Analysis of Palierne's emulsion model in the case of viscoelastic interfacial properties

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Synopsis

The quantitative understanding of rheological experiments on compatibilized binary polymer blends requires the consideration of viscoelastic interfacial properties. The Palierne model offers these capabilities but a systematic analysis has not been performed yet. Starting from the Palierne model containing a Maxwell ansatz for complex interfacial shear or dilatational moduli and which considers a particle-size distribution function, we find that this model combines parameter and material functions in an ambiguous way. Consequently, a simplified version of the model—frequency-independent interfacial moduli and monomodal particle-size distribution—was introduced. Formulas have been derived for the relaxation times, the form relaxation time, and one additional still longer time which is associated with viscoelastic interfacial properties. We have found a good agreement between the predictions of the model and experimental data as well as the characteristic times in the relaxation time spectrum and the derived time constants for a PS/PMMA blend compatibilized with different amounts of a corresponding symmetric block copolymer. These results reveal that from the rheological point of view, the interface is of almost elastic nature, either shear or dilatational. © *1999 The Society of Rheology.* [S0148-6055(99)01406-6]

I. INTRODUCTION

Little experimental work has been published regarding the influence of interfacial agents on the rheological behavior of polymer blends. Most often these papers deal with polymeric systems in which (i) the morphology is not a simple ''spheres in matrix morphology'' [Brahimi *et al.* (1991); Haaga and Friedrich (1994); Riemann *et al.* (1994)], (ii) the concentration of the dispersed phase is too high [Valenza *et al.* (1991); Wippler (1991); Kim *et al.* (1993); Bousimina *et al.* (1995); Germain *et al.* (1994); Gleinser *et al.* (1994)], (iii) a too high compatibilizer concentration is used, leading to the formation of micelles [Kim *et al.* (1993); Germain *et al.* (1994); Wippler (1991)], or (iv) reactive compatibilizers are added for which the amount of interface active agent created is not known [Germain *et al.* (1994); Lacroix *et al.* (1996a,b)]. All these facts complicate a quantitative analysis of the results obtained in terms of rheological models.

Recently, we have presented experimental facts [Riemann *et al.* (1996, 1997)], which describe the influence of block copolymers, e.g., P(S-*b*-MMA), on the relaxation behavior of polystyrene (PS)/poly(methyl methacrylate) (PMMA) blends. For blends with 7.5 wt % of dispersed phase, it was observed that the form relaxation process is shifted

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slightly towards higher frequencies, depending on the amount of interfacial active species. This relaxation process is characterized by the relaxation time λ_F, which the deformed spherical particles need to attain their original spherical shape.

Moreover, at times longer than the form relaxation time, a new relaxation process, which heavily depends on the amount and the nature of the block copolymer used, was observed. The characteristic time of that process, λ_β, was given by an equation that is based on Palierne's emulsion model. This model contains a deformation-dependent interfacial shear modulus which makes the interfacial stress state nonisotropic. The assumptions made, the derivation itself and the extension to an interfacial dilatational modulus were not given in the previous paper and it is one of our objectives to present these results here.

The theoretical description of the rheological properties of compatibilized blends is a long-term research subject. It is based on the assumption that the addition of interfacial active species does not only alter the coefficient of interfacial tension α but leads to a more general interfacial stress state which becomes area dependent. Models have been developed to analyze either the influence of compatibilizers on the deformation of individual particles [Flumerfelt (1980); Gottier *et al.* (1986); Prieditis *et al.* (1987); Pozrikidis (1994)] or to derive material functions like the complex shear modulus G^* and its components, the storage modulus G' and the loss modulus G'' [Oldroyd (1953), (1955); Palierne (1990), (1991)].

In his pioneering work on emulsions of viscous blend components, Oldroyd investigated the case of an interface whose properties are characterized by interfacial viscoelasticity. He analyzed the solely elastic and the solely viscous interface more in detail and found that an interface characterized by a constant interfacial viscosity changes the zero-shear viscosity of the blend, and no further relaxation process with a time longer than the form relaxation time occurs. In the case of an emulsion with solely elastic interfacial properties characterized by an interfacial modulus, the zero-shear viscosity of the blend is not changed. However, an additional relaxation process arises. Oldroyd has not derived the characteristic relaxation time of that process. We will do this exercise here.

Palierne's model applies for emulsions in which the matrix as well as the dispersed phase might show viscoelastic properties. The assumptions made for the rheology of the interface are similar to those established by Oldroyd. For deformation-independent interfacial properties, Palierne's model has successfully been applied to describe the rheological response of different blend systems [Brahimi *et al.* (1991); Kim *et al.* (1993); Graebling *et al.* (1993); Friedrich *et al.* (1995); Lacroix *et al.* (1996a,b, 1997)]. It was also shown by Friedrich *et al.* (1995) that particle-size distributions can be derived from measured blend data if the interfacial tension is known. A detailed analysis of Palierne's model for the case of complex interfacial stress states does not yet exist.

Riemann's data (1997) indicate the relevance of viscoelastic interfacial properties for the understanding of experimental phenomena in the case of compatibilized blends. Therefore, it is our objective to analyze Palierne's model for relevant interfacial stress states. Starting from the continuous version of Palierne's model, which allows us to include a distribution function $v(R)$ of the particle radius R, numerical simulations are performed to show the applicability of the model. Furthermore, a special version of this continuous model is used to describe our experimental data. By using a volume averaged radius R_V instead of $v(R)$, we analyze the properties of the so-called monomodal Palierne model. We derive the formulas for the form relaxation process and the mentioned additional relaxation process. The theoretical predictions are verified at the example of new experimental results on compatibilized PS/PMMA blends.

