Interfacial Relaxation in Polymer Blends and Gibbs Elasticity

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ABSTRACT: We have investigated the influence of different amounts of symmetric block copolymers such as poly(styrene-*b*-methyl methacrylate) on the form and interfacial relaxation times of a polymer blend containing mainly 7.5% polystyrene as a dispersed phase in a poly(methyl methacrylate) matrix. Special emphasis was put on the investigation of the effect of the compatibilizer molecular weight on these times. For this purpose, we combined predictions of the extended Palierne model with assumptions on the changes of interfacial tension with the amount of compatibilizer. It turned out that the identification of the interfacial modulus in Palierne's model with the Gibbs elasticity modulus as the intrinsic property of a surfactant-laden interface, responsible for the reconstitution of an equilibrium surfactant distribution, is the key point for a quantitative understanding of the ongoing processes and the interfacial relaxation time scaling. On the basis of the assumption that Gibbs elasticity is the important interfacial parameter, the scaling relation for the interfacial relaxation time was derived. A similar treatment of the form relaxation times leads to a more complex scaling relation that is determined by the same set of parameters.

Introduction

Compatibilizers, either formed in situ by reactive processing or premade as block copolymers (BCPs), are of crucial importance during the formation and stabilization of polymer blends. These polymeric surfactants reduce the interfacial tension, α, between the blend components, and due to their ability to accumulate preferentially in the interface, they stabilize the obtained morphology against coalescence.[1,2] Small amounts of these species in the range of parts of percent are already active.

While the principles of their action in polymer blends are well understood (see, e.g., Milner and Xi,[3] Van Puyvelde et al.,[4] and Lyu et al.[5]), interfacial dynamics influenced by various amounts of compatibilizer have been little investigated. In a polystyrene (PS)/poly(methyl methacrylate) (PMMA) blend compatibilized with the corresponding symmetric BCP, Riemann et al.[6] discovered a relaxation process at frequencies lower than the inverse form relaxation time, which could be entirely attributed to the action of the used BCP at the interface. They found that, with increasing concentration of BCP, the relaxation time associated with this process, τ_β, decreased. The changes in the interfacial relaxation time with the changes in the morphological, rheological and compositional properties of this blend system could be analyzed quantitatively on the basis of the Palierne model.[7,8] Using an extended version of the Palierne model that, besides the interfacial tension, takes into account the interfacial elasticity in form of an interfacial dilatational modulus, β'', these authors were able to derive a formula connecting all relevant parameters. This formula will be the starting point of our scaling analysis given in the discussion part of this paper.

Later, Jacobs et al.[9] analyzed the extended Palierne model in more detail. Starting from an interfacial constitutive equation that takes into account the interfacial viscoelasticity (e.g., the interfacial Maxwell model), they found that changes in the interfacial elasticity due to the presence of different amounts of surface-active species are the only cause of the observed phenomena.

Although the phenomenology of the relaxation processes occurring in neat and compatibilized blends is well understood, the physical origin of the interfacial relaxation time and its dependence on the structural parameters of the compatibilizer molecule remain vague. The results of two recent publications by Van Hemelrijck et al.[1,2] have shed some light on this problem. First of all, these authors confirmed the existence of the interface-governed relaxation time and its dependence on the morphological and rheological parameters of polydimethylsiloxane/polyisoprene blends with the corresponding, not necessarily symmetric, BCP. Second, they analyzed the τ_β evolution with the structural parameters of their blends, and in doing so, they were able to sketch the influence of parameters like the surface coverage of BCP, c_0 (their c_0 is identical to the inverse of our Σ, the interfacial area per copolymer molecule), the ratio of the viscosities of the dispersed-to-matrix phases, $p = \eta_d/\eta_m$, and, most importantly, the interfacial tension gradient, $d\alpha/dc$, on the interfacial relaxation time. In particular, the last parameter is known as the physical cause of a variety of effects in compatibilized blends, such as coalescence suppression or drop deformability (see, e.g., Pawar and Stebe,[10] Li and Pozrikidis,[11] Velankar et al.,[12] and Jeon and Macosko[13]). Velankar et al.[12] as well as Van Hemelrijck et al.[1,2] identified local interfacial stress gradients as the most probable origin of the interfacial relaxation time. As a result, they were able to scale their experimental data obtained for BCPs of different molecular weights, different block symmetries (ratio of the molecular weights of both blocks), and with varying concentrations of dispersed phase and viscosity ratios, on one master curve. According to their analysis, the interfacial relaxation time scales in the following way:

$$\tau_\beta \propto \frac{R_V}{c_0}\,\frac{1}{k_B T}\,\delta^{-2/3}\,\frac{{\eta_m}^2}{\eta d} \tag{1}$$

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Table 1. Characterization of the Blend Components and BCPs

material	M_n[a] (kg/mol)	M_w/M_n[a]	w_{MMA}[b] (wt %)	η_0 at T_{ref} (Pa s)	K
PMMA	31	1.19		7.0×10^4	
PS	100	1.03		8.6×10^3	
SM17	17	1.16	51.3		25.5
SM35	35	1.30	52.5		30.1
SM55	55	1.11	52.6		48.8
SM105	105	1.12	55.2		88.8
SM144	144	1.17	51.9		97.2
SM169	169	1.17	53.8		99.2

[a] GPC, PS standard. [b] Determined by ^{1}H NMR.

