Interpretation of a New Interface-Governed Relaxation Process in Compatibilized Polymer Blends

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ABSTRACT: We have analyzed the influence of different amounts w_{bc} of two diblock copolymers, poly(styrene-*b*-methyl methacrylate) (sm blend series) and poly(cyclohexyl methacrylate-*b*-methyl methacrylate) (cm blend series), on the morphological and rheological characteristics of a blend containing $w =$ 7.5 wt % polystyrene in poly(methyl methacrylate) matrix. The morphological analysis is based on the sphere size distribution function, which was determined from the image analysis of the transmission electron micrographs. Using this function and assuming that all block copolymers are located at the interface, the interfacial area per copolymer joint, Σ, was calculated. From its hyperbolic dependence on w_{bc} the value at the critical micelle concentration, Σ_{cmc}, was found to be about 10 nm^2 for both systems. The rheological analysis reveals that in addition to the form relaxation process, well-known for polymer blends, a new relaxation process is observed for these systems. Its relaxation time, τ_β, has been studied in dependence on the amount of added block copolymers. The observed phenomena for each blend series, i.e. constant blend viscosity, slight shift of the form relaxation times τ_1, and systematic shift of the interface governed relaxation time τ_β ($\tau_\beta > \tau_1$), have been interpreted quantitatively. In contrast to τ_1, τ_β is less influenced by the interfacial tension but is mainly governed by an additional contribution, the interfacial shear modulus. Formulas were derived from an expanded version of the Palierne emulsion model which allows the determination of the proposed interfacial properties from rheological measurements. In general, the interfacial tension decreases with increasing amount of block copolymer, and the decrease is more pronounced for the cm blend series. The interfacial shear modulus increases during compatibilization from 0 to amounts which are in the range of 20−30% of the interfacial tension. The decrease of interfacial tension is in good agreement with predictions from Leibler's brush model extended by Dai et al. In conclusion, it was found that the Palierne model with an nonisotropical interfacial stress state is quantitatively correct to describe the observed phenomena for those blends.

Introduction

Heterogeneous polymeric systems may consist of droplets dispersed in a matrix. They generally exhibit bad phase adhesion as a consequence of the weak interaction of both components. The addition of adequate block copolymers which accumulate preferentially at the interface causes a decrease in particle size and an improved adhesion between the blend components.[1−3] From a microscopic point of view, the presence of block copolymers enlarges the thickness of the interphase separating the domains of both polymers. The understanding of the interactions in this transitional region is of fundamental importance for the understanding of the process of compatibilization. Besides the interfacial thickness, there are two other important parameters characterizing the interaction between both components from its phenomenological point of view: the thermodynamic interaction parameter χ and the coefficient of interfacial tension α_0.[4]

Among the methods for the characterization of block copolymer interactions, the determination of the coefficient of interfacial tension is of great importance.[5] Within the category of methods, rheological techniques start to play an important role, too. Their principle is based on the fact that heterogeneous polymer blends in the molten state are emulsions. One of the most striking properties of emulsions is the ability to change the shape of inclusions during deformation. For droplets dispersed in a continuous matrix, the balance of the viscous forces outside the particles and the Laplace pressure originating from the interfacial tension determine the equilibrium form of the inclusions. The process associated with the re-formation of a deformed particle to its primarily spherical form is called the form relaxation process. This process possess a characteristic time τ_1, the form relaxation time which is larger than the terminal relaxation times of the blend components. It depends on the particle radius, R, the viscosity of the matrix, η_m, the viscosity of the minor phase, η_d, and the interfacial tension. Knowing the morphology and rheology of the blend quantitatively, it is possible to derive the interfacial tension from the form relaxation time. This was first mentioned by Graebling et al.[6] Fitting Oldroyd's emulsion model[7] to the moduli curves, the coefficient of interfacial tension was determined quantitatively correct.[8] Later on for neat blends consisting of polystyrene (PS) and poly(methyl methacrylate) (PMMA), Gramespacher and Meissner[9] used a simple empirical mixing rule for the moduli of the blend components and of the interface to determine the interfacial tension. The ansatz for interface moduli originates from the Choi−Schowalter[10] model. The authors concluded that it is possible to determine the coefficient of interfacial tension by shear oscillation tests. They found for a PS/PMMA blend at a temperature of about 190 °C an interfacial tension of about 2 mN/m. A similar result for this system was presented by Friedrich et al.,[11] who applied the Palierne model[12] formulated on the basis of a continuous distribution function for the particle radii in order to determine from rheology both the coefficient of interfacial tension and the distribution function. They found that only for concentrations of the minor phase up to 15% could quantitatively correct results be obtained.