II. THEORY

A. Continuous Palierne model with interfacial viscoelasticity

1. The model

Similar to Oldroyd, Palierne assumes that the interfacial stress state is characterized by the following interfacial stress tensor α_{ij}:

$$\alpha_{ij} = \alpha \delta_{ij} + \beta_{ij}, \tag{1}$$

where $i, j = 1,2$ for a two-dimensional interface. $\alpha \delta_{ij}$ is the isotropic interfacial tension with δ_{ij} being the unit tensor, while β_{ij} is the dynamic, nonisotropic part, proportional to the interfacial strain γ_{ij}:

$$\beta_{ij}(\omega) = \tfrac{1}{2}\beta'(\omega)\delta_{ij}\gamma_{kk} + \beta''(\omega)(\gamma_{ij} - \tfrac{1}{2}\delta_{ij}\gamma_{kk}). \tag{2}$$

$\beta_{ij}(\omega)$ consists of a complex interfacial dilatation modulus $\beta'(\omega)$, which is conjugate to the relative area variation, and a complex interfacial shear modulus $\beta''(\omega)$, which is conjugate to shear without change of area.

Under these assumptions, Palierne's model for the complex shear modulus $G_b^*(\omega)$ of the blend reads as

$$G_b^*(\omega) = G_m^*(\omega) \frac{1 + 3\displaystyle\int_0^\infty \frac{E(\omega,R)}{D(\omega,R)}\nu(R)dR}{1 - 2\displaystyle\int_0^\infty \frac{E(\omega,R)}{D(\omega,R)}\nu(R)dR}, \tag{3}$$

with

$$E(\omega,R) = [G_d^*(\omega) - G_m^*(\omega)][19G_d^*(\omega) + 16G_m^*(\omega)] + 4\frac{\alpha}{R}[5G_d^*(\omega) + 2G_m^*(\omega)]$$

$$+ \frac{\beta'(\omega)}{R}[23G_d^*(\omega) - 16G_m^*(\omega)] + \frac{2\beta''(\omega)}{R}[13G_d^*(\omega) + 8G_m^*(\omega)]$$

$$+ 24\beta'\frac{\alpha}{R^2} + 16\beta''\frac{\alpha + \beta'(\omega)}{R^2}, \tag{3a}$$

and

$$D(\omega,R) = [2G_d^*(\omega) + 3G_m^*(\omega)][19G_d^*(\omega) + 16G_m^*(\omega)] + \frac{40\alpha}{R}[G_d^*(\omega) + G_m^*(\omega)]$$

$$+ \frac{2\beta'(\omega)}{R}[23G_d^*(\omega) + 32G_m^*(\omega)] + \frac{4\beta''(\omega)}{R}[13G_d^*(\omega) + 12G_m^*(\omega)]$$

$$+ 48\beta'(\omega)\frac{\alpha}{R^2} + 32\beta''(\omega)\frac{\alpha + \beta'(\omega)}{R^2}. \tag{3b}$$

E and D are functions, which contain all model parameters and material functions, including the one for of the interface. $G_m^*(\omega)$ and $G_d^*(\omega)$ are the complex shear moduli of the matrix and the dispersed phase, respectively. Compared to the original Palierne model [Palierne (1990, 1991)], Eq. (3) contains an integral over the volume-weighted

sphere-size distribution $v(R)$ instead of a sum. We will call this variant of the Palierne model the ''continuous'' model since it allows us to consider a continuous distribution in size of the dispersed droplets.

The properties of the interface in Palierne's model are characterized by the material parameter α and the material functions $\beta'(\omega)$ and $\beta''(\omega)$. A first inspection of Eq. (3) shows that β' and β'' enter into terms having the same structure. Therefore, it seems that the role of these parameters can be exchanged (see Fig. 2 later on) and that the parameter ambiguity is a consequence if this model is used for parameter determination. This is the reason why we analyze the model for the condition $\beta'(\omega) = 0$ or $\beta''(\omega) = 0$, which for the functions E and D amounts to

$$E(\omega,R) = [G_d^*(\omega) - G_m^*(\omega)][19G_d^*(\omega) + 16G_m^*(\omega)]$$

$$+ 4\frac{\alpha}{R}[5G_d^*(\omega) + 2G_m^*(\omega)] + E_{1(2)},$$

$$E_1 = \frac{\beta'(\omega)}{R}\left[24\frac{\alpha}{R} + 23G_d^*(\omega) - 16G_m^*(\omega)\right], \quad \text{for } \beta'' = 0, \tag{4}$$

with

$$E_2 = \frac{2\beta''(\omega)}{R}\left[8\frac{\alpha}{R} + 13G_d^*(\omega) + 8G_m^*(\omega)\right], \quad \text{for } \beta' = 0, \quad \text{and}$$

$$D(\omega,R) = [2G_d^*(\omega) + 3G_m^*(\omega)][19G_d^*(\omega) + 16G_m^*(\omega)]$$

$$+ 40\frac{\alpha}{R}[G_d^*(\omega) + G_m^*(\omega)] + D_{1(2)},$$

$$D_1 = \frac{2\beta'(\omega)}{R}\left[24\frac{\alpha}{R} + 23G_d^*(\omega) + 32G_m^*(\omega)\right], \quad \text{for } \beta'' = 0,$$

with

$$D_2 = \frac{4\beta''(\omega)}{R}\left[8\frac{\alpha}{R} + 13G_d^*(\omega) + 12G_m^*(\omega)\right], \quad \text{for } \beta' = 0.$$

