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Linear viscoelastic behavior of molten polymer blends: A comparative study of the Palierne and Lee and Park models

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Abstract The linear viscoelastic properties of several molten blends with immiscible components of different viscosity ratio have been investigated. All the blends show a morphology of emulsion type. At low frequencies, the behaviors of these blends are essentially governed by the interface. The Palierne (1990) model is shown to well predict the linear behavior of all the blends. The Lee and Park model (1994), developed to take into account the relationship between the rheological behavior and morphological changes under large strain flows, is also shown to well describe the storage and loss moduli of the blends by adjusting a single fitting parameter. Based on the

weighted relaxation spectra, a comparison of both model predictions is made focussing on the time associated to the interface. An approximate method is then proposed to evaluate the interface parameter introduced in the Lee and Park model. At high frequency, discrepancies are observed for the Lee and Park predictions when the viscoelastic properties of both components are considerably different. The description of the bulk properties of the blend, i.e., the mixing rule used by Lee and Park, is modified to obtain a better description of the high frequency data.

Key words Blends – linear viscoelasticity – emulsion models

Introduction

The development of new polymer blends of specific properties is intimately related to the nature of the phases and to the control of the morphology. The rheology of multi-phase systems is very complex mainly due to the flow history dependence of the morphology. Rheological models can be a powerful tool to relate microscopic and macroscopic quantities. Nevertheless, considerable effort needs to be devoted to take into account the viscoelastic nature of the polymers under the different types of flow generally encountered in processing. In the case of small amplitude oscillatory flow, the Palierne Model (1990) has been shown to be very useful for predicting the rheological behavior of the immiscible blends (Brahimi et al., 1991; Graebling et al., 1990;

1993; Bousmina and Muller, 1993; Carreau et al., 1994; Germain et al., 1994; Bousmina et al., 1995). Satisfactory predictions are obtained up to relatively high concentrations of the dispersed phase. Estimation of unknown interfacial tension (Graebling et al., 1993, 1994; Lacroix et al., 1996), determination of particle size distribution (Friedrich et al., 1995), and analysis of the deformation of droplets under elongational flow (Delaby et al., 1994) have also been successfully carried out, using the Palierne model.

Recently, Lee and Park (1994) have developed a new model for multiphase systems based on the Doi and Ohta theory (1991). The model is not restricted to dilute or semi-dilute concentrations of the dispersed phase and accounts for coalescence and breakup phenomena. In principle, it is able to describe the rheological behavior of polymer blends for any type of flow,

especially for small amplitude oscillatory flow, assuming that the Cox-Merz rule is valid for the blend components.

More recently, Guenther and Baird (1996) have applied the Doi-Ohta theory (1991) to a PET/PA blend, of which the components exhibited almost a Newtonian behavior. The theory could be used to qualitatively describe the effects of the interfacial tension on the steady shear viscosity and primary normal stress difference. Overshoots and undershoots observed experimentally during transient experiments could not be described by the Doi-Ohta theory. The Doi and Ohta (1991) theory has also been used to relate the morphology of blends to steady state normal stress data (Vinckier et al., 1996). In this case, several blends of nearly inelastic polymers with various concentrations and viscosity ratios have been analyzed with the Doi and Ohta theory.

As far as we know, except for Lee and Park who have compared and validated their model predictions to experimental data of a PS/PE system over a wide range of composition, not attempt has been made to show that the Lee and Park model (or the Doi-Ohta model) can adequately describe the linear viscoelastic properties of immiscible blends. The aim of this paper is to compare the predictions of the Palierne and the Lee and Park models in the linear viscoelastic domain. This is the first step needed before assessing the Lee-Park model for large deformation flows. The experimental data of these different polymer blends, covering a wide range of viscoelastic properties, are used for the assessment of the models. The limitations of the two models are underlined and in light of experimental results, a modification of the Lee and Park model is proposed.

Theoretical background

Since both Palierne and Lee and Park models are based on two completely different approaches, the major assumptions are recalled and limitations of the results are also discussed.

Palierne model (1990, 1991)

By analogy with an electric formalism, Palierne derived an equation for predicting the complex modulus of molten (emulsion type) blends, G_B^* , is a function of the complex moduli of both phases G_M^* (for the matrix) and G_I^* (for the inclusions or dispersed phase) taking into account several important features of a multiphase system. The viscoelasticity of both phases, the hydrodynamics interactions, the droplets size and size distribution and the interfacial tension are indeed included in this formulation. Neglecting the effects of gravity and

inertia, G_B^* can be expressed as function of volume fractions ϕ_i of droplets of radius R_i by:

$$G_B^*(\omega) = \frac{1 + 3 \sum_i \phi_i H_i^*(\omega)}{1 - 2 \sum_i \phi_i H_i^*(\omega)} G_M^*(\omega) \quad (1)$$

with H_i^* given by:

$$H_i^*(\omega) = \frac{4 \left(\frac{\alpha}{R_i}\right) [2 G_M^*(\omega) + 5 G_I^*(\omega)] + [G_I^*(\omega) - G_M^*(\omega)] [16 G_M^*(\omega) + 19 G_I^*(\omega)]}{40 \left(\frac{\alpha}{R_i}\right) [G_M^*(\omega) + G_I^*(\omega)] + [2 G_I^*(\omega) + 3 G_M^*(\omega)] [16 G_M^*(\omega) + 19 G_I^*(\omega)]} \quad (2)$$

where α is the interfacial tension between the two polymer blend components. Equation (1) is restricted to linear viscoelasticity, that is: the case of small amplitude oscillatory shear flow. Therefore morphological changes during the flow, such as breakup or coalescence cannot be predicted by the model. Theoretically, a general behavior of the interface was considered by Palierne (1990) by introducing two parameters: $\beta'(\omega)$ which expresses the dependence of the interfacial tension α on local changes of the interfacial area, $\beta''(\omega)$ which describes the effect of local shear. Since these parameters are virtually impossible to determine experimentally, they are usually set equal to zero (Bousmina and Muller, 1993), as it is the case for Eqs. (1 and 2). Recently, Friedrich et al. (1996) have empirically made use of β' and β'' to account for the effect of adding a copolymer as a compatibilizer.

The rheological properties of an emulsion are strongly dependent on the morphology. The behavior of an emulsion may also be affected by steric interactions or anisotropic effects which occur often in concentrated systems. In such cases, failures have been reported (Bousmina and Muller, 1993; Carreau et al., 1994) limiting the use of the Palierne model to moderate concentrations. Nevertheless, the Palierne model very well describes emulsions of viscoelastic fluids up to relatively high concentrations under small amplitude oscillatory flow. For a polydispersity of the droplet size d_v/d_n (ratio of the volume and number average diameter respectively) less than 2, it has been shown that the model predictions can be calculated assuming monodispersed droplets and using the volume average diameter (Graebing et al., 1993; Bousmina et al., 1995). For a monodisperse droplet size distribution and for Newtonian components the Oldroyd expression (1953, 1955) is retrieved. Because the symmetry, the dipole-dipole interactions included in the Palierne approach do not contribute to the deviatoric stress tensor. Several others relations, such as the Einstein equation can be retrieved as special cases. Another particular case is obtained by setting $\alpha = 0$. The Palierne model then yields the following expression:

$$G_B^* = \left(\frac{1 + 3/2 H^*}{1 - H^*} \right) G_M^* \quad (3)$$

with H^* given by

$$H^* = \sum_i \phi_i \frac{2(G_I^*(\omega) - G_M^*(\omega))}{2G_I^*(\omega) + 3G_M^*(\omega)} \quad (4)$$

This result justifies the generalization to viscoelastic components of Dickie's results (1973) obtained from the work of Kerner for a dispersion of Hookean inclusions dispersed in a Hookean matrix. Equation (3) reduces to Einstein's expression for rigid inclusions in a Newtonian matrix.