In this equation, R_V is the volume-averaged particle radius, δ is the parameter taking into account the asymmetry in block length of the BCP, k_B is the Boltzmann constant, and T is the temperature. This relation is, to some extent, similar to a definition of a characteristic time responsible for the relaxation of surfactant inhomogeneities by Marangoni stresses, given by Vlahovska et al.[14] These authors define their characteristic time constant in the following way:

$$\tau_{\Delta\alpha} = \frac{\eta_m(1+p)R_V}{\Delta\alpha} \tag{2}$$

Here $\Delta\alpha = \alpha(0) - \alpha(\Gamma)$, $\alpha(0)$ ($=\alpha_0$) is the interfacial tension in the absence of surfactant, and $\alpha(\Gamma)$ is the equilibrium interfacial tension if surfactant is present. Γ is the areal number density of the surfactant, as a measure of its interfacial concentration. Assuming that $\Delta\alpha = k_BT\,\Gamma$ and that $\Gamma \approx R_h^2$, where R_h is the hydrodynamic radius of the surfactant molecule, they derived the following equation:

$$\tau_{\Delta\alpha} = \frac{(\eta_m + \eta_d)R_VR_h^{\,2}}{k_BT} \tag{2_1}$$

In the case of a BCP as surfactant, we would identify R_h with the hydrodynamic radius of a BCP block.

The aim of this paper was 2-fold. First of all, we wanted to provide additional data on the interfacial relaxation times in polymer blends, in order to enlarge the data basis of available interfacial relaxation times. Therefore, we analyzed the viscoelastic properties of PS/PMMA polymer blends compatibilized with symmetric poly(styrene-*b*-methyl methacrylate) (P(S-*b*-MMA)) of different molecular weights, and determined the characteristic times as described by Riemann et al.[6] and Jacobs et al.[9] Second, we verified the dependence of the interfacial relaxation time on the structural parameters of the blend and the BCPs, experimentally and theoretically. To this end, we combined the results of the extended Palierne model with reliable assumptions about the interfacial tension reduction by a compatibilizer. Elucidating the influence of the amount and the structure of a symmetric BCP on τ_β was one of the main objectives of this paper. Additionally, we analyzed the influence of the above-mentioned parameters on the form relaxation time, and we explain why the form relaxation time might increase or decrease in comparison to the neat blend in dependence on the molecular weight of the BCP.

Experimental Section

1. Polymers. The key properties of the polymers used in these experiments, such as molar mass, M_w, polydispersity index, M_w/M_n, weight fraction of the MMA block in the BCP, w_{MMA}, and the K factor are shown in Table 1. PS and PMMA were supplied by BASF (Ludwigshafen, Germany). Symmetric BCPs were prepared by anionic polymerization as described elsewhere.[6] The PS homopolymer and the PS part of the BCPs are atactic.

Symmetric P(S-*b*-MMA) BCPs with molecular weight averages M_{bc} = 17, 35, 55, 105, 144, and 169 kg/mol (hereafter referred to as SM17, SM35, SM55, SM105, SM144, and SM169) were used as compatibilizers in the PS−PMMA blends. The interfacial tension, α_0, between both blend components has been reported to be $(1.8 \pm 0.3) \times 10^{-3}$ N/m at the relevant temperature of 190 °C (see Gramespacher and Meissner[15]) and agrees with data calculated from blend rheology of neat blends (see Friedrich et al.[16]).

2. Blends. Samples were prepared as described by Riemann et al.[6] and Jacobs et al.[9] The blend components and the compatibilizer were dissolved in tetrahydrofuran (10 wt % solution) and then precipitated in methanol. The precipitate was dried in vacuo for at least 2 days at 60 °C. For rheological and morphological studies, the blends were annealed for 30 min at 180 °C in vacuo, and then molded in a vacuum press into 1 mm thick disks, 25 mm in diameter. This procedure guarantees that the fine morphology observed during the solution processing is preserved in the molded samples during the rheological experiments.[9] This fact was verified by comparing the results of the morphological analysis for untreated and treated samples. The blends contained ($92.5 - 0.5\,w_{BC}$) wt % matrix material (PMMA) and ($7.5 - 0.5\,w_{BC}$) wt % dispersed phase (PS), with the weight fraction of the BCP, w_{BC}, between 0 and 2.0%. One blend was made of 12% dispersed phase and the corresponding amount of BCP. The volume fractions of the dispersed phase, ϕ, and of the BCP used, ϕ_{bc}, were calculated on the basis of their corresponding densities, ρ and ρ_{bc}, at 190 °C.

For the morphological measurements, ultrathin (about 60 nm thick) sections from the blends were made on a Leica Ultracut-E microtome. Before imaging, they were stained with RuO_4. From these samples, transmission electron microscopy (TEM) elastic brightfield images were taken on a Zeiss CEM902 (ESI mode). The droplet morphology of the dispersed phase in the matrix was quantitatively analyzed using the image processing system IBAS 2000 (Kontron). The sphere size distribution and from that the number- and volume-averaged sphere radii, R_n and R_V, respectively, were calculated from the section size distributions according to a method developed by Gleinser et al.[17] The ϕ_{bc} dependence of R_V was used to calculate the K parameter given in Table 1. Its physical meaning is related to the BCP's ability to change the particle size with incipient compatibilization: $K = -d\ln(R_V)/d\phi_{bc}|_{\phi_{bc}=0}$. The interfacial area per BCP molecule, Σ, was calculated according to a procedure outlined elsewhere.[6] We assume that all BCP molecules reside at the interface, and there are several reasons to assume that this is true. First, the low viscosity level during solution processing allows the BCPs to easily arrive at the interface. Second, thermodynamic reasoning (see Israels et al.[21]), based on the fact that the chemical potential of a symmetrical BCP molecule in a micelle is always higher than the chemical potential of that molecule in an equilibrium monolayer, leads to the conclusion that in a ternary system the BCP should remain at the interface when the system is thermodynamically equilibrated. Therefore, micellization sets in for the BCPs when used at concentrations exceeding the realized concentrations. We checked this fact experimentally by searching for micellas in the blend compatibilized with 2% SM105, by high-resolution TEM. Knowing the dimensions of micellas from the neat matrix−BCP system, we were able to exclude micellization. Moreover, we calculated the critical concentration for micellization for all BCPs (see text above eq 8_1) and found that micellization is of no importance in our case. What cannot be excluded and what is hard to estimate is the dissolution of some BCP molecules in one or the other blend component. However, the strong tendency of all BCPs to reduce the particle dimensions with increasing BCP concentration (expressed by the K parameter) is, according to the reasoning of Favis and co-workers,[24,25] a strong indication for the BCPs' tendency to segregate to the interface. Although we cannot exclude dissolution, especially for BCPs with the lowest molecular weights (also lowest K values), we consider the calculated Σ values as apparent values.