Later on, we will show that our measurements can be described well by an even more reduced model. Moreover, the analysis of the reduced model ($\beta' = 0$ or $\beta'' = 0$), following in the next paragraph, shows that the relationship between the data and the parameters is not unique without the use of additional simplifying assumptions. This is the reason why our analysis is based on a simple ansatz for $\beta'(\omega)$ or $\beta''(\omega)$. A single Maxwell mode with interfacial modulus β_{10} or β_{20} and interfacial relaxation times λ_{if1} or λ_{if2} is used:

$$\beta'^{(\prime\prime)}(\omega) = \beta_{10(20)}\frac{i\omega\lambda_{if1(2)}}{1 + i\omega\lambda_{if1(2)}}. \tag{5}$$

The introduced relaxation time governs the balance of interfacial viscosity and interfacial elasticity. λ_{if1} or λ_{if2} are not identical to the time λ_β found by Riemann *et al.* (1996 and 1997). We will see later that the experimentally found relaxation time λ_β is a consequence of a solely elastic interface (λ_{if1} or λ_{if2} is infinite).

The resulting version of the Palierne model is given by Eq. (3) with Eqs. (4) and (5). The distribution function $v(R)$, the material functions $G_m^*(\omega)$, and $G_d^*(\omega)$, and the interfacial parameters α, $\beta_{10(20)}$, and $\lambda_{\mathrm{if1(2)}}$ have to further be specified for our simulation demands.

2. Test of uniqueness

Now it is our aim to test whether the relationship between the data $G_b^*(\omega)$ on one hand, and the parameters of the model and the distribution function $v(R)$ on the other are unique or not. For that purpose, in a preliminary step we create data for $G_b^*(\omega)$ using with the model presented by Eqs. (3), (4), and (5) for a given set of parameters (here, we chose α, β_{20}, and λ_{if2}, the results will be similar for the other set of parameters: α, β_{10}, and λ_{if1}), and for a given Gaussian distribution function $v(R)$, which is chosen for reasons of convenience. The conclusions drawn do not depend on the individually particularly chosen function. For the rheological properties of the phases we assume single relaxation time Maxwell models [Eq. (6)]. This assumption represents no serious simplification because the effects to be discussed are associated with the terminal rheological properties of participating phases:

$$G_m^*(\omega) = \frac{i\omega\eta_m}{1+i\omega\lambda_m}, \quad G_d^*(\omega) = \frac{i\omega\eta_d}{1+i\omega\lambda_d}. \tag{6}$$

In order to test the uniqueness, the parameters α, β_{20}, and λ_{if2} are assumed to be unknown and are estimated from the simulated, noisy data. If the model presented above is unique, the parameters used for the generation of rheological data for the blend system must result from the estimation. The values used and recalculated for the interfacial parameters agree fairly well if the particle-size distribution function is given. The calculations have been performed similarly as described by Friedrich *et al.* (1995). Therefore, we conclude that the relationship between the data $G_b^*(\omega)$ and the parameters is unique and we are not able to determine the particle-size distribution function by this technique as presented for uncompatibilized blends by Friedrich *et al.* (1995).

Anyway, values for the interfacial parameters may be obtained by fitting the parameters of the model [Eqs. (3), (4), and (5)] to the experimental data $G_b^*(\omega)$ if $v(R)$, $G_m^*(\omega)$, and $G_d^*(\omega)$ are given, e.g., by transmission electronic microscopy (TEM) for $v(R)$. Alternatively, the volume average radius R_v can be included in the model instead of using the whole sphere-size distribution $v(R)$ leading to an equation for $G_b^*(\omega)$ which can be treated by analytical methods.

B. Monomodal Palierne model with interfacial elasticity

According to Graebling *et al.* (1993), the sphere-size distribution $v(R)$ in Eq. (3) can be replaced by a volume-averaged Radius R_v in the case of the Palierne model with $\beta'(\omega) = \beta''(\omega) = 0$ if the polydispersity parameter R_v/R_n (R_n: number averaged radius) is below 2.3. We assume that this replacement is also justified for the model with more complex interfacial properties. Therefore, a volume-averaged sphere radius R_v is used in the following instead of $v(R)$. This leads to a model which we call the monomodal Palierne model.