Lee and Park model (1994)

The model proposed by Lee and Park is based on the theory developed by Doi and Ohta to predict the rheology of texture fluids. Lee and Park modified the Doi-Ohta theory (1991), originally developed for an equal mixture of two immiscible fluids with the same viscosity and density undergoing flows at low Reynolds number, to account for a mismatch in the viscosities of the polymers. They started from the general expression of the stress tensor for an emulsion given by Mellema and Willemsse (1983) and references cited therein:

$$\sigma_{ij} = \eta_M \dot{\gamma}_{ij} + \lim_{V \rightarrow \infty} \frac{1}{V} (\eta_I - \eta_M) \int (u_i n_j - n_i u_j) dS + \lim_{V \rightarrow \infty} \frac{1}{V} \int a \left(\frac{1}{3} \delta_{ij} - n_i n_j \right) dS - P \delta_{ij} \quad (5)$$

where $\dot{\gamma}_{ij} = \kappa_{ij} + \kappa_{ji}$ are the components of the rate of deformation tensor and κ_{ij} are the components of the velocity gradient tensor. The integrals are over the entire area of the interface S , δ_{ij} is the Kronecker delta, \mathbf{n} the unit vector normal to the interface, \mathbf{u} the velocity vector, η_M and η_I are the viscosities of the matrix and the inclusion respectively. Lee and Park associated the third term on the right of Eq. (5) as the anisotropy tensor term in Doi-Ohta theory, and as Doi and Ohta, Lee and Park used the interface tensor \mathbf{q} defined by Onuki (1987):

$$q_{ij} = \lim_{V \rightarrow \infty} \frac{1}{V} \int \left(n_i n_j - \frac{1}{3} \delta_{ij} \right) dS \quad (6)$$

Thus, Eq. (5) only differs from that of Doi-Ohta by its second right-hand term (called the viscosity ratio term). Considering almost spherical particles ($a \rightarrow \infty$), a pure straining motion, and first order volume fractions, Schowalter et al. (1968) expressed this viscosity ratio term as a function of the volume fraction of inclusions ϕ , and of matrix and inclusion viscosities by:

$$\lim_{V \rightarrow \infty} \frac{1}{V} (\eta_I - \eta_M) \int (u_i n_j - n_i u_j) dS = \frac{6}{10} \left(\frac{\eta_I - \eta_M}{\eta_I + \eta_M} \right) \eta_M \phi \dot{\gamma}_{ij} \quad (7)$$

Replacing Eq. (6) and (7) in Eq. (5) leads for constant a to:

$$\sigma_{ij} = \left(1 + \frac{6(\eta_I - \eta_M)}{10(\eta_I + \eta_M)} \phi \right) \eta_M \dot{\gamma}_{ij} - a q_{ij} - P \delta_{ij} \quad (8)$$

The interface tensor is assumed to be determined by two factors: the flow which enlarges and orients the interface, and the interfacial tension which opposes the effects of the flow. These effects are accounted for separately:

$$\frac{dq_{ij}}{dt} = \left(\frac{dq_{ij}}{dt} \right)_{flow} + \left(\frac{dq_{ij}}{dt} \right)_{interfacial \ tension} \quad (9)$$

Lee and Park have considered the same flow terms as those derived by Doi-Ohta for a 50/50 mixture of two immiscible Newtonian fluids with the same viscosity and assuming affine deformation. The evolution equation for the tensor \mathbf{q} for the flow contribution is then given by:

$$\left(\frac{dq_{ij}}{dt} \right)_{flow} = -q_{ik} \kappa_{kj} - q_{jk} \kappa_{ki} + \frac{2}{3} \delta_{ij} \kappa_{lm} q_{lm} - \frac{Q}{3} \dot{\gamma}_{ij} + \left(\frac{q_{lm} \kappa_{lm}}{Q} \right) q_{ij} \quad (10)$$

where the first three terms represent the upper convected derivative and Q is the area of the interface per unit volume. The variation of Q with time under the effect of the flow is given by:

$$\left(\frac{dQ}{dt} \right)_{flow} = -\kappa_{ij} q_{ij} \quad (11)$$

Lee and Park considered three different mechanisms of relaxation: coalescence, shape relaxation, and break up by interfacial tension (the relaxation mechanisms by interfacial tension proposed by Doi-Ohta did not account explicitly for the break-up phenomena). The relaxation rates are assumed to be controlled by a , Q and $\eta_M(\dot{\gamma})$ only, and a dimensional analysis leads to the following kinetics equations for the relaxation of the interfacial area Q , and its anisotropy q_{ij}/Q :

$$\left(\frac{dQ}{dt} \right)_{interfacial \ tension} = -c_1 \frac{a}{\eta_M} Q^2 - c_3 \frac{a}{\eta_M} q_{ij} q_{ij} \quad (12)$$

$$\frac{d}{dt} \left(\frac{q_{ij}}{Q} \right)_{interfacial \ tension} = -c_2 \frac{aQ}{\eta_M} \left(\frac{q_{ij}}{Q} \right), \quad (13)$$

where c_1, c_2, c_3 are dimensionless parameters which may depend on the volume fraction of the inclusions ϕ . Equations (12) and (13) can be rearranged to get:

$$\left(\frac{dq_{ij}}{dt}\right)_{\text{interfacial tension}} = -d_1 \frac{a}{\eta_M} Q q_{ij} - d_1 d_3 \frac{a}{\eta_M} \left(\frac{q_{lm} q_{lm}}{Q}\right) q_{ij} \quad (14)$$

$$\left(\frac{dQ}{dt}\right)_{\text{interfacial tension}} = -d_1 d_2 \frac{a}{\eta_M} Q^2 - d_1 d_3 \frac{a}{\eta_M} q_{ij} q_{ij} \quad (15)$$

where $d_1 = c_1 + c_2$, $d_2 = c_1/(c_1 + c_2)$ and $d_3 = c_3/(c_1 + c_2)$, respectively λ, μ and ν in the Lee and Park paper, and denoted as degrees of total relaxation, size relaxation, size relaxation, and break up and shape relaxation, respectively. The time evolution of the interface tensor under the opposite effects of the flow and of the relaxation by interfacial tension is found by substituting Eqs. (10) and (14) in Eq. (9).

$$\begin{aligned} \frac{dq_{ij}}{dt} = & -q_{ik} \kappa_{kj} - q_{jk} \kappa_{ki} + \frac{2}{3} \delta_{ij} \kappa_{lm} q_{lm} - \frac{Q}{3} \dot{\gamma}_{ij} \\ & + \left(\frac{q_{lm} \kappa_{lm}}{Q}\right) q_{ij} - d_1 \frac{a}{\eta_M} Q q_{ij} \\ & - d_1 d_3 \frac{a}{\eta_M} \left(\frac{q_{lm} q_{lm}}{Q}\right) q_{ij} \end{aligned} \quad (16)$$

and the time evolution of interfacial area per unit volume Q is given by:

$$\frac{dQ}{dt} = -\kappa_{ij} q_{ij} - d_1 d_2 \frac{a}{\eta_M} Q^2 - d_1 d_3 \frac{a}{\eta_M} q_{ij} q_{ij} \quad (17)$$