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The Palierne model is the most used emulsion model at the moment due to its ability to describe quantitatively the linear viscoelastic properties of blends and the possibility to derive the interfacial tension from these data.[11,13,14]

The influence of compatibilizers on blend properties is a long-term research subject. Whereas the influence of polymeric emulgators on the morphology of blends, especially for blends with spherical inclusions, is well understood,[15−18] the results concerning the rheology of compatibilized blends are contradictory.[19−29] In most cases the blends were not properly designed to study the form relaxation process, and consequently, the material response did not cover the form relaxation region or, eventually, slower relaxation processes.[21,22,24,27] In other cases,[18,23] the matrix exhibits great polydispersity or the inclusions themselves have a complex morphology, for instance the "salami type" morphology of high impact polystyrene. Moreover, the addition of block copolymers may induce a strong change in morphology,[25,26] and thus the emulsion theories based on spherical inclusions cannot be applied further. In many cases the concentration of inclusions is so high that the models cannot be applied quantitatively.[24,27] Nevertheless, many authors tried to calculate the interfacial tension for compatibilized blends applying the formulas found to be adequate for neat blends. The correctness of such a procedure is questionable.

Recently for a PS (7.5 wt %)−PMMA (92.5 wt %) blend it was found by the authors[28] that the addition of 1 wt % of symmetric diblock copolymer poly(styrene-*b*-methyl methacrylate), P(S-*b*-MMA), or poly(cyclohexyl methacrylate-*b*-methyl methacrylate), P(CHMA-*b*-MMA), leads to an additional relaxation process with a longer relaxation time than the form relaxation. Thus, the dynamic moduli of such a blend cannot be described by emulsion models which do not take into consideration the rheological consequences of block copolymers residing at the interface.

It is the aim of the present work to study and to quantify the morphological changes during compatibilization of the previously mentioned blends. In addition, the new relaxation process shall be analyzed in dependence on the type and the amount of added block copolymer. We describe the observed phenomena quantitatively in terms of a modified emulsion model including interfacial rheological properties such as interfacial shear modulus and derive a procedure that allows the determination of these parameters from rheological measurements.

Experimental Section

Materials. All materials, the polymer for the matrix and for the dispersed phase as well as the block copolymers, were polymerized anionically, exhibiting low molecular weight polydispersity. PMMA, was used as matrix material and PS as the dispersed phase. As compatibilizers symmetric diblock copolymers P(S-*b*-MMA) and P(CHMA-*b*-MMA) are used. The second block copolymer is a polymeric emulgator, where the poly(cyclohexyl methacrylate) block is miscible with PS. Blends containing the P(S-*b*-MMA) block copolymers we will call the "sm blend" series whereas the other series is called "cm blend" series. Details concerning weight average molecular weights, M_w, polydispersity, M_w/M_n, and the block composition, w_{bc}, are listed in Table 1.

Blend Preparation. For the investigations presented here, blends with ($92.5 - w_{bc}/2$) wt % PMMA as matrix material, and ($7.5 - w_{bc}/2$) wt % PS as dispersed phase, with $w_{bc} = 0$, 0.3, 0.6, 1, 1.5, and 2 wt % of the block copolymers, were prepared. The mixture without block copolymer ($w_{bc} = 0$) with 92.5 wt % PMMA and 7.5 wt % PS was used as the neat (reference) blend. Details concerning the precise composition and the names of the blends are given in Tables 2 and 3 for the sm and cm series, respectively. This procedure of compatibilization has the advantage that the ratio between PS and PMMA is always identical in all blends investigated, independent of the amount of block copolymer. Blends were prepared from a 10 wt % solution of blend components in tetrahydrofuran and subsequent precipitation into 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 to 1 mm thick disks, 25 mm in diameter.

Table 1. Characterization of the Blend Components and Block Copolymers

material	M_w[a]	M_w/M_n[a]	w_{bc}, wt %[b]
PS	100	1.03	
PMMA	31	1.19	
P(S-*b*-MMA)	105	1.12	0.52
P(CHMA-*b*-MMA)	87	1.4	0.49

[a] Gpc., PS standard. [b] Determined from ^{1}H NMR.