Our experiments (see Table II) as well as the data of Riemann *et al.* (1997) indicate the existence of an additional relaxation time, and no or only a very slight increase in the viscosity of the blends during compatibilization. Such a scenario is in accordance with Oldroyd's analysis of a blend with a purely elastic interface, and, therefore, we make use
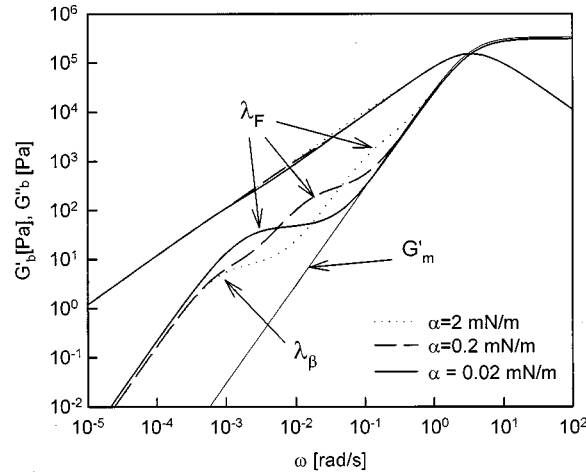
FIG. 1. Influence of the interfacial tension α on the storage modulus $G'_b(\omega)$ and the loss modulus $G''_b(\omega)$ of the blend for the parameters $\beta_{20} = 0.01$ mN/m, $R_v = 0.1\ \mu$m, $\eta_m = 10^5$ Pa s, $\eta_d = 10^4$ Pa s, $\phi = 0.075$, $\lambda_m = 0.3$ s, and $\lambda_d = 0.1$ s.

of this assumption, too. If in Eq. (5) $\lambda_{\text{if1(2)}}$ tends to infinity, the interfacial shear modulus $\beta''(\omega)$ becomes constant $[\beta'(\omega) = \beta_{10}$ or $\beta''(\omega) = \beta_{20}]$. Thus, the complex shear modulus $G^*_b(\omega)$ of the blend is obtained from the corresponding versions of Eq. (4). By simulation we would like to explore in more detail the properties of this model.

1. Simulation for viscoelastic phases

In this paragraph we show which influence the different parameters have on the storage and loss moduli of the blends. For this purpose, we use once more Eq. (6), together with the already presented values of the parameters for blend components. In addition, we assume $R_v = 0.1\ \mu$m and $\beta_{20} = 0.1$ mN/m. The concentration in all cases is $\phi = 0.075$.

The influence of the interfacial tension α on the storage modulus $G'_b(\omega)$ and the loss modulus $G''_b(\omega)$ of the blend is shown in Fig. 1, in which the position of the corresponding relaxation processes is given by the arrows. The influence of the processes associated with the interface on the blend properties can be acknowledged by comparing the storage modulus of the blend with the one of the matrix. Here, and in the following figures, the curve for G''_m is omitted for the sake of clarity of the presentation. The most striking feature of the G' curve is the appearance of an additional relaxational process characterized by λ_β without introducing an additional time constant. For decreasing values of the interfacial tension α the plateau value corresponding to the form relaxation process decreases and its relaxation time λ_F increases. The process associated with λ_β remains nearly unchanged. However, if the values of α and β_{20} are of the same order of magnitude, the shoulder of the form relaxation process covers the longest relaxation process and λ_β is not detectable anymore (see the curve for $\alpha = 0.02$ mN/m). The limiting ratio of α/β_{20} to observe λ_β is about 10. Thus, for higher values of this ratio, the two relaxation processes are well separated.

In Fig. 2 the influence of the interfacial shear modulus β_{10} or β_{20} on the storage modulus $G'_b(\omega)$ and the loss modulus $G''_b(\omega)$ of the blend is shown. The variation of β_{10}
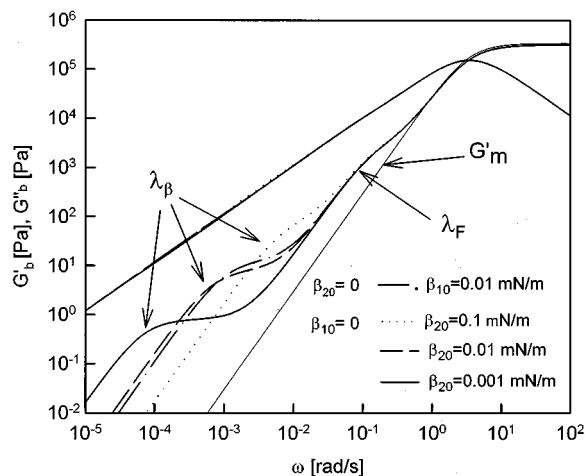
FIG. 2. Influence of the interfacial shear modulus β_{10} or β_{20} on the storage modulus $G'_b(\omega)$ and the loss modulus $G''_b(\omega)$ of the blend for the parameters $\alpha = 2$ mN/m, $R_V = 0.1~\mu$m, $\eta_m = 10^5$ Pa s, $\eta_d = 10^4$ Pa s, $\phi = 0.075$, $\lambda_m = 0.3$ s, and $\lambda_d = 0.1$ s.

or β_{20} mainly influences the interfacial relaxation process, while the form relaxation process remains nearly unchanged. However, if the value of β_{20} is of the order of the value of α, the interfacial relaxation process is covered by the form relaxation process again. Figure 2 shows that for decreasing values of β_{20}, the interfacial relaxation time λ_β is shifted to longer times and the corresponding plateau value decreases. Figure 2 also shows (compare the dash-dotted line with the dash-short-dashed line) that the use of the interfacial dilatational modulus instead of the interfacial shear modulus (or vice versa) only leads to small quantitative differences in blend responses.

For increasing radii R_V from 0.1 to 10 μm both relaxation times become longer, while the values of the corresponding plateaus decrease. The results are not presented here. The simulated curves overlay in such a way that the appearance of a power-law behavior for a very broad particle-size distribution can be anticipated. In this case, no individual relaxation process associated with a certain particle size can be recognized, and it cannot be distinguished between both processes. It seems that a narrow sphere-size distribution with a mean around several hundred nanometers is a necessary prerequisite to find the different relaxation processes well separated.