For a given velocity gradient tensor component κ_{ij} and for initial values of interfacial area per unit volume $Q(0)$ and its anisotropy $q_{ij}(0)$, the stresses occurring in a blend are calculated using Eqs. (8), (16) and (17). Lee and Park obtained the following results for oscillatory shear flow of a viscoelastic blend by applying the Cox-Merz rule to the pure components. Equation (8) becomes:

$$G_B^* = \left(1 + \frac{6(G_I^* - G_M^*)}{10(G_M^* + G_I^*)} \phi\right) G_M^* + G_{\text{interface}}^* \quad (18)$$

where $G_{\text{interface}}^*$ is the contribution of the interface to the complex modulus. The transformation of Eq. (8) using the Cox-Merz rule also constitutes a point of discussion. Lee and Park assumed that the Cox-Merz rule is valid for the pure components and that the evolution with time of the anisotropy tensor \mathbf{q} is expressed here as the special case of oscillatory shear flow. This approach is empirical since the original evolution equa-

tions for \mathbf{q} and Q have been developed considering the viscosities of both components to be similar so that the interface is affected only by the interfacial tension. Clearly the Cox-Merz rule does not apply to the blend, mainly because of the morphology evolution during shear flow (Han et al., 1995; Bousmina and Muller, 1996) and also, because of the non linearity of the contributions of the bulk properties and interfacial effect. Applying the set of Eqs. (16) and (17) for a polymer blend of different viscosities constitutes a crude approximation which can be probably overcome by using a fitting parameter. Such an empiricism is nevertheless quite useful for describing the blend morphology under large deformation flow.

For an imposed small amplitude shear strain $\gamma(\omega) = \gamma^0 \sin(\omega t)$, the resulting stress due to the interface, $-a q_{12}(\omega)$, will also vary sinusoidally with the stress amplitude $\sigma_{\text{interface}}$, but will be out of phase with respect to the strain. $\sigma_{\text{interface}}$, and its phase lag $\delta_{\text{interface}}$ are calculated by solving Eqs. (16) and (17) with initial values $Q(0)$ and $q_{ij}(0)$. The interfacial moduli are then calculated by using the following definitions exactly like in the work of Lee and Park:

$$G'_{\text{interface}} = \frac{\sigma_{\text{interface}}}{\gamma^0} \cos(\delta_{\text{interface}}) \quad (19)$$

$$G''_{\text{interface}} = \frac{\sigma_{\text{interface}}}{\gamma^0} \sin(\delta_{\text{interface}}) \quad (20)$$

Experimental

Three different types of blends were studied: polystyrene, polyethylene (PS/PE), polyethylene terephthalate glycol, ethylene vinyl acetate (PETG/EVA) and polypropylene (PP)/EVA blends. These blends have been chosen for comparing the predictions of the models because of their wide range of the zero-shear viscosity ratio (η_{I0}/η_{M0}) varying from 0.1 to 1. The experimental procedure concerning the PETG/EVA system has already been discussed elsewhere (Lacroix et al., 1996). For the other two systems, the commercial polymers were a PP (PP3020GN3) and an EVA (EVATANE 2805) supplied by Elf-Atochem while a PS (Styron D685) and a PE (LLDPE Tufin) products were obtained from Dow Chemical and Union Carbide, respectively.

Blending procedure

For each type of blend, as well as for the unblended components, the following blending procedures have also been applied, so that the thermomechanical history of the blends and of the components would be the same.

PE/PS blends

The blends were prepared using a Brabender internal mixer under nitrogen atmosphere at 200 °C and 50 rpm during 300 s, time long enough to reach a constant torque value. The samples extracted from the chamber were compression molded at 200 °C during 6 min, the pressure load progressively was increased from 200 kPa to 1.1 MPa. Blends of composition by volume of 90/10, 80/20, and 20/80 were prepared.

PP/EVA blends

The pellets were first dry-blended and melted in the Brabender at a set temperature of 200 °C and with a rotor speed of 20 rpm. Then, once all the pellets were loaded and melted, the speed was increased to 40 rpm and the components were mixed during 200 s. This time was sufficient to reach a constant torque value. The melt processing was carried out under nitrogen atmosphere to prevent degradation. The samples were extracted from the chamber and quenched in cold water. Samples for rheological measurements were then compression molded at 200 °C during 7 min. The pressure load was progressively increased from 200 kPa to 1.4 MPa. The samples were then quenched in cold water. Blends of composition by weight percent of 90/10, 80/20, 70/30 and 65/35 (corresponding to particles volume concentrations of 0.095, 0.19, 0.285 and 0.332) were investigated.

Scanning electron microscope

The morphological stability of the blends was checked by extracting from the rheometer the samples at different times. The morphologies were frozen with dry air, which allows the temperature inside the samples to decrease by about 150 °C in 2 min. The blend morphologies were determined by using a Jeol JSM-840 scanning electron microscope, for fractured samples in liquid nitrogen and coated with 50/50 gold palladium to avoid charging. To account for the fact that the observation plane does not necessarily cut through the particles at their equator, the Scharwz-Saltikhov (1967) corrections were applied, using the program developed by Lavallée (1990). The number and volume average diameters d_n and d_v were determined from the surface analysis of at least 300 particles with a digitalizing device. Our estimate of the accuracy of the measurements is at best $\pm 10\%$.

Rheological measurements

The linear viscoelastic properties of the molten blends were measured as a function of frequency using a Boh-

lin CSM rheometer with a concentric disk geometry. The diameter of the plates was 25 mm and the gap about 1.5 mm. The measurements were carried out under nitrogen at a set temperature of 200 °C except for the PETG/EVA blends for which the temperature was 210 °C and the frequency range investigated was 0.001–10 Hz. The samples were found to be stable with time by running repeated frequency sweep experiments or experiments at a low constant frequency for periods of over 1 h. To keep the response in the viscoelastic linear domain, the applied stress was controlled to keep the total deformation at around 0.05, except for very low frequencies where larger stresses input were used to increase the sensitivity.

Results and discussions

Figures 1 to 6 report the linear viscoelastic data for the different blends. The PETG/EVA, PP/EVA and PS/PE blends exhibit the typical rheological behavior observed for blends with an emulsion type morphology. For the three systems investigated, the viscosity ratio (η_I/η_M) is lower than 1 over almost the whole frequency range. For relatively low concentrations of the dispersed phase (10% and 20%), the loss modulus of the blends coincide almost with that of the matrix. By increasing the amount of the dispersed phase of lower viscosity, the loss modulus tends to decrease progressively compared to that of the major phase. The storage modulus is characterized by a shoulder in the low frequency region compared to that of the matrix (dashed line in Fig. 1).