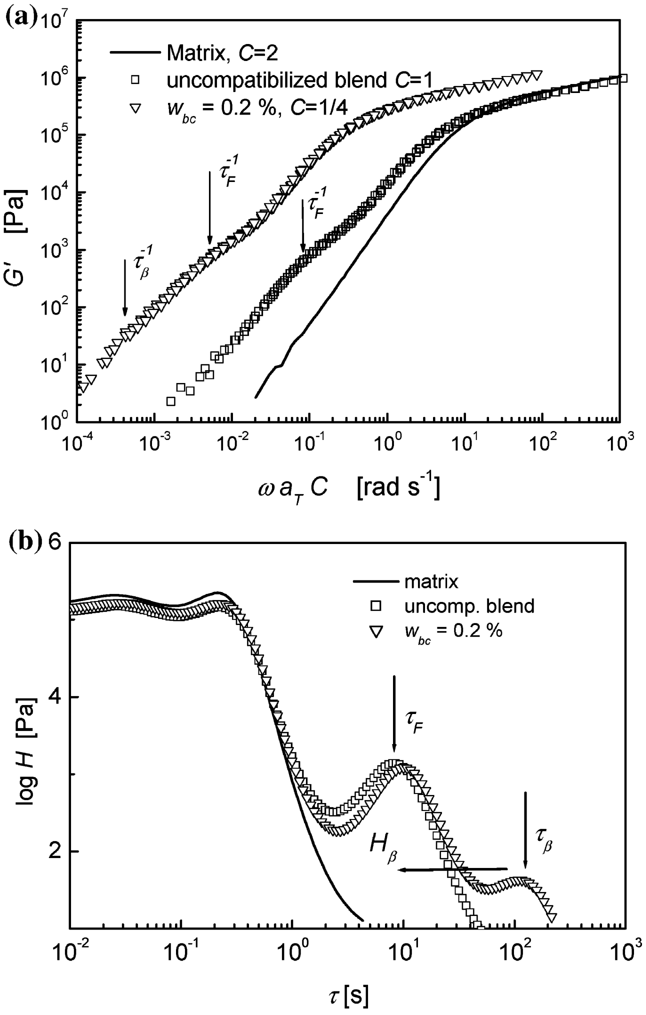

Figure 1. (a) Storage moduli of the matrix, the neat and the compatibilized blend. The curves are shifted by factor C to avoid overlap. (b) Relaxation time spectra $H(\tau)$ of samples presented in Figure 1a.

Knowing the particle dimensions from TEM, Σ can be calculated in the following way: $\Sigma = 3\phi M_{bc}/(\phi_{bc}\rho_{bc}R_V N_A)$. In this equation, ϕ is the volume fraction of the dispersed phase, ϕ_{bc} is the volume fraction of the BCP, ρ_{bc} is the density of the BCP (we assume 1 g/cm^3), and N_A is the Avogadro number.

3. Rheology. The rheological measurements were made on a Rheometrics mechanical spectrometer RMS800 applying a parallel plate geometry with a diameter of 25 mm. Isothermal frequency sweeps at a deformation amplitude of 2% were recorded between 170 and 230 °C, in steps of 10 K. The isotherms were shifted to master curves with a reference temperature $T_{ref} = 190$ °C. The shift factors followed WLF behavior. Details concerning the applicability of the time−temperature superposition principle in the case of compatibilized blends with blend components of similar thermorheological properties are given elsewhere.[9] From the master curves, relaxation time spectra were computed using the program NLREG.

Results and Discussion

1. Form and Interfacial Relaxation Times. Master curves of the storage modulus, G', for a blend composed of 7.5 wt % dispersed phase and compatibilized with 0.2% SM55, together with the curves for the neat blend and the matrix, are shown in Figure 1a. Arrows indicate the positions of characteristic relaxation times as determined from the corresponding relaxation time spectra shown in Figure 1b.

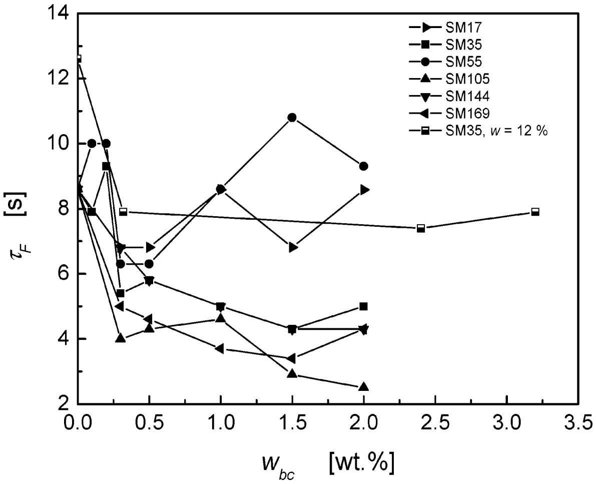

Figure 2. Form relaxation times of all samples under investigation in dependence on the weight fraction of the BCPs. Lines are drawn to guide the eye.