Table 2. Some Characteristic Parameters of the Investigated sm Blend Series

blend	w_{bc} wt %	τ_1, s	τ_β, s	R_v, nm	$10^{-5}\ \eta_0^{exp}$, Pa·s	α_0, mN/m	β_{20}, mN/m
b075	0	6.3		110	1,02	2.28	0
sm03	0.29	5.6	89.2	102	1,13	2.31	0.16
sm06	0.59	5.6	70.7	93	1,17	2.1	0.18
sm1	0.98	4.5	35.4	90	1,08	2.47	0.36
sm15	1.58	3.5	25.1	78	1,13	2.73	0.44
sm2	1.94	3.2	17.7	75	1,25	2.79	0.62

Table 3. Some Characteristic Parameters of the Investigated cm Blend Series

blend	w_{bc}, wt %	τ_1, s	τ_β, s	R_v, nm	$10^{-5}\ \eta_0^{exp}$, Pa·s	α_0, mN/m	β_{20}, mN/m
cm03	0.25	5	177	73	1.3	2.29	0.06
cm05	0.49	5.6	89	75	1.17	2.06	0.14
cm1	1	3.9	70.7	56	1.3	2.05	0.23
cm15	1.54	4.46	35.5	71	1.3	1.96	0.28
cm2	2.01	5.01	31.8	64	1.3	1.55	0.29

Transmission Electron Microscopy (TEM). 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, TEM elastic bright-field images were taken on a ZEISS CEM 902 (ESI mode).

The droplike morphology of the PS phase dispersed in PMMA was quantitatively analyzed using the image processing system IBAS 2.0 (Kontron). If the average diameter of the spheres dispersed in the blends are larger than the thickness of sections made by microtoming (here about 60 nm), the droplets are cut and one gets the dimensions of the corresponding circular sections. Between 3000 and 5000 circular sections of PS were evaluated to get the section size distribution of the blends. The sphere size distributions and from that the number- and volume-weighted sphere radii, R_n and R_v respectively, were calculated from the section size distributions according to a method developed by Gleinser et al.[30]

Rheology. The rheological measurements were performed on a Rheometrics Mechanical Spectrometer RMS 800 applying parallel plate geometry with a diameter of 25 mm. Isothermal frequency sweeps were recorded between 170 and 230 °C, in steps of 10 K. The isotherms were shifted to mastercurves with a reference temperature $T_{ref} = 190$ °C. The shift-factors showed WLF behavior. More details concerning the shiftability are given by Friedrich et al.[11] From the master curves relaxation time spectra were computed with the program NLREG developed by Weese.[31]

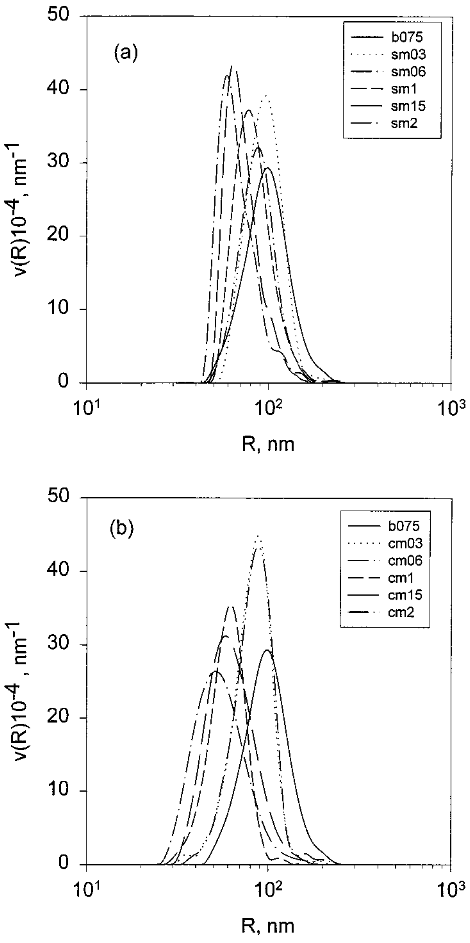

Figure 1. Volume weighted sphere radius distribution $v(R)$ for blends compatibilized using the P(S-*b*-MMA) block copolymer (a) and the P(CHMA-*b*-MMA) block copolymer (b). The area under the distribution function gives the volume percentage of dispersed material.

Results and Discussion

Morphology. Blends, with a volume concentration of the minor phase 0−12% exhibit drops of quite uniform size, with a drop diameter in the order of 1 μm.[3] In our case, where the blends were prepared by a solution process, the dimensions of the particles are even smaller. The morphologies of the blends are stable during the period of measurements. This was checked by repeated determination of $v(R)$ after the blends have been inside the rheometer. Consequently, we may assume that stability of dimensions is guaranteed by our blend preparation and measuring procedure.