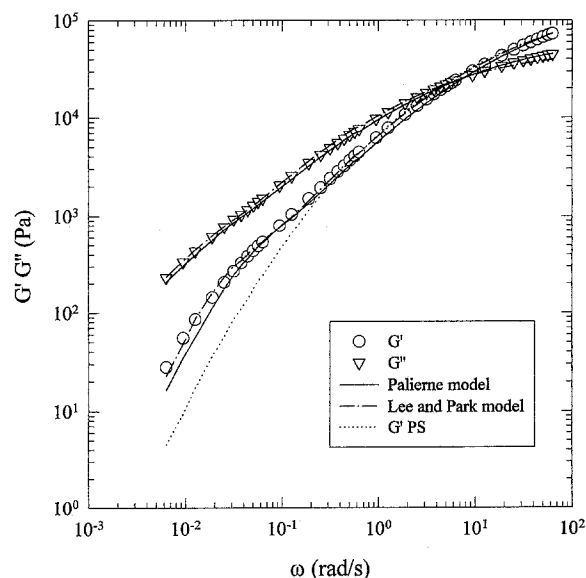


Fig. 1 Comparison between experimental data and model predictions for the 80/20 PS/PE blend; $T=200\text{ °C}$

The shoulder is quite visible in Figs. 3, 4. This increase in elasticity in the terminal zone of the matrix has been attributed to the deformability of the suspended droplets (Bousmina et al., 1995; Carreau et al., 1994, Bousmina and Muller, 1993; Graebling et al., 1993; Graebling and Muller, 1990; Scholtz et al., 1989). It results that the terminal zone of the blends is shifted towards lower frequencies compared to that of the matrix. In order to observe such effects, measurements have to be carried out at sufficiently low frequencies, for which the oscillation period is long enough to observe the relaxation of the deformable droplets. We report also in the figures the predictions of the Palierne and Lee-Park models. The comparison is discussed in the following section and limitations of these two models are underlined. The models are also used to estimate the relaxation times associated with the droplet deformation.

PS/PE blends

From the knowledge of the rheological behavior of the components and from the determination of the particle size distribution and the interfacial tension, the behavior of the blends can be predicted by using Eq. (1), and this without adjustable parameters. On the other hand, if unknown, the interfacial tension can be determined by fitting the theoretical predictions to the experimental data. For the PS/PE blends as well as the two others blends (PETG/EVA and PP/EVA) considered later, the polydispersity in size (d_v/d_n) of the inclusions did not exceed 2, so that we could consider the system as monodisperse in particle size and use the volume average diameter for calculating the model predictions (Graebling et al., 1993; Bousmina et al., 1995). The morphology was checked during the measurements and the stabilized values of the volume average diameter were used (see Table 1). Recall that the Palierne model implicitly assumes no coalescence and that the droplets remain almost spherical.

Even if the Lee and Park model is fundamentally different, especially regarding the treatment of the inter-

face, it can be used to describe the linear rheological behavior of polymer blends. The anisotropy tensor as well as the interfacial area variations with time are required to assess the interfacial contribution in the Lee-Park model. The evolution with time of the quantities characterizing the interface (q_{ij} and Q) is obtained from the solution of the non linear set of coupled Eqs. (16) and (17). In small amplitude oscillatory flow, (for sufficiently low deformations) coalescence is negligible. So, as in the analysis done by Lee and Park, d_2 associated to coalescence is set equal to zero and d_3 , v in the original Lee and Park article, associated to simultaneous shape relaxation and break-up is set equal to $1 - \phi$. We assume that the system is initially isotropic, so we set $q_{ij}(0)$ equal to zero. $Q(0)$ is determined from the quantitative analysis of the morphology, the interfacial stress and the phase lag ($\sigma_{interface}$ and $\sigma_{interface}$) can be estimated from the established solution of the governing interface equations. $G'_{interface}$ and $G''_{interface}$ are then calculated by using Eqs. (19) and (20). The complex modulus of the blend is finally obtained from Eq. (18). The parameter d_1 is adjusted to give the best fit between the model predictions and the experimental data in the low frequency region because as we will show in a following section, the relaxation time associated to the interface in the blend is dependent on the d_1 value.

Figure 1 compares both model predictions to the data for a 80/20 PS/PE blend. For the Palierne model, we assume the interfacial tension to be equal to 5.0 mN/m (Wu, 1971) and use the morphological data given in Table 1. Without any fitting parameter, the data can be well predicted by the Palierne model as shown in the figure. A slightly better fit of the lower frequency data could be obtained by using a lower value of the interfacial tension. Also reported on the figure are the G' data for the matrix (dashed line). The parameters used to calculate the predictions of the Lee-Park model are presented in Table 1. The results of both Lee-Park and Palierne models are very similar and, over the whole frequency range, the experimental data are correctly described by both Palierne and Lee-Park models.

All predictions of the Lee-Park model were obtained in the same way. A single fitting parameter was used (d_1) and adjusted to get the best fit in the low frequency region. The relaxation mechanism induced by the interfacial tension indeed becomes predominant at low frequencies. The influence of the parameter d_1 is shown in Fig. 2 for the 80/20 PS/PE blend. In the low frequency region, the model predictions are quite sensitive to d_1 , which is shown in Table 1 to depend on the volume fraction of the dispersed phase as well as on the viscosity ratio. A decrease of d_1 corresponds to an increase in elasticity and to a shift of the terminal zone towards lower frequencies for the blend.

Table 1 Morphological data, interfacial tension and parameters used for predicting the rheological behavior

Blends	ϕ	R_v (μm)	a (mN/m)	d_1	d_2	d_3
PS/PE @ 200°C	0.1	1.15	5.0±0.5	1.3	0	0.9
	0.2	2.4	5.0±0.5	0.6	0	0.8
PETG/EVA @ 210°C	0.1	0.55	4.0±0.5	1.5	0	0.9
	0.2	1.23	4.0±0.5	0.6	0	0.8
PP/EVA @ 200°C	0.095	0.3	1.0±0.2	2	0	0.905
	0.19	1.4	1.0±0.2	1.2	0	0.81
	0.285	2.8	1.0±0.2	0.5–0.7	0	0.715
	0.332	4.1	1.0±0.2(0.6)	0.6	0	0.668

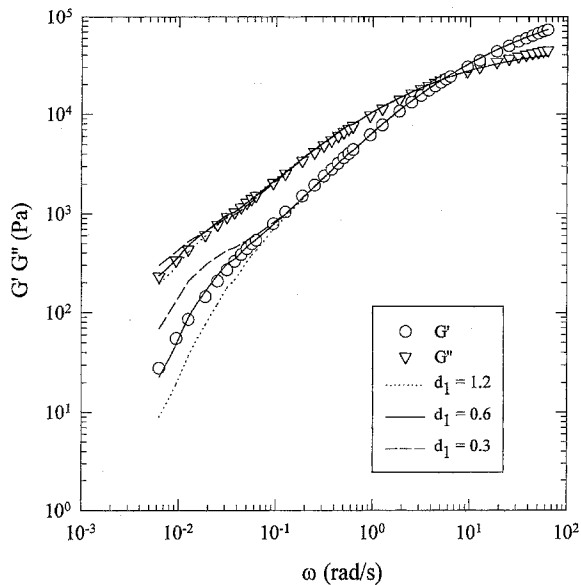


Fig. 2 Influence of the parameter d_1 on the predictions of the Lee and Park model for the 80/20 PS/PSE blend; $T=200^\circ\text{C}$