These results reveal that the two relaxation processes strongly depend on the parameters characterizing the rheology of the interface and of the blend components. Experimentally, these processes can best be detected for a polymer blend with high interfacial tension, with $K \ll 1$, and for R_V values in the submicron range with high uniformity. Our model polymer blend meets all these requirements and, therefore, is suitable for an analysis of the interfacial rheological properties.

2. Derivation of formulas for λ_F and λ_β

Now, formulas for the two relaxation times λ_F and λ_β will be presented, which describe the dependence on several parameters in a more quantitative way. A further simplification must be introduced because an exact analytical solution of the corresponding equations with respect to λ_F and λ_β is only possible if both phases behave like Newtonian liquids: $G_m^*(\omega) = i\omega\eta_m$ and $G_d^*(\omega) = i\omega\eta_d$. This assumption is justified

because the relaxation times of interest appear at frequencies for which the stresses in both phases are already relaxed ($\lambda_m, \lambda_d \ll \lambda_F, \lambda_\beta$).

In order to quantify the two relaxation times λ_F and λ_β, the monomodal Palierne model is rewritten for the case of viscous components as follows:

$$G_b^*(\omega) = i\omega\eta \frac{(i\omega)^2 + i\omega/\lambda_{21} + 1/(\lambda_{21}\lambda_{22})}{(i\omega)^2 + i\omega/\lambda_{11} + 1/(\lambda_{11}\lambda_{12})}, \tag{7}$$

with the four auxiliary times

$$\lambda_{11} = \frac{R_\nu \eta_m}{4\alpha} \frac{(19K+16)[2K+3-2\phi(K-1)]}{10(K+1) + \dfrac{\beta_{20}}{\alpha}(13K+12) - 2\phi\left((5K+2) + \dfrac{\beta_{20}}{2\alpha}(13K+8)\right)}, \tag{8}$$

$$\lambda_{12} = \frac{R_\nu \eta_m}{8\beta_{20}} \frac{10(K+1) + \dfrac{\beta_{20}}{\alpha}(13K+12) - 2\phi\left((5K+2) + \dfrac{\beta_{20}}{2\alpha}(13K+8)\right)}{(1-\phi)}, \tag{9}$$

$$\lambda_{21} = \frac{R_\nu \eta_m}{4\alpha} \frac{(19K+16)[2K+3+3\phi(K-1)]}{10(K+1) + \dfrac{\beta_{20}}{\alpha}(13K+12) + 3\phi\left((5K+2) + \dfrac{\beta_{20}}{2\alpha}(13K+8)\right)}, \tag{10}$$

$$\lambda_{22} = \frac{R_\nu \eta_m}{8\beta_{20}} \frac{10(K+1) + \dfrac{\beta_{20}}{\alpha}(13K+12) + 3\phi\left((5K+2) + \dfrac{\beta_{20}}{2\alpha}(13K+8)\right)}{(1-\frac{3}{2}\phi)}, \tag{11}$$

and

$$\eta = \eta_m \frac{[2K+3+3\phi(K-1)]}{[2K+3-2\phi(K-1)]}. \tag{12}$$

Equations (8)–(11) correspond to the case $\beta_{10} = 0$. If β_{10} is considered instead of β_{20} the following changes occur: the term $(13K+12)$ is replaced by $0.5(23K+32)$, the term $(13K+8)$ by $0.5(23K-16)$, and the 8 in the denominator of Eqs. (9) and (11) by 12.

The four equations for the times λ_{11}, λ_{12}, λ_{21}, and λ_{22} do not define the characteristic relaxation times of the monomodal model. Because the relaxation or retardation times are the poles of the complex modulus [Tschoegl (1989)], Eq. (7) must be rewritten:

$$G_b^*(\omega) = i\omega\eta \frac{\left(i\omega + \dfrac{1}{\lambda_{F2}}\right)\left(i\omega + \dfrac{1}{\lambda_{\beta2}}\right)}{\left(i\omega + \dfrac{1}{\lambda_F}\right)\left(i\omega + \dfrac{1}{\lambda_\beta}\right)}. \tag{13}$$

Now λ_{F2} and $\lambda_{\beta2}$ are the characteristic retardation times, and λ_F and λ_β the characteristic relaxation times. The latter are related to the times λ_{11} and λ_{12} as

$$\lambda_F = \frac{\lambda_{12}}{2}\left[1 - \left(1 - 4\frac{\lambda_{11}}{\lambda_{12}}\right)^{0.5}\right], \tag{14}$$

TABLE I. Characterization of blend components and block copolymer.