The spectra (see Figure 1b) give quantitative access to characteristic times. It can be clearly seen that in addition to the well-known form relaxation time, τ_F (see, e.g., Graebling et al.[18]), a longer time, τ_β, is present that does not exist in the case of the uncompatibilized blend. Rieman et al.[6] reported for the first time about the existence of such a characteristic time, which is the longest relaxation time in the blend.

Following the same procedure as outlined above, we determined the form and interfacial relaxation times for all blends compatibilized with different BCPs, with the exception of SM17. In the latter case, no additional process to form relaxation was detectable. The collection of all data determined in this way is presented in Figures 2 and 3.

Figure 2 shows the form relaxation time in dependence on the amount of used BCP for different BCP molecular weights. For the discussion of this time, we use the weight fraction of BCP, a concentration measure of the emulsifier, because, in contrast to Σ, only this concentration permits to present the times for the noncompatibilized blend. In the case of the interfacial relaxation time, where the corresponding time does not exist, we compare and discuss the results on the basis of both concentration measures. The data in Figure 2 show that the form relaxation time decreases with compatibilization. While this trend is well developed for the BCPs with the highest molecular weights, shorter BCPs show a large scatter around the value for the neat blend. It is not obvious whether this scatter may even obscure an increase in the form relaxation time for SM17 and SM55. We will discuss this problem later, together with the derived scaling relations. It is worth mentioning that the increase in dispersed phase weight fraction (compare SM35 with SM35 12%) from 7.5 to 12% leads to a significant increase in the form relaxation times, which is in accordance with predictions of the Palierne model.

Figure 3a shows the interfacial relaxation time in dependence on the weight fraction of the added compatibilizer for the different BCPs used. Obviously, with increasing concentration of BCP, the interfacial relaxation time decreases strongly. This behavior was first observed by Riemann et al.[6] and was later confirmed by Jacobs et al.[9] and Van Hemelrijck et al.[1,2] Moreover, the high-molecular-weight BCPs appear to result in longer interfacial relaxation times. However, a clear ordering among the emulsifiers with smaller molecular weights cannot be observed. Taking into account particle size and particle size distribution, the interfacial relaxation times are presented in dependence on the interfacial area per BCP (Figure 3b).

Presentation of the data using Σ as concentration measure, as shown in Figure 3a, does not result in a better separation of the curves and therefore does not help to answer the question concerning the influence of the BCP molecular weight. However, the strong dependence of the interfacial relaxation time on the interfacial area per BCP, $\tau_\beta \propto \Sigma^1$, is confirmed. Moreover, the relaxation strength of this process, H_β (not presented here), decreases in such a way that the product $\tau_\beta H_\beta$ is vanishing with increasing Σ. Later, we will see which combinations of parameters will be responsible for an appropriate τ_β scaling.

A comparison of all data in Figures 2 and 3 reveals that the interfacial relaxation time depends more strongly on the concentration of the surfactant than the form relaxation time. While the form relaxation time changes by only over half a decade in the covered concentration range, the interfacial relaxation time changes by more than one decade.

2. Scaling Relations. Now the question arises as to how the differences between the curves that are due to structural differences between different samples can be scaled. The starting point for the derivation of a scaling relation for both characteristic times, in dependence on all important blend parameters and structural parameters of the compatibilizers, are the equations for these times on the basis of the extended Palierne model, as given by Riemann et al.[6] and Jacobs et al.[9]

$$\tau_\beta = \frac{t_2}{2}\left[1 + \left(1 - 4\frac{t_1}{t_2}\right)^{0,5}\right] \tag{3}$$

and

$$\tau_F = \frac{t_2}{2}\left[1 - \left(1 - 4\frac{t_1}{t_2}\right)^{0,5}\right] \tag{4}$$

with the auxiliary times

$$t_1 = \frac{R_V \eta_m}{4\alpha} \times \frac{(19p + 16)(2p + 3 - 2\phi(p - 1))}{10(p + 1) + \frac{\beta''}{\alpha}(13p + 12) - 2\phi\left[(5p + 2) + \frac{\beta''}{2\alpha}(13p + 8)\right]}$$

and

$$t_2 = \frac{R_V \eta_m}{8\beta''} \times \frac{10(p + 1) + \frac{\beta''}{\alpha}(13p + 12) - 2\phi\left[(5p + 2) + \frac{\beta''}{2\alpha}(13p + 8)\right]}{(1 - \phi)}$$

We will analyze these equations under simplifying assumptions that are valid for the blends under consideration: $\phi \ll 1$, $\beta''/\alpha \ll 1$. These conditions are also valid for the literature data presented by Riemann et al.,[6] Jacobs et al.,[9] and Van Hemelrijck et al.[1,2] Under these conditions, the ratio t_1/t_2 is also much smaller than 1. Using these restrictions, we observe the following modifications of eqs 3 and 4