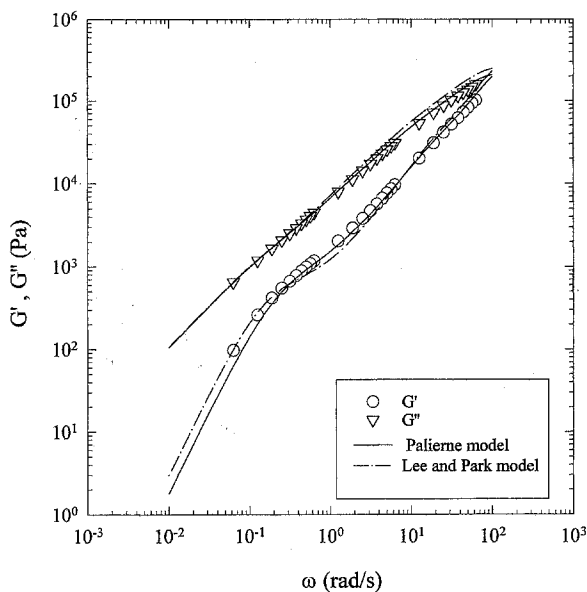


Fig. 3 Comparison between experimental data and model predictions for the 80/20 PETG/EVA blend; $T=210^\circ\text{C}$

PETG/EVA blends

The interfacial tension between these two polymers was initially unknown. A very good agreement between the model predictions and the experimental data had been found for values of a around 4.0 mN/m using the Palierne model (Lacroix et al., 1996) and this, for the two compositions investigated at 210°C . This previously determined interfacial tension value of 4 mN/m was used to test the Lee-Park model. Figure 3 compares the pre-

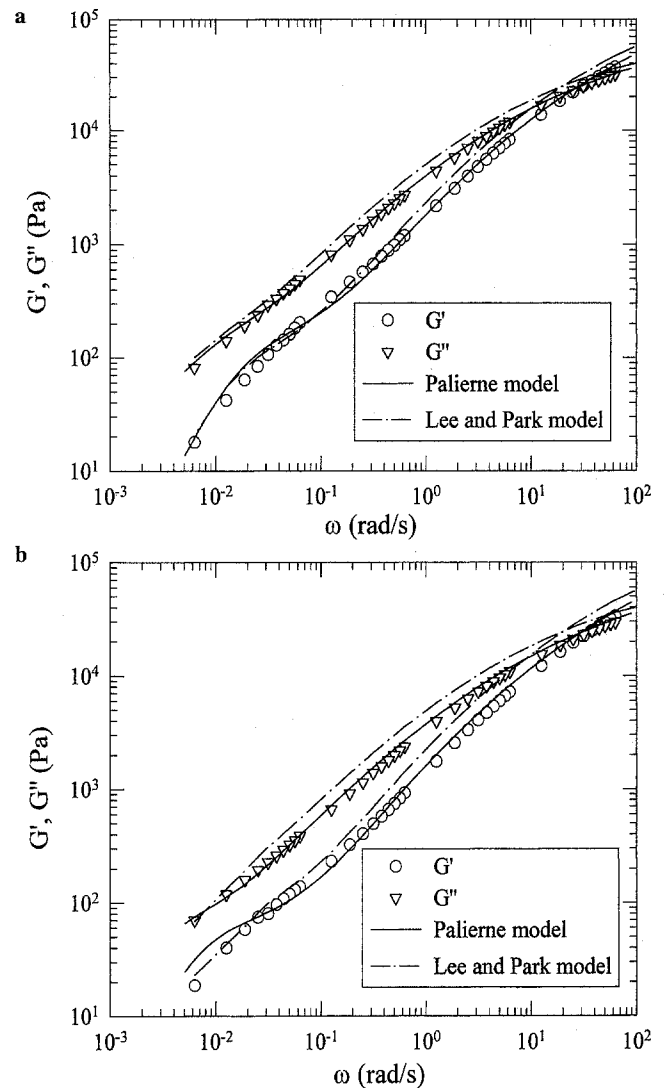


Fig. 4 Comparison between experimental data and model predictions for two PP/EVA blends: a) 70/30 PP/EVA, b) 65/35 PP/EVA; $T=200^\circ\text{C}$

dictions of both models for the 80/20 PETG/EVA blend. Both models give a good description of the data over the whole frequency range and the increase in elasticity in the low frequency region is well described. We must nevertheless keep in mind that if the interfacial tension is known the Palierne model does not contain any adjustable parameter. Table 1 summarizes the values of d_1 used to obtain the best fits of the Lee-Park model for the 90/10 and 80/20 PETG/EVA blends.

PP/EVA blends

The two previous blends investigated have shown that the Lee-Park model leads to a good description of the

linear viscoelastic properties. For the third system analyzed in this study, the differences of the rheological behavior of both components are much more pronounced. The zero-shear viscosity ratio is lower (η_{I0}/η_{M0} is around 0.1 instead of 0.3 for the PS/PE blends and around 0.7 for the PETG/EVA blends) and, over the whole frequency range the viscosity ratio between the components is lower compared to the PS/PE and PETG/EVA blends.

Figure 4 compares the predictions of both models for the 70/30 and 65/35 PP/EVA blends. The Palierne model predictions were determined by adjusting the interfacial tension to fit the experimental data. For almost all the compositions, the rheological behavior over the whole frequency range, as well as the increase in elasticity at low frequencies, are well predicted by the model. Slight discrepancies between the Palierne model and the 80/20 PP/EVA data occurred for the low frequency region (not shown in the figure). Nevertheless, the values of the interfacial tension found by adjusting the model predictions to the data are in agreement with the value obtained using the harmonic mean equation, 1.2 mN/m, except for the 65/35 PP/EVA blend where a best fit of the rheological data is obtained for $\alpha=0.6$ mN/m (Fig. 5). With increasing concentration of the dispersed phase up to 30% by weight of EVA, the terminal zone of the emulsion is shifted towards the low frequency region and the magnitude of the shoulder associated with the presence of the interface is increased.

The sensitivity of α on the Palierne model predictions is shown in Fig. 5 for the 65/35 PP/EVA blend.

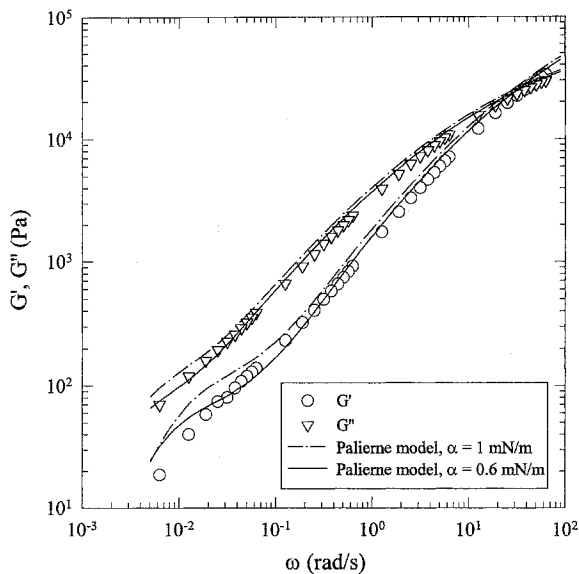


Fig. 5 Comparison between experimental data and the Palierne emulsion model predictions for the 65/35 PP/EVA blend; influence of the interfacial tension value on the model predictions; $T=200$ °C

Using the lower value, $\alpha=0.6$ mN/m, an overall better fit of the experimental data is observed, but the lowest frequency data for this blend are still not very well predicted. At this concentration, steric interaction as well as partial miscibility are not to be excluded, and this may explain the lower elastic modulus at low frequencies compared to the model predictions. Moreover, the experimental data at very low frequencies are not necessarily very accurate.