Parts a and b of Figure 1 show the volume-weighted sphere radius distribution function $v(R)$ of the sm and cm blend series, respectively. By integration of these distribution functions, the volume percentage of dispersed material is recovered. Figure 1 also shows that the size distributions are monomodal and narrow. The polydispersity parameter R_v/R_n, which is a measure for the width of the particle size distribution, and R_v are given in Tables 2 and 3. In the following we will use the volume average particle radius R_v, because it was found[13] that this radius is most suitable for calculations with the emulsion models.

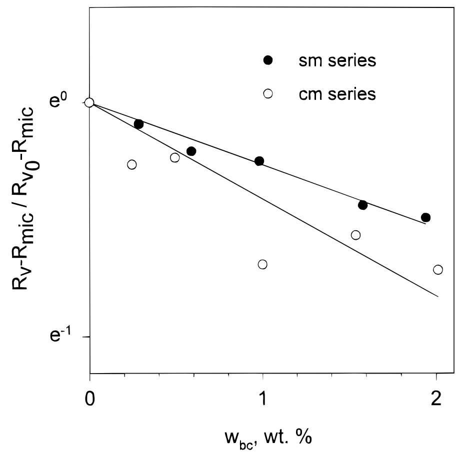

Figure 2. Semilogarithmic plot of the decrease of drop radius for both blend series. The solid lines correspond to linear regression (eq 2).

Tables 2 and 3 show that the radii R_v decrease from 110 nm for the uncompatibilized blend to 75 nm for the blend sm2 and to 64 nm for cm2. This is due to the well-known dispersion effect of block copolymers caused by their presence at the interface and the subsequent lowering of the interfacial tension. Although the dispersed particles are very small for the uncompatibilized blend, the addition of the block copolymers leads to a significantly lower average particle radius. The course of R_v with content of block copolymer can be described with an exponential decrease.[20,32] The dependence of drop radius R_v on the amount of added block copolymer w_{bc} is given by

$$R_v = R_{mic} + (R_{v0} - R_{mic})\, e^{-Kw_{bc}} \tag{1}$$

K is a decay parameter for the change of drop radius with w_{bc}. R_{v0} is the average radius of the dispersed phase particles in case of the neat blend and was found to be 110 nm. R_{mic} is the radius of the block copolymer micelles. With the mixing procedure for the blend preparation used in this work, where the overall minor phase concentration is kept constant, R_{mic} is reached at a block copolymer content of 15 wt %. At this concentration all minor phase would be built by the PS blocks or PCHMA blocks respectively of the block copolymers and, therefore, only micelles would be present. In our case, R_{mic} was especially determined by TEM for a blend containing 2% block copolymers. We found $R_{mic}^{sm} = 20$ nm for sm blend series, and due to the similar molecular weight we assume that micelles have the same radius for cm blend series. From eq 1, we get

$$\ln\left(\frac{R_v - R_{mic}}{R_{v0} - R_{mic}}\right) = -Kw_{bc} \tag{2}$$

The data for our blends are displayed in Figure 2 in a semilogarithmic plot. The exponential behavior is verified, and decay parameters of $K_{sm} = 25.2$ and $K_{cm} = 41.3$ can be determined. The behavior corresponding to eq 2 is depicted by the solid lines in Figure 2.

Knowing the particle size distribution and the blend composition, it is possible to calculate the specific interfacial area of particles per gram blend, I:

$$I = \frac{w_A \bar{O}_A}{\rho_A \bar{V}_A} \tag{3}$$

w_A is the weight fraction and ρ_A the density of the minor phase A, irrespective whether the polymer stems from the inclusion material (≡PS) or from the block copolymer (≡*b*-PS or *b*-PCHMA). In the case of cm series we

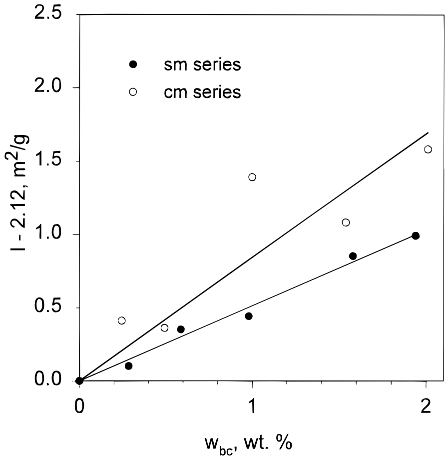

Figure 3. Specific interfacial area per mass of blend, I, as a function of block copolymer concentration for both blend series. The line corresponds to the linear regression (eq 6).