$$\tau_\beta \approx \frac{\eta_m(1 + p)R_V}{\beta''} \tag{3$_1$}$$

and

$$\tau_F \approx \frac{\eta_m R_V}{\alpha} \times f(p) \tag{4$_1$}$$

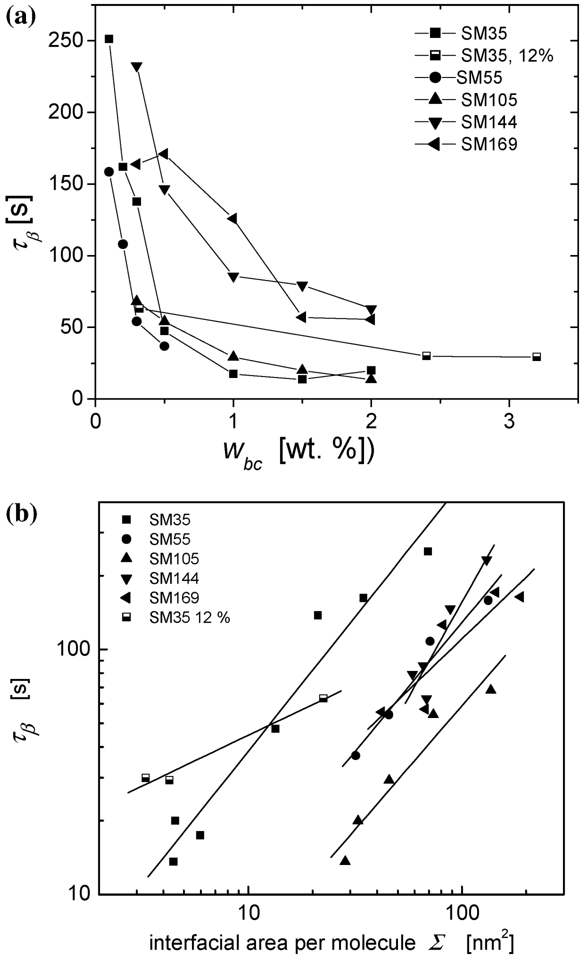

Figure 3. (a) Interfacial relaxation time in dependence on the weight fraction of the BCPs. The lines are added to guide the eye. (b) Double-logarithmic plot of interfacial relaxation time in dependence on the interfacial area occupied by a BCP. The lines are linear fits having, on average, a slope of about 1.

where $f(p)$ is a more complex expression accounting for the weak influence of the viscosity ratio. This function changes from a value close to 1 for small p to 2 for viscosity ratios around 1. As already mentioned, within the Palierne model, α and β'' are entirely phenomenological parameters describing the interfacial rheological stress state. They do not have any relationship to structural parameters, and only by identification of these parameters with models based on structural parameters, the wanted scaling relations can be derived.

Let us assume that at low surfactant concentration, $\rho^{if}/\rho^{if}_{sat} \ll 1$, where the surfactant's surface density, ρ^{if}, is much smaller than its value at saturation, ρ^{if}_{sat}, the interfacial tension in dependence on the amount of compatibilizer can be given in the following way[19]

$$\alpha(\rho^{if}) = \alpha(0) - RT\rho^{if}/M_{bc} \tag{5}$$

with $\alpha(0) = \alpha_0$. This is the simplest possible ansatz describing changes in the interfacial tension with changing amounts of compatibilizer, excluding interactions between these molecules. In terms of interfacial area per surfactant molecule, this equation can be expressed as follows:

$$\alpha(\Sigma) = \alpha_0 - \frac{k_B T}{\Sigma} \tag{5$_1$}$$

The concentrations defined so far correspond to an equilibrium

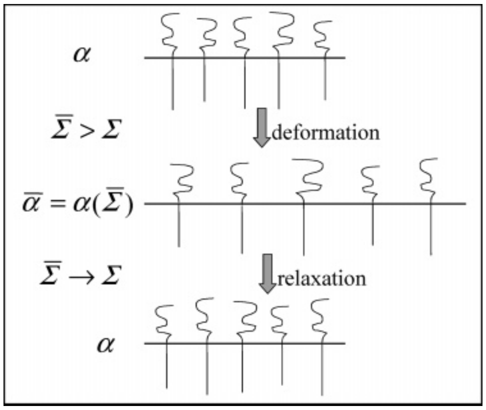

Figure 4. Scheme presenting the changes in interfacial concentration during the deformation and relaxation of the interface.

situation in which the blends are at rest, meaning that deformation of the blend, and therefore of the interface, is absent. If, due to shearing of the blend, the interfacial area enlarges and the same number of surfactant molecules (we assume that no surfactant molecule is leaving the interface during deformation) is distributed over a larger area, the interfacial tension increases. The instantaneous value, which characterizes the out-of-equilibrium state, will be designated by overbars: $\bar{\alpha} = \alpha(\bar{\Sigma})$. This situation is depicted in Figure 4.

Although there are no significant interfacial tension gradients acting, there is a driving force that pulls back the interface to equilibrium. This force is the "surface pressure", $\pi = \alpha - \bar{\alpha}$, which is related to the reduced surface concentration of the compatibilizer molecules, $\bar{\rho}^{\mathrm{if}}_{\mathrm{red}} = (\bar{\rho}^{\mathrm{if}} - \rho^{\mathrm{if}})/\rho^{\mathrm{if}} = -(\bar{\Sigma} - \Sigma)/\bar{\Sigma}$, in the following way: $\pi = \beta_{\mathrm{G}}\, \bar{\rho}^{\mathrm{if}}_{\mathrm{red}}$. The material parameter that connects both quantities is the so-called "Gibbs elasticity" and is defined as follows (see, e.g., Edwards et al.[19]):

$$\beta_{\mathrm{G}} = -\left(\frac{\mathrm{d}\alpha}{\mathrm{d}(\ln \rho^{\mathrm{if}})}\right) \tag{6}$$

According to Edwards et al.,[19] the interfacial adsorption of BCP molecules at the interface may result in a dependence of the interfacial stress on deformation of the interface, and such behavior is accounted for by elasticity. Gibbs elasticity is an intrinsic property of a modified interface. At the same time, this kind of elasticity can also arise from interfacial tension gradients and might be considered as a special case of all of those effects associated with the interfacial tension gradients named after Marangoni. Because of the fact that, for a sparsely compatibilized interface, the reduced interfacial concentration $\bar{\rho}^{\mathrm{if}}_{\mathrm{red}}$ can be identified with the interfacial deformation, $\epsilon^{\mathrm{if}} = -\bar{\rho}^{\mathrm{if}}_{\mathrm{red}}$ (see, e.g., Ivanov et al.[20]), this state equation is actually an interfacial rheological constitutive equation of Hooke type. This formal similarity allows us to identify the interfacial modulus in the Palierne model with the Gibbs elasticity: $\beta'' \equiv \beta_{\mathrm{G}}$. Using eq 5, one can present β'' in the following way:

$$\beta'' = \rho^{\mathrm{if}}_{\mathrm{bc}} \frac{RT}{M_{\mathrm{bc}}} = \frac{k_{\mathrm{B}}T}{\Sigma} \tag{6$_1$}$$