Figure 4 shows also that the loss and storage moduli are overpredicted by the Lee and Park model in the high frequency region. It can also be noted that these discrepancies are more significant for the larger concentration of dispersed EVA phase. Nevertheless, the behavior in the low frequency region, and related to the interface, is correctly described. The low frequency G' data for the 80/20 PP/EVA blend are better described by the Lee-Park model (not shown here), and globally the deviations are reasonable. In the high frequency region, where discrepancies between the Lee-Park model predictions and the data are observed for the PP/EVA blends, the contribution of the interface is negligible compared to those of the bulk properties of both phases (mixing rule). In the Lee and Park model, the behavior of the blend at high frequencies is dominated by the first term of Eq. (18). This viscoelastic term comes from an extension of the work of Schowalter et al. (1968), initially developed for a mixture of Newtonian fluids in which the particles are kept almost spherical ($a \rightarrow \infty$), and applying the Cox-Merz rule to both components. Assuming that the interfacial tension contribution is negligible (this is clearly valid at high frequency), the limiting case of this model can be written as follows:

$$G_B^* = \left(1 + \frac{6(G_I^* - G_M^*)}{10(G_M^* - G_I^*)} \phi \right) G_M^* \quad (21)$$

As shown in the previous paragraphs, the Palierne model is able to very well predict the behavior of the blends over the whole frequency range. By setting $\alpha=0$ in the Palierne model, Dickie's results (1973) are then retrieved and can be expressed as follow:

$$G_B^* = \left(\frac{1 + 3/2 H^*}{1 - H^*} \right) G_M^* \quad (22)$$

with

$$H^* = \phi \frac{2(G_I^*(\omega) - G_M^*(\omega))}{2G_I^*(\omega) + 3G_M^*(\omega)} \quad (23)$$

This corresponds to the Palierne model predictions in the limit of high frequency where the interfacial effects become negligible. Although the two high frequency limits are different (Eqs. (21) and (22)), the behavior of the PS/PE and the PETG/EVA blends are correctly described by both models because the viscoelastic proper-

ties of the two components for these blends are not much different. For the 80/20 PETG/EVA blend, a slight overestimation of the loss modulus can be detected at very high frequencies. For the PP/EVA blends which show the lower viscosity ratio over the whole frequency range, more significant discrepancies are observed.

Considering that the Palierne model leads to a good description of the high frequency data, we choose to modify Eq. (18) as follows:

$$G_B^* = \left(\frac{1 + 3/2 H^*}{1 - H^*} \right) G_M^* + G_{interface}^* \quad (24)$$

with H^* given by Eq. (23). $G_{interface}^*$ is calculated according to the same procedure as described in the case of the Lee-Park model.

The use of the Lee and Park model (Eq. (18)) as well as of the modified model (Eq. (24)) requires further comments. In developing Eq. (18), Lee and Park have associated the anisotropy tensor term, $-a q_{ij}$, to the limit of the morphology-dependent term (Mellema and Willemse, 1983) by assuming a constant interfacial tension. If one considers the limit of non deformable spheres, q_{ij} is equal to zero and then Eq. (18) does not reduce to the well known Einstein formula. In such a case, the limit of the morphology-dependent term will differ from that implicit in Schowalter et al. (1968) and derived by Mellema and Willemse (1983). The modified Lee and Park model (Eq. (24)) correctly reduces to the Einstein expression for rigid inclusions in Newtonian fluids. On the other hand, as indicated by one of the reviewers, the viscosity ratio term and the morphology-dependent term were obtained by Schowalter and Mellema and Willemse for almost spherical non deformable spheres at low volume fractions. Adding the limits of these two terms leads to the following form of the Eq. (18):

$$G_B^* = \left(1 + \frac{5k + 2}{2k + 2} \phi \right) G_M^* + G_{interface}^* \quad (25)$$

which is a generalized Taylor equation. We have tested this form (Eq. (25)) and found considerable disagreement with our data at high frequencies. Note that this result is considerably different from that of Palierne at high frequencies where the contribution of $G_{interface}^*$ becomes negligible. However this form may prove to be more appropriate for other conditions.

Figure 6 compares the predictions of both the Lee-Park and modified (Eq. (24)) models for the 70/30 and 65/35 PP/EVA blends. The results have been obtained by using the same value of d_1 as previously determined (Table 1). The figure shows that the modification significantly improves the predictions at high frequencies and, as expected, both the modified Lee and Park and the Palierne models are equivalent at high frequencies.

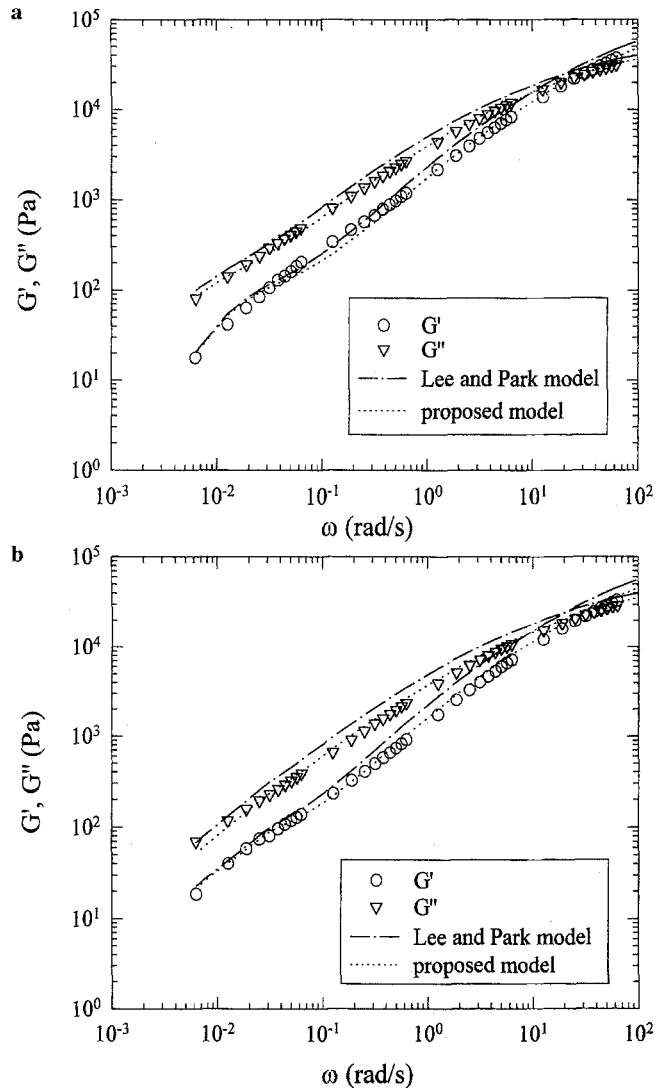


Fig. 6 Comparison between the Lee-Park and modified Lee-Park model predictions for two PP/EVA blends: a) 70/30 PP/EVA, b) 65/35 PP/EVA; $T=200^\circ\text{C}$

It is therefore believed that the mixing rule for the bulk properties embedded in the Palierne model is more appropriate. For the other blends, good agreement is also found with this modified model, but no significant differences could be observed.

