</td>
</tr>
<tr>
<td>( R_0 ) (µm)</td>
</tr>
<tr>
<td>( \sigma ) (mN/m)</td>
</tr>
<tr>
<td>( \phi )</td>
</tr>
<tr>
<td>( \mu )</td>
</tr>
<tr>
<td>( \lambda )</td>
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<tr>
<td>( \nu )</td>
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</table>
decreasing times), decreases in the normalized loss moduli of interfaces arise, reflecting the relaxation time of interfaces $\tau_i$. Observation of these curves reveals a peculiar feature, which can be stated as follows: between the two frequency ranges comparatively little energy, on interfaces, is dissipated in periodic deformation, while the energy stored is retained. Thus, in such a region $G''_{\text{int}}/G''_{b}$ tends to be considerably less than $G''_{\text{inl}}/G''_{b}$.

In order to facilitate our analysis as suggested by Chuang and Han (1984), we shall consider logarithmic plots of $G'_b(\omega)$ and $G''_b(\omega)$ to correlate the dynamic viscoelastic properties of polymer blend systems. They observed that such plots were very sensitive to the morphological state of heterogeneous polymer systems. In Fig. 12 the theoretical influence of inclusion size, when assumed to be monodisperse, is shown in the log $G'_b$-log $G''_b$ plot. In each case there are four frequency regions and three characteristic relaxation times: $\tau_{R_0}$, $\tau_{S_R}$, and $\tau_{P_0}$. Similar observations were made by Graebling and co-workers (1993). For higher frequency ($\omega > 1/\tau_N$) a quadratic region appears on these curves (here, $\tau_N$ is the shortest relaxation time of blend and can be regarded as mean relaxation time of both the phases). Since the relaxation times of matrix and dispersed phase on the basis of a rheological model having a single relaxation time were chosen to be 0.1 (s) equally, the curve changes direction at 10 (rad/s). A secondary region between frequency $(1/\tau_{P_0})$ and $(1/\tau_N)$ is shown to be very
close, $G'_b \sim (G''_b)^2$, and then a plateau on the third region appears, which is directly related to the interfacial tension with the longest relaxation time, $\tau_{R_0}$. After all, it may be noted that the terminal region at frequency lower than $(1/\tau_{R_0})$ is reached, where there arises an apparent limiting behavior of $G'_b \sim \omega^2$ and $G''_b \sim \omega$. It should be noted that in keeping with the above pattern, decreasing the size of the inclusion amounts to increasing the plateau value of $G'_b$, as well as the frequency at which the terminal region appears. That is, the relaxation time of interfaces is reduced as follows:

\[
\tau_{R_0/5} < \tau_{R_0} < \tau_{5R_0}
\]  \hspace{1cm} (28)

The log $G'_{int}$ vs log $G''_{int}$ plots are shown in Fig. 13. This clearly shows the relaxation time dependence, having features similar to those of the pure phases (see the $\tau_N$ of Fig. 12). Therefore, from such a plot it is possible to deduce the relaxation time of interfaces in dynamic oscillatory flow experiments. As shown in Fig. 14, an analogous behavior is found for the PS/LLDPE system. It is possible to assess their relaxation times, $\tau_{PS10} \sim 0.25$ (s), $\tau_{PS30} \sim 0.4$, and $\tau_{PS90} \sim 0.5$ even though experiments of PS70 ($\tau_{PS70} > 10$) have never been carried to sufficiently low frequency (i.e., very long-time relaxation) to test the prediction, so that the following relation can be written:
\[ \tau_{PS10} < \tau_{PS30} \quad \text{and} \quad \tau_{PS90} \ll \tau_{PS70}. \quad (29) \]

Significantly, it is also consistent with the SEM observations for systems having the same matrix. However, when PS is the continuous phase, in spite of the smaller inclusion size, the interfacial relaxation time \( \tau_{PS90} \) is longer than that \( (\tau_{PS10} \text{ and } \tau_{PS30}) \) where LLDPE is continuous. The reason is that PS has longer relaxation times than LLDPE due to its higher molecular weight as shown in Fig. 4. Accordingly, it seems that the interfacial relaxation time is also dependent upon the relaxation time of the continuous phase.

V. CONCLUSION

In this paper, a new constitutive equation to describe the rheological properties of the two-phase system was proposed. When the theoretical prediction applied to dynamic oscillatory flow was compared with experiments in immiscible polymer blends (PS/LLDPE), its validity was confirmed not only for the whole frequency range but also for all compositions. From the experimental point of view, the changes in morphology due to the controlled shear strength and interfacial tension have been observed.
FIG. 14. Theoretical prediction of log $G'_\text{int}$ vs log $G''_\text{int}$ according to our model, for PS/LLDPE blends based on Fig. 10.

Furthermore, in the frame of our model the contribution of morphological effects on modulus, $G'_{\text{int}}$, can be determined, and hence it has given us an insight into the long relaxation time of interfaces caused by surface tension between the two phases.

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