Material	M_w (kg/mol)[a]	M_w/M_n[a]	c_{MMA} (wt %)[b]	η (10^4 Pa s)	λ (s)
PS	149	1.03	$\cdots$	0.86	0.2
PMMA	41	1.19	$\cdots$	7.05	0.1
P(S-b-MMA)	55	1.11	0.52	$\cdots$	$\cdots$

[a]Size Exclusion chromatography, PS standard.
[b]Weight fraction in the block copolymer of PMMA, determined from ^{1}H NMR.

$$\lambda_\beta = \frac{\lambda_{12}}{2}\left[1+\left(1-4\frac{\lambda_{11}}{\lambda_{12}}\right)^{0.5}\right]. \tag{15}$$

Both relaxation times λ_F and λ_β depend on the interfacial tension α and the interfacial modulus β_{10} or β_{20}. However, for the limiting case $\beta_{10} = 0$ and $\beta_{20} = 0$, the form relaxation time λ_F coincides with the form relaxation time for the Palierne model with isotropic interfacial tension [Graebling *et al.* (1993)] and λ_β becomes infinite:

$$\lambda_F = \frac{R\eta_m}{4\alpha}\frac{(19K+16)[2K+3-2\phi(K-1)]}{10(K+1)-2\phi(5K+2)} \quad \text{and} \quad \lambda_\beta \to \infty. \tag{16}$$

The zero-shear viscosity of the blend η_b of the complete model, taking into consideration β_{10} or β_{20}, is obtained from Eq. (7) for vanishing frequencies ω:

$$\eta_b = \lim_{\omega \to 0}\frac{G_b^*(\omega)}{i\omega} = \eta_m\frac{\lambda_{11}\lambda_{12}}{\lambda_{21}\lambda_{22}} = \eta_m\frac{1+\frac{3}{2}\phi}{1-\phi}. \tag{17}$$

η_b is independent of interfacial properties and also independent of the viscosity ratio K, depending only on the amount of dispersed phase. This result was first obtained by Oldroyd (1955) and indicates that in the low-frequency zone the droplets behave like solid spheres if their interface is characterized by α and β_{10} or β_{20}. From the viewpoint of continuum mechanics, the compatibilization leads to an entirely elastic interface. Observations made by Riemann *et al.* (1997) and by Milner and Xi (1996) support such a position and the latter authors give some hints how this result can be understood from the molecular point of view. With Eqs. (8), (9), (14), and (15), values for the interfacial tension α and interfacial shear modulus β_{10} or β_{20} can be obtained from rheological measurements. Recently, we have published values for the interfacial tension α and interfacial shear modulus β_{20} [Riemann *et al.* (1997)] by using these equations. For this purpose, the relaxation times λ_F and λ_β have been received from relaxation time spectra and R_V has been obtained from TEM data.

III. RESULTS AND DISCUSSION

Here, we would like to discuss experimental data on compatibilized PS/PMMA blends recently obtained in our laboratory. These experiments have been done in extension of Riemann's work, in order to test the emulsification ability of symmetric block copolymers but of different molecular weights. The preparation of the blends as well as the realization of experiments on the determination of rheological and morphological properties are the same as described by Riemann *et al.* (1997). Some data on the used blend components and the block copolymer used are summarized in Table I. The blends consist of 7.5 wt %PS and 92.5 wt % PMMA compatibilized with up to 2.0 wt % block copolymer. We assume that the block copolymers are distributed even among the particles due
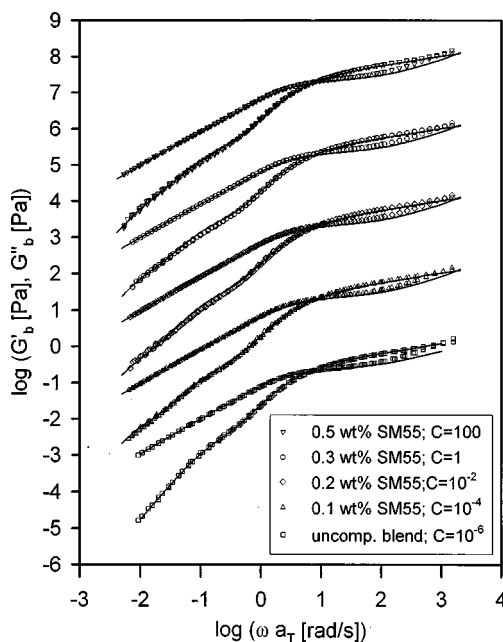
FIG. 3. Master curves (symbols) of the storage modulus $G'_b(\omega)$ and loss modulus $G''_b(\omega)$ vs frequency ωa_T for the blend series plotted together with the fits (solid lines) for the continuous Palierne model. The curves are shifted vertically by the factor C to avoid overlap.

to thermodynamical reasons [see also Riemann *et al.* (1997)]. Here, we will only discuss such blends which show the interfacial relaxation process. While the block copolymers used by Riemann show this effect up to 2 wt %, the (shorter) block copolymer used here can rheologically be seen only up to 0.5 wt %. Therefore, we analyze only these results.

The master curves ($T_{\text{ref}} = 190\,°C$) of storage modulus $G'_b(\omega)$ and the loss modulus $G''_b(\omega)$ of the blend series under consideration versus the reduced frequency $a_T\omega$ are shown in Fig. 3 (symbols). Some aspects pointing to the validity of the time–temperature superposition principle for our systems are presented in the appendix.

The zero-shear viscosities η_b of the blends have been determined from the Cole–Cole plots of the components of the complex viscosity and are listed in Table II. It is found that the values are almost independent of the amount of the block copolymers added, even if the values appear to be too high for the theory. This is similar to the findings of Riemann *et al.* (1997) for the same blend system but different compatibilizer.