For high concentrations of the dispersed phase, the empirically modified Lee-Park model with an adjustable parameter d_1 is more flexible than the Palierne model. Comparing Figs. 5 and 6, it is clear that a better fit of the low frequency data is obtained with the modified Lee-Park model for this 65/35 PP/EVA blend. The original Lee-Park model can account for particle-particle interactions, coalescence and breakup under large strain flows through adjustable parameters. These features could be of major interest in relation to the processing

of polymer blends. This parameter d_1 is related to the shape relaxation of the deformed droplets in the relaxation mechanism of Lee and Park. By adjusting its value, the anisotropy relaxation rate is modified (see Eq. (13)). The relaxation time associated to the interface in the blend is then dependent on the d_1 value. Based on this observation, Guenther and Baird (1996) have chosen another way of determining the parameter related to the anisotropy relaxation rate in the Doi-Ohta model, equivalent to the parameter d_1 in this case. We will discuss this approach in the following section in light of the relaxation times determined from the weighted spectra.

Interface relaxation times

The comparison of the plots of the weighted relaxation spectra $\lambda H(\lambda)$ as a function of $\log(\lambda)$ for the blend and the components is an efficient way to show the additional relaxation mechanism associated with interfacial tension (Gramespacher and Meissner (1992)). The relaxation spectrum $H(\lambda)$ is related with G' and G'' by:

$$G'(\omega) = \int_{-\infty}^{+\infty} H(\lambda) \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} d \ln \lambda \quad (26)$$

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\lambda) \frac{\omega \lambda^2}{1 + \omega^2 \lambda^2} d \ln \lambda \quad (27)$$

We have applied a modified Tikhonov regularization method (Weese (1993), Honerkamp and Weese (1993)) to calculate the spectra. The weighted relaxation spectra of the PS, PE and 80/20 PS/PE blend are given in Fig. 7. The blend spectrum exhibits two maxima. The first one coincides with that of the matrix, suggesting that the matrix governs the rheological behavior of the blend at high frequency. The second peak detected at longer relaxation times is associated with the shape relaxation of the droplets. The same features are observed for the PP/EVA blends in Fig. 8 for different concentrations of the dispersed phase. As the dispersed phase concentration is increased, we observe a shift of the additional peak towards longer times (i.e., an increase of the relaxation time, characteristic of the interface). Similar results observed for the PETG/EVA blends are not illustrated here.

Expressions for the characteristic time associated with the relaxation of the shape of the interface can be obtained from the Palierne and Lee and Park models. Graebing et al. (1993) reported the time associated with the droplets deformation for the emulsion model of Palierne. They pointed out that if a secondary plateau in G' associated with the shape relaxation of the

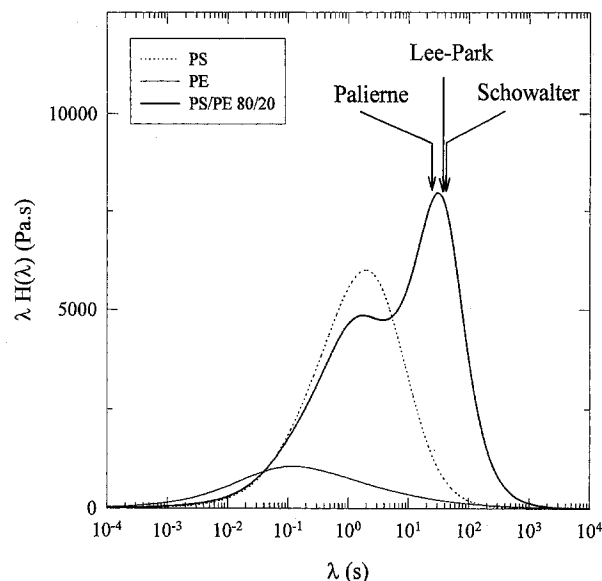


Fig. 7 Weighted relaxation spectra for the PS, PE and the 80/20 PS/PE blend; $T=200^\circ\text{C}$

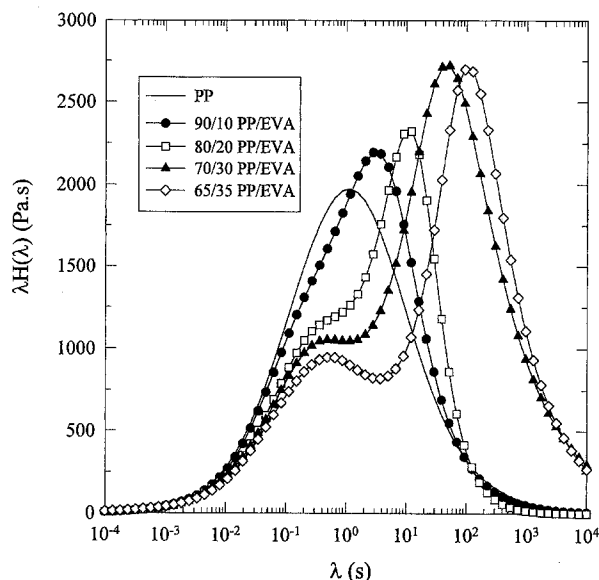


Fig. 8 Weighted relaxation spectra for the PP and the PP/EVA blends for various compositions of EVA; $T=200^\circ\text{C}$

droplets exists for a blend of viscoelastic polymers, it occurs in a frequency range where $G_M^* \sim i\omega\eta_M$ and $G_I^* \sim i\omega\eta_I$. They considered that the contribution to the storage modulus of the emulsion arising from the relaxation of the droplets can be calculated as if the phases were Newtonian liquids. Assuming that the droplets are monodispersed ($R_i = R$) they showed that the Palierne model is analogous to a Jeffreys model. The following expression for the time associated with

the relaxation of the shape of the droplets is then obtained:

$$\lambda_1 = \frac{R\eta_M}{4a} \frac{(19k+16)(2k+3-2\phi(k-1))}{10(k+1)-2\phi(5k+2)} \quad (28)$$

where $k = \eta_I/\eta_M$.

For the Lee and Park model, the relaxation of the anisotropy of the interface under the effect of the interfacial tension is described by Eq. (13). It is a first order kinetic equation and the inverse of the relaxation rate gives a relaxation time λ_2 expressed as:

$$\lambda_2 = \frac{\eta_M}{aQd_1} \quad (29a)$$

which reduces in the case of spherical monodisperse droplets of radius R to:

$$\lambda_2 = \frac{R\eta_M}{a} \frac{1}{3\phi d_1} \quad (29b)$$

The expressions for the time constants (Eq. (28) and (29b)) are quite similar and, by taking $\lambda_1 = \lambda_2$ the Lee and Park parameter d_1 can be calculated from physical parameters. Identification of the characteristic times associated with the relaxation of the interface was also considered by Guenther and Baird (1996). They identified the characteristic time equivalent to λ_2 in the Doi-Ohta theory with the relaxation time derived by Choi and Schowalter (1975). In this constitutive equation developed for semi diluted emulsions of two Newtonian fluids the expression for the relaxation time λ_3 , associated with interfacial tension, can be expressed as:

$$\lambda_3 = \lambda_0 \left(1 + \frac{5\phi(19k+16)}{4(k+1)(2k+3)} \right) \quad (30a)$$

with

$$\lambda_0 = \frac{R\eta_M}{4a} \frac{(19k+16)(2k+3)}{10(k+1)} \quad (30b)$$

The Guenther and Baird approach was partly based on the results presented by Gramespacher and Meissner (1992). For PMMA/PS blends, they found that the relaxation time λ_3 calculated using Eqs. (30a) and (30b) was equal to the experimentally obtained, value corresponding to the peak in the weighted relaxation spectra associated with the interfacial tension.