The picture we have developed is certainly only correct if no or negligible interfacial tension gradients are present. This is the case if also the deformation of the particles is small. In contrast, for large deformations, one can expect significant interfacial tension gradients. These gradients can only relax by diffusion of the surfactant molecules at the interface. Van Hemelrijck et al.[1,2] already mentioned this situation and stated that under these conditions the interfacial relaxation times should be much greater than the observed values. Moreover, if the relaxation of the interfacial tension gradients happens by diffusion, then the observed time constants should depend on deformation. Therefore, we determined the interfacial relaxation times of a 7.5% blend compatibilized by different amounts of SM144, by measuring the storage and loss moduli for deformation amplitudes between 1 and 40% and by analyzing the data in the way described above. The result is presented in Figure 5.

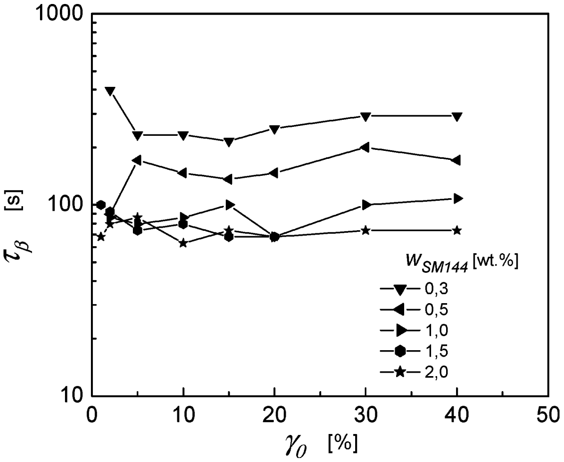

Figure 5. Interfacial relaxation time in dependence on the deformation amplitude during the oscillatory test.

One can clearly recognize that the interfacial relaxation time does not depend on the applied shear amplitude in the covered range, and therefore, we conclude that an interfacial relaxation process prevails that does not rely on the existence of interfacial tension gradients.

Combining eq 3_1 with eq 6_1, one arrives at the desired scaling relation:

$$\tau_\beta \approx \frac{(\eta_{\mathrm{m}} + \eta_{\mathrm{p}})}{k_{\mathrm{B}}T} R_{\mathrm{V}}\Sigma = \frac{(\eta_{\mathrm{m}} + \eta_{\mathrm{p}})}{k_{\mathrm{B}}T} \frac{3\phi}{\phi_{\mathrm{bc}}} V_{0\mathrm{bc}} \tag{7}$$

In these equations, $V_{0\mathrm{bc}} = M_{\mathrm{bc}}/\rho_{\mathrm{bc}}N_{\mathrm{A}}$ represents the volume occupied by one BCP molecule, and this is the only structural parameter that is relevant for the understanding of the interfacial relaxation time. Especially the second part of eq 7 promotes the understanding of the experimental fact presented in Figure 3a: the hyperbolic dependence of the interfacial relaxation time on the volume fraction of the added emulsifier. Moreover, the order of times with decreasing volumes of emulsifier molecule, proportional to their molecular weight, is explained.

Figure 6 summarizes all experimental results and literature data within this scaling representation. Here, we included our own actual measurements and data published by Jacobs et al.[9] and Van Hemelrijck et al.[1,2] Let us first discuss the points that correspond to our data. While the thick line represents the best fit for all data points, the scaling according to eq 7 is given by the thin dashed line. Interestingly, the data include the results of a blend (see Jacobs et al.[9]) compatibilized with a symmetric BCP whose outer block (interaction with matrix PS) is made of poly(cyclohexyl methacrylate), which is miscible with PS. To show that interfacial relaxation times smaller than the form relaxation times of the blends are not accessible, we included the form relaxation times obtained for the blend compatibilized with SM17. These times do not follow this scaling relation, and we will justify the differences between these times later on.

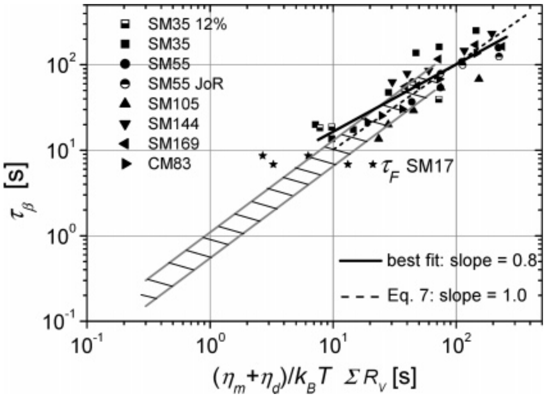

Figure 6. Verification of scaling relation (eq 7) on the example of the available blend systems compatibilized with symmetric BCPs. The points corresponding to SM55 JoR were taken from ref 9.

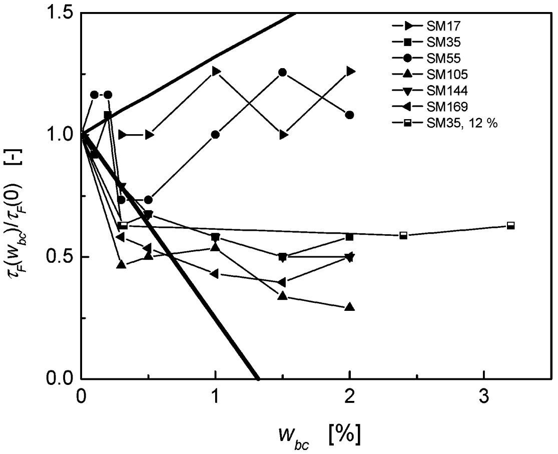

Figure 7. Relative form relaxation time in dependence on the weight fraction of the added compatibilizer. The lines connecting the points are drawn to guide the eye. The two bold straight lines correspond to calculations (eq 8_2) for SM17 (upward) and SM169 (downward).