TABLE II. Some parameters of the investigated blend series.

	w_{bc} (wt %)	R_V (nm)	R_V/R_n	$\lambda_{F,\text{calc}}$ (S)[a]	λ_F (S)[b]	λ_β (S)[b]	η_b (10^4 Pa s)[c]
sm00	0	110	1.14	4.98	5.01	$\cdots$	7.01
sm01	0.1	107.3	1.05	8.14	7.94	100	9.14
sm02	0.2	91	1.03	8.23	7.94	79.4	8.94
sm03	0.3	85.3	1.03	8.35	7.94	63.1	9.34
sm05	0.5	78.1	1.11	8.53	6.31	50.1	9.48

[a]Determined by using Eq. (16) for the conventional Palierne model.
[b]Determined from relaxation time spectra.
[c]Obtained from Cole–Cole plots.

TABLE III. Values for the interfacial parameters α and β_{10} for the blend series.

	α (mN/m)[a]	β_{10} (mN/m)[a]	α (mN/m)[b]	β_{10} (mN/m)[b]	α (mN/m)[c]	β_{10} (mN/m)[c]
sm00	2.18	$\cdots$	2.06	$\cdots$	2.29	$\cdots$
sm01	2.75	0.07	2.2	0.1	2.18	0.12
sm02	3.01	0.1	3.07	0.18	2.06	0.14
sm03	2	0.11	2.3	0.14	2.19	0.19
sm05	1.9	0.1	2.06	0.17	2.26	0.2

[a]Determined from the fits to the continuous model.
[b]Determined from the fits to the monomodal model.
[c]Determined by using Eqs. (14) and (15).

For the blend series, three characteristic relaxation times have been found, which are easier to detect if the corresponding relaxation time spectra are calculated [see, e.g., Riemann *et al.* (1997)]. The relaxation process appearing at the highest frequencies (not shown in the tables) is associated with the relaxation within both phases and, consequently, that time is comparable to the terminal relaxation time of the matrix λ_m. The values of the relaxation times of the two longest processes are λ_F and λ_β and are given in Table II.

λ_F is the form relaxation time of the dispersed droplets as can be seen from Table II, in which the experimental values are compared with the values calculated with the conventional Palierne model [Graebling *et al.* (1993)], which is based on the isotropic, deformation-independent interfacial tension only. The calculations are performed with a value for the interfacial tension which corresponds to the uncompatibilized case ($\alpha = 2.0 \, \text{mN/m}$). Experimental and calculated values are in good agreement. For the blend series, the λ_F values show the expected slight decrease with increasing block copolymer content due to decreasing particle dimensions. λ_β is the relaxation time which was associated with interfacial properties as stated by Riemann *et al.* (1997). The relaxation time λ_β decreases at an increasing amount of block copolymer. The physical origin of this time will not be discussed here, but Milner and Xi (1996) gave a first explanation of the rheological consequences caused by the presence of these molecules at the interface and our further work on the compatibilization with block copolymers of different molecular weights points in this direction.

The parameters of the continuous Palierne model [Eqs. (3) and (4)] with interfacial viscoelasticity (shear or dilatational) have been determined by fitting the model to the measured rheological data of our blend series under the assumption that $v(R)$ and G^* of both components are given. The free parameters to be evaluated during the fitting procedure are the interfacial tension α, the interfacial shear modulus β_{10} or β_{20} and the relaxation time λ_{if1} or λ_{if2}. The values for α and $\beta_{10}(\beta_{20})$ are listed in Tables III and IV for the blend series.

In Fig. 3, the model data (solid lines) for the blends are shown along with the measured data (symbols). The Palierne model quantitatively describes the experiments in the investigated frequency range very well. The relaxation time λ_{if1} or λ_{if2} tends to infinity, which indicates that the interface of the blends behaves mainly elastic. This is a proof that the relaxation process of the interface which we assigned as the relaxation time λ_β is not identical with that time λ_{if1} or λ_{if2}, which governs the viscoelasticity of the interface. On the basis of the fit results we are not able to distinguish between shear or dilatational elasticity of the interface.

The interfacial tension α shows a certain degree of dispersion around a constant value. This result is not surprising because for the higher molecular weight block copolymers a

TABLE IV. Values for the interfacial parameters α and β_{20} for the blend series.

	α (mN/m)[a]	β_{20} (mN/m)[a]	α (mN/m)[b]	β_{20} (mN/m)[b]	α (mN/m)[c]	β_{20} (mN/m)[c]
sm00	2.18	⋯	2.16	0	2.29	⋯
sm01	2.68	0.16	2.48	0.14	2.12	0.18
sm02	2.39	0.07	2.57	0.2	1.99	0.22
sm03	2	0.15	2.3	0.16	2.09	0.3
sm05	1.9	0.18	2	0.18	2.16	0.31

[a]Determined from the fits to the continuous model.
[b]Determined from the fits to the monomodal model.
[c]Determined by using Eqs. (14) and (15).

small decrease in α has been observed only over a larger concentration range [see Riemann *et al.* (1997)]. The values of the interfacial shear modulus β_{20} rise with increasing amounts of block copolymers. The value of the interfacial shear modulus β_{20} is smaller than the interfacial tension α (by almost one decade) for all blends.

We have also determined the parameter $(\alpha, \beta_{10(20)}, \lambda_{if1(2)})$ using the monomodal version of the Palierne model. The parameters are presented in Tables III and IV. We have found a good agreement between both types of models and the experimental data.