Table 2 lists the relaxation times associated with the interface for the Palierne, Lee and Park, and Choi and Schowalter models, and those determined from the second peak of the weighted relaxation spectra as shown in Figs. 7 and 8. When considering the whole time scale under investigation, the times associated with the different models are found, for any given blend, to fall in the same range of values. Discrepancies between the times are, however, observed. They can be important (up to 100%), and they vary from one system to an-

Table 2 Comparison of different interface relaxation times

Blends	Composition	λ_1 (s)	λ_2 (s)	λ_3 (s)	λ_{peak} (s)
PS/PE	90/10	10.4	16	15	8
	80/20	24	37	43	30
PETG/EVA	90/10	2.2	2.4	3.0	0.8
	80/20	5.4	6.6	9.0	4.8
PP/EVA	90/10	5.5	6.8	7.8	2.8
	80/20	27	26	50	12
	70/30	60	70	128	51.8
	65/35	93	85	207	92.9

other. For the PP/EVA and PETG/EVA blends the Palierne and the Lee and Park characteristic times are quite similar (the differences do not exceed 20%), but the times obtained from the Choi and Schowalter equation are 50% to 100% higher. By contrast, for the PS/PE blends, the Choi and Schowalter and the Lee and Park characteristic times are quite similar, while the times associated with the Palierne model are now about 50% lower. The characteristic times determined from the models are roughly consistent with the estimation from the weighted relaxation spectra using the peak associated with interfacial tension. The time corresponding to this peak is, however, generally lower, especially at low dispersed phase concentrations where the distinction of the peaks associated with the matrix and the interface is difficult. Coupling effects between the peaks could then made the determination of the characteristic time associated with the interface less reliable.

The Lee and Park model predictions for the PS/PE blends (systems for which the discrepancies between the Palierne and Lee and Park characteristic times are the largest), using the parameter d_1 calculated by taking $\lambda_1 = \lambda_2$, are reported in Fig. 9 and compared to the data for two concentrations of the dispersed phase. Also shown by the solid lines are the best fits obtained by adjusting d_1 . The model with d_1 given by Eq. (29) is found to underestimate the storage modulus of the blend in the low frequency range. The global agreement is, however satisfactory, so that setting the interface characteristic time of the Lee and Park model equal to the characteristic time of the Palierne model is believed to be a simple way of determining an approximate value of d_1 .

Finally, in calculating the Lee and Park model predictions presented so far the parameter d_3 had been taken equal to $1 - \phi$. In the case of the PS/PE blends and when d_1 is calculated by taking $\lambda_1 = \lambda_2$, the adjustment of d_3 did not make it possible to improve the fit between the model predictions and the experimental data. For small amplitude oscillatory flow the predictions of the model are almost insensitive to the value of this parameter.

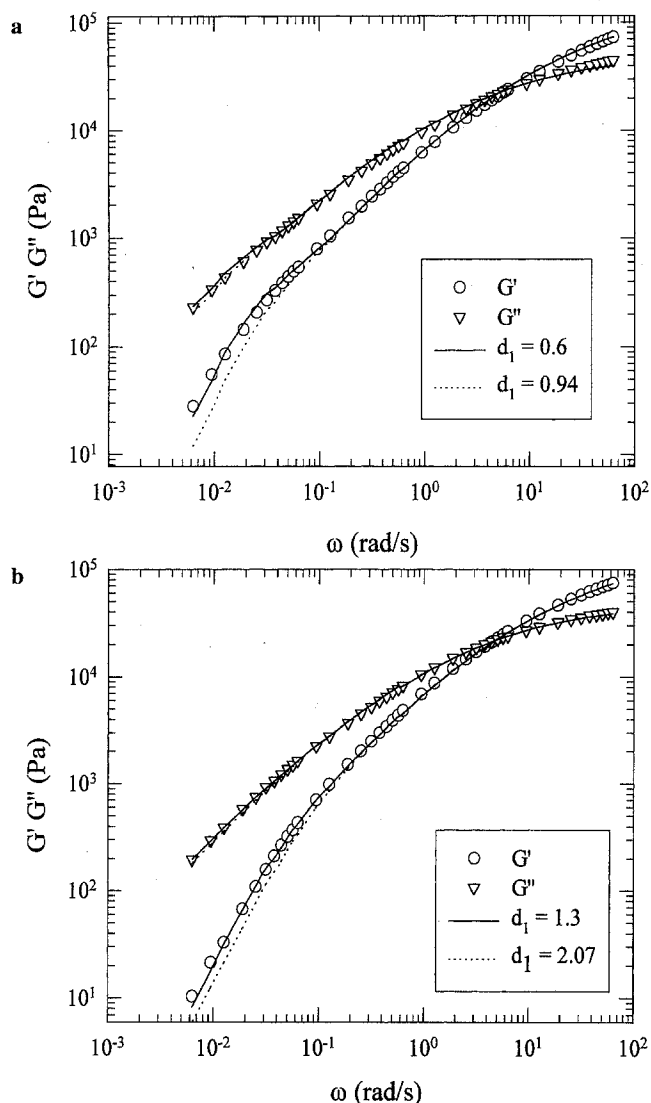


Fig. 9 Comparison between experimental data and the Lee and Park model predictions for two PS/PE blends; a) PS/PE 90/10, b) PS/PE 80/20; — best fits; using d_1 calculated from Eq. (24)

Conclusions

We have confirmed for three different systems the ability of the Palierne model to predict the linear viscoelastic behavior of immiscible blends. The linear viscoelastic data of the same blends could also be relatively well described by the Lee-Park model using a single fitting parameter related to the relaxation of the interface. For the more concentrated emulsions, when particle-particle interactions become important, the Lee-Park model with an adjustable parameter appears to be more flexible than the Palierne model to describe the low frequency behavior although some empiricism remains in the development of such an equation. The times associated with the relaxation of the shape of the interface derived from Lee and Park and Palierne models were found to be of similar magnitude and in relative agreement with the characteristic time determined from the peak of the weighted relaxation spectra. As a first approximation, the parameter d_1 associated with the interface relaxation in the Lee-Park model can be estimated using the characteristic time derived from the Palierne equation. For a blend with a relatively different viscosity ratio between the components, the Lee and Park model overestimates the data in the high frequency range. So, in light of these experimental results, a modification of the Lee-Park model is proposed to obtain a better description of the linear viscoelastic data. This modified model reduces to the Palierne equation for high frequencies and the Einstein equation is recovered for the case of rigid spheres diluted in a Newtonian fluid.

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