The data documented by Van Hemelrijck et al.[1,2] for their symmetric BCPs in blends with $p = 1$ fall within the region given by the shaded area. Their data show less scatter and follow the trend of our data, thereby also confirming scaling relation (7). Their empirically established scaling relation (eq 1) is similar to ours, except for the treatment of the influence of matrix and dispersed phase viscosities. Because of the fact that their samples have viscosity ratios close to 1, the difference is not significant. However, for polymer blends with viscosity ratios around 0.1 (this corresponds to their efforts to scale our old data within their scaling relation), significant differences can be seen (see our data in their Figures 9 and 10; caution, these authors used $1/\tau$ as abscissa!).

Next, we discuss the similarity of our scaling relation to eq 2 presented by Vlahovska et al.[14] They defined a longest relaxation time for a surfactant-covered drop that, in their opinion, is associated with the relaxation of the surfactant distribution by Marangoni stresses. Instead of a material property like β'', as we did, they used the driving force of surfactant redistribution, $\alpha_0 - \alpha$, as the relevant parameter in their equation. Although there is a principal difference between their approach and ours, the consequence for the definition of time is the same: $\alpha_0 - \alpha = k_B T/\Sigma = \beta_G = \beta''$. Using the hydrodynamic radius of a surfactant molecule for the calculation of interfacial occupancy, they give an estimate of the lower limit of the interfacial relaxation time rather than a general equation valid for different amounts of surfactant molecules at the interface. Only in the case of an almost perfectly covered interface is the relation $\Sigma \approx \Sigma_{\mathrm{cmc}} \approx R_h^2$ valid, where Σ_{cmc} is the smallest value of interfacial area at which micella formation sets in. Most interfacial relaxation times determined by us correspond to the situation where $\Sigma \gg R_h^2$.

Now, we discuss the dependence of the form relaxation time on the degree of compatibilization. For this purpose, we have to express the particle radius as well as the interfacial tension in dependence on the degree of compatibilization. We make use of an equation derived by Riemann et al.[6] (their eqs 5 and 5_1). Assuming $f(p) \approx 1$, eq 4_1 changes to

$$\tau_F \approx \tau_{F0} \frac{\exp(-K\phi_{bc}) + \dfrac{R_{\mathrm{cmc}}}{R_{V0}}(1-\exp(-K\phi_{bc}))}{1-\dfrac{k_B T}{\alpha_0 \Sigma}} \tag{8}$$

where τ_{F0} is the form relaxation of a particle with a neat interface. The K parameter for the BCPs can be found in Table 1.

Using Riemann's eq 9, one can express the interfacial area per BCP through the volume fraction of the BCP: $\Sigma \approx \Sigma_{\mathrm{cmc}} + a_2/\phi_{bc}$. With $a_2 = 3\phi M_{bc}/(\rho_m R_{V0} N_A)$ and $\Sigma_{\mathrm{cmc}} = a_2 K$, we arrive at the following equation

$$\tau_F \approx \tau_{F0} \frac{\exp(-K\phi_{bc}) + \dfrac{R_{\mathrm{cmc}}}{R_{V0}}(1-\exp(-K\phi_{bc}))}{1-\dfrac{A\phi_{bc}}{1+K\phi_{bc}}} \tag{8_1}$$

where $A = k_B T/(\alpha_0 a_2)$.

Assuming furthermore that $K\phi_{bc} \ll 1$, one can present the form relaxation time in an even simpler form

$$\frac{\tau F}{\tau_{F0}} \approx (1 - K'\phi_{bc})(1 + A\phi_{bc}) \approx 1 - (K' - A)\phi_{bc} + O(\phi_{bc}^{\;2}) \tag{8_2}$$

with $K' = K(R_{V0} - R_{\mathrm{cmc}})/R_{V0}$.

Figure 7 shows the scaled form relaxation times of all samples together with calculations for two BCPs (SM17 and SM169) based on the application of eq (8_2). These calculations make use of the facts that the neat, noncompatibilized particle has a radius of $R_{V0} = 110$ nm and that the micellas have a radius of R_{cmc} (=20 nm in the case of SM105). A report on the determination of the latter quantity can be found elsewhere.[6] The calculations (see the two straight lines) are in qualitative agreement with experimental facts: For the shortest BCP (SM17), the compatibilization leads to an increase in the form relaxation time, because with the addition of compatibilizer, the reduction in interfacial tension is stronger than the reduction in particle size. For the compatibilizer with the highest molecular weight, the opposite situation holds true: The reduction in particle size wins over the reduction in interfacial tension and therefore leads to decreasing form relaxation times. Use of eq 8_1 instead of eq 8_2 leads to the observed leveling of relaxation times with increasing concentrations of emulsifier.

In general, eq 8 explains under which conditions—different amounts of dispersed phase and different compatibilizers—increasing or decreasing form relaxation times can be observed.