The analytical formulas [Eqs. (14) and (15)] allow a simple calculation of α and β_{20}. The results for both interfacial parameters are also listed in Table III for β_{10} and in Table IV for β_{20}. We have already shown [Riemann *et al.* (1997)] that for compatibilized blends it is possible to obtain values for the interfacial tension α and the interfacial shear modulus β_{20} from measured blend data with these equations.

The statistical analysis of all values of interfacial tension determined by the different methods reveals no significant differences. Strikingly, the values of β_{10} and β_{20}, for the monomodal model are always higher than those determined from the continuous one. However, the values the two different methods provided are of the same magnitude and show a similar course with respect to the amount of block copolymer.

Since α, when obtained from Eqs. (14) and (15), is sometimes higher than the value for the neat PS/PMMA blend, we believe that the values from the continuous model are more reasonable. The consideration of only one characteristic size of the domains or one characteristic time from the relaxation time spectra for the form relaxation time and the interfacial relaxation time seems to be too restrictive. At the moment, we cannot decide which of these factors, size or temporal factors, is more important. Nevertheless, the consideration of the whole relaxation as well as the whole domain-size spectra represents the more accurate description of the systems under investigation. Having this in mind, the fit of the continuous model to the experimental data, which are a representation of the relaxation time spectrum, is the superior method.

IV. CONCLUSIONS

Palierne's emulsion model represents the only rheological constitutive equation which is suitable for the description of the viscoelastic behavior of polymer blends containing polymeric interfacial agents. For that purpose, the model has to be specified with respect to the rheological properties of the interface, which build up between the two phases of the blends. We formulate the Palierne model in different degrees of complexity corresponding to particle size (distribution function versus monomodale particles in size) and to (nonisotropic) interfacial properties. Concerning the latter case, we assume that besides the isotropic interfacial tension a Maxwell mode either of the interfacial dilatation modu-
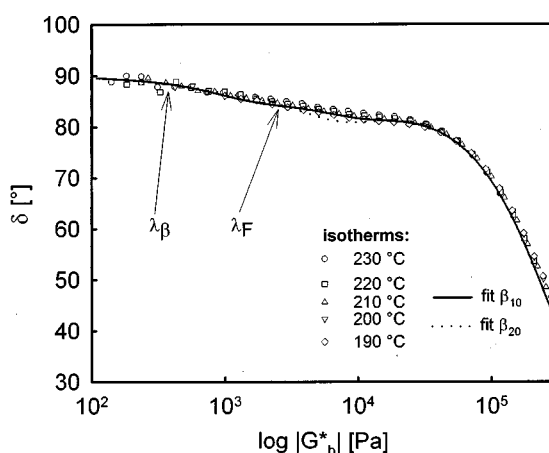
FIG. 4. Presentation of phase angle $\delta(= \arctan(G''/G'))$ vs the modulus of the complex modulus of the blend $|G_b^*| (= (G_b'^2 + G_b''^2)^{1/2})$. The symbols correspond to experimental data of five isotherms and the two lines are the corresponding fits taken from Fig. 3. The arrows indicate the position of the form and interfacial relaxation processes.

lus or of the interfacial shear modulus has to be considered. The adjustment of the models for our experimental data on compatibilized PS/PMMA blends reveal that the compatibilized interface is of almost elastic nature. The determined values for the interfacial tension and the interfacial shear or dilatational modulus are in reasonable ranges. Our data do not allow us to distinguish between shear or dilatational elasticity. This is a consequence of the structure of how these parameters are imbedded in the model.

We conclude that the consideration of a nonisotropic interfacial stress state in the Palierne model, which envolves from the consideration of deformation-dependent interfacial shear or dilatational elasticity, is necessary for the description of all experimentally found relaxation transitions in our compatibilized PS/PMMA blends. The results obtained give rise to hope that rheology will become a tool for the investigation of interfacial rheological properties for compatibilized blends.

ACKNOWLEDGMENT

APPENDIX: VALIDATION OF THE TIME–TEMPERATURE SUPERPOSITION (TTS) PRINCIPLE FOR COMPATIBILIZED PS/PMMA BLENDS

Here, we check whether the time–temperature superposition (TTS) is fulfilled or not for our polymer blends. Usually, it is assumed that polymer blends do not obey the TTS due to the differences in the thermorheological properties of the components and the differences in the temperature dependence of bulk and interfacial properties. Following van Gurp (1998), we check this superposition principle for our blends by analyzing the blend isotherms in the coordinates $\delta(= \arctan G'/G'')$ vs $|G^*| (= (G''^2 + G''^2)^{1/2})$. The result is given in Fig. 4 for the isotherms between 190 and 230 °C (see the different symbols) for the PS/PMMA blend containing 0.5 wt % block copolymer. The resulting curve is of the same accuracy as those for which van Gurp stated the validation of this principle. The same plots can be drawn for the blends presented by Riemann *et al.*

(1997). This is not unexpected because we have analyzed the thermorheological properties of our blends qualitatively in an earlier paper [Friedrich *et al.* (1995)] and have found that the TTS holds due to similar c_1 and c_2 values for both blend components and a corresponding temperature dependence of the interfacial tension. In this case, additionally, the temperature dependence of the interfacial moduli is such that the TTS is not violated. Furthermore, we have checked the morphology before and after the rheological measurements and have obtained the same radii. This is proof of sufficient thermal stability of the morphology, at least at the time of our experiments.

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