Finally, we would like to mention that the derived formulas for the form and interfacial relaxation times can be used for the characterization of interfacial properties (the interfacial tension and the interfacial modulus) in dependence on the amount of compatibilizer. The procedure and its utility were demonstrated by Riemann et al.[19] Due to the lack of values for the coefficient of interfacial tension of compatibilized PS−PMMA blends, they compared their calculations with model predictions. Statistical thermodynamic theories by Leibler[22] and by Noolandi and Hong[23] have been used in this case. The comparison of calculations on the basis of thermodynamic theories and predictions using form and interfacial relaxation times yielded a good agreement and revealed the application potential of such a method. Whether the determined interfacial moduli are reasonable is hard to assess due to missing theories and missing experimental values for comparison. However, the derived scaling relations might be the basis of a procedure that allows at least the indirect determination of the interfacial properties that are difficult to measure by alternative techniques.

Conclusions

We have investigated the influence of different amounts of symmetric BCPs such as P(S-*b*-MMA) on the form and interfacial relaxation times of a polymer blend containing mainly 7.5% of PS as dispersed phase in a PMMA matrix. Special emphasis was put on the investigation of the effect of the compatibilizer molecular weight on these times. Using image analysis and rheological procedures developed previously (see Riemann et al.[6] and Jacobs et al.[9]), we were able to highlight the influence of all processing (volume fraction of dispersed phase and compatibilizer) and structural (molecular weight of BCP) parameters. For this purpose, we combined predictions of the extended Palierne model with assumptions on the changes of interfacial tension with the amount of compatibilizer. It turned out that the identification of the interfacial modulus in Palierne's model with the Gibbs elasticity modulus as the intrinsic property of a surfactant-laden interface, responsible for the reconstitution of an equilibrium surfactant distribution, is the key point for a quantitative understanding of the ongoing processes and the interfacial relaxation time scaling. On the basis of the assumption that Gibbs elasticity is the important interfacial parameter, the scaling relation for the interfacial relaxation time was derived. It turned out that the parameter complex $R_V(\phi_{bc})\Sigma(\phi_{bc}) = V_{0bc} 3\phi/\phi_{bc}$ controls the development of the interfacial relaxation time with compatibilization. The roles of the matrix and the dispersed phase viscosities were highlighted as well. A similar treatment of the form relaxation times leads to a more complex scaling relation that is controlled by the same set of parameters.

In conclusion, Gibbs elasticity is the important material parameter of the compatibilized interface controlling the ongoing rheological relaxation processes.

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References and Notes

(1) Van Hemelrijck, E.; Van Puyvelde, P.; Velankar, S.; Macosko, C. W.; Moldenaers, P. *J. Rheol.* **2004**, *48*, 143−159.
(2) Van Hemelrijck, E.; Van Puyvelde, P.; Macosko, C. W.; Moldenaers, P. *J. Rheol.* **2005**, *49*, 783−798.
(3) Milner, S. T.; Xi, H. W. *J. Rheol.* **1996**, *40*, 663−687.
(4) Van Puyvelde, P.; Valenkar, S.; Moldenaers, P. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 457−463.
(5) Lyu, S. P.; Jones, T. D.; Bates, F. S.; Macosko, C. W. *Macromolecules* **2002**, *35*, 7845−7855.
(6) Riemann, R. E.; Cantow, H. J.; Friedrich, Chr. *Macromolecules* **1997**, *30*, 5476−5484.
(7) Palierne, J. F. *Rheol. Acta* **1990**, *29*, 204−214.
(8) Palierne, J. F. Correction. *Rheol. Acta* **1991**, *30*, 497.
(9) Jacobs, U.; Fahrländer, M.; Winterhalter, J.; Friedrich, Chr. *J. Rheol.* **1999**, *43*, 1495−1509.
(10) Pawar, Y.; Stebe, K. J. *Phys. Fluids* **1969**, *8*, 1738−1751.
(11) Li, X.; Pozrikidis, C. *J. Fluid Mech.* **1997**, *341*, 165−194.
(12) Velankar, S.; Van Puyvelde, P.; Mewis, J.; Moldenaers, P. *J. Rheol.* **2001**, *45*, 1007−1019.
(13) Jeon, H. K.; Macosko, C. W. *Polymer* **2003**, *44*, 5381−5386.
(14) Vlahovska, P.; Blawzdziewicz, J.; Loewenberg, M. *J. Fluid Mech.* **2002**, *463*, 1−24.
(15) Gramespacher, H.; Meissner, J. *J. Rheol.* **1992**, *36*, 1427−1441.
(16) Friedrich, Chr.; Gleinser, W.; Korat, E.; Maier, D.; Weese, J. *J. Rheol.* **1995**, *39*, 1411−1415.
(17) Gleinser, W.; Maier, D.; Schneider, M.; Weese, J.; Friedrich, Chr.; Honerkamp, J. *J. Appl. Polym. Sci.* **1994**, *53*, 39−50.
(18) Graebling, X.; Muller, R.; Palierne, J. F. *Macromolecules* **1993**, *26*, 320−329.
(19) Edwards, D.A.; Brenner, H.; Wasan, D. T. *Interfacial Transport Processes and Rheology.* Butterworth-Heinemann: Boston, MA, 1991.
(20) Ivanov, I. B.; Danov, K. D.; Ananthapadmanabhanb, K. P.; Lips, A. *Adv. Colloid Interface Sci.* **2005**, *114−116*, 61−93.
(21) Israels, R.; Jasnow, D.; Balazs, A. C.; Krausch, G.; Sokolov, J.; Rafailovich, M. J. *Chem. Phys.* **1995**, *102*, 8149−8157.
(22) Leibler, L. *Makromol. Chem. Makromol. Symp.* **1988**, *16*, 1−17.
(23) Noolandi, J.; Hong, K. M. *Macromolecules* **1984**, *17*, 1531−1537.
(24) Cigana, P.; Favis, B. D.; Jerome, R. J. *Polym. Sci. Polym. Phys.* **1996**, *34*, 1691−1700.
(25) Li, J.; Favis, B. D. *Polymer* **2002**, *43*, 4935−4945.

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