suppose that the PCHMA block of the cm block copolymer behaves similar to the PS block of the sm block copolymer. Therefore, we assume $w_A = 0.075$ and $\rho_A = \rho_{PS}(T = 25\ °C) = 1.05$ g/mL in all cases. $\bar{O}_A$ and $\bar{V}_A$ are the surface area and the volume of an average drop of the minor phase A, respectively. $\bar{O}_A$ and $\bar{V}_A$ are given as

$$\bar{O}_A = 4\pi\frac{\int q(R)R^2\,dR}{\int q(R)\,dR};\quad \bar{V}_A = \frac{4}{3}\pi\frac{\int q(R)R^3\,dR}{\int q(R)\,dR};$$

$$q(R) = \frac{v(R)}{R^3} \qquad (4)$$

$q(R)$ is the number-weighted sphere radius distribution function.

Figure 3 shows the specific interfacial area I calculated from eq 3 vs the amount of added compatibilizer for both blend series. The specific interfacial area increases linearly with block copolymer content, from 2.1 m²/g for the neat blend to 3.1 m²/g for the sm2 blend and to 3.7 m²/g for the cm2 blend, respectively. Such an increase can be explained on the basis of discussed formulas using some simplifying assumptions. In the monodisperse case one gets for eq 3, $I = 3w_A/\rho_A R_v$. Assuming $(R_{v0} - R_{mic}) \approx R_{v0}$ and expanding the e-function of eq 1 in a Taylor series up to order 1, this equation yields

$$R_v = R_{mic} + (R_{v0} - R_{mic})e^{-Kw_{bc}} \approx R_{mic} + (R_{v0} - R_{mic})(1 - Kw_{bc}) \approx R_{v0}(1 - Kw_{bc}) \qquad (5)$$

With this relation, an approximation of the specific interfacial area can be calculated:

$$I \approx \frac{3w_A}{\rho_A R_{v0}}\frac{1}{1 - Kw_{bc}} \approx \frac{3w_A}{\rho_A R_{v0}}(1 + Kw_{bc}) \qquad (6)$$

The curves corresponding to eq 6 are given in Figure 3 by the straight lines. The decay parameter K derived from the slope of that line yields values of $K_{sm} = 26.8$ and $K_{cm} = 39.7$ which are in good agreement with the values derived above from relation 2.

Now, the interfacial area per copolymer joint, Σ, can be calculated. Assuming that all block copolymers are residing at the interface, Σ is the ratio of I divided by the number of block copolymers per gram blend, N_{bc}:

$$\Sigma = \frac{I}{N_{bc}} = \frac{w_A\bar{O}_A M_{n\ bc}}{\rho_A\bar{V}_A w_{bc} N_A} \qquad (7)$$

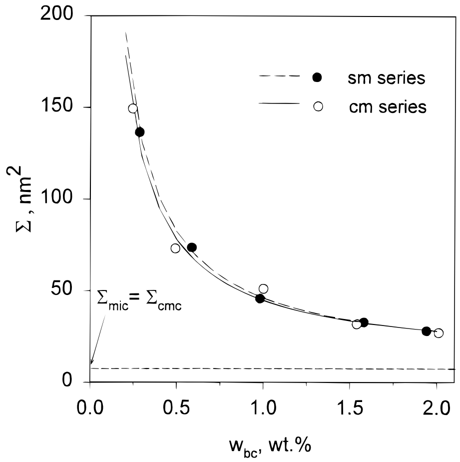

Figure 4. Interfacial area per copolymer joint, Σ, vs block copolymer concentration for both blend series. Σ shows a hyperbolic decrease (solid lines) which corresponds to eq 9.

In this equation, $M_{n\ bc}$ is the molecular weight of the block copolymer and N_A is Avogadro's number.

Israels et al.[33] found from calculations using the self-consisted field (SCF) theory that micelles of symmetric block copolymers in a ternary system are not stable. They derived the fact that the chemical potential of a copolymer in a micelle is always higher than the chemical potential of a copolymer in an equilibrium monolayer. Consequently, in a ternary system, all copolymers should rest at the interface when the system is thermodynamically equilibrated. For that reason and from a careful analysis of high resolution TEM pictures, our assumption that all block copolymers are located at the interface seems to be correct.

With some simple rearrangements and for the assumption of monodisperse particles with radius R_v, where $\bar{O}_A/\bar{V}_A = 3/R_v$, one gets Paul's relation:[42]

$$\Sigma = \frac{3\phi_A M_{n\ bc}}{\phi_{bc}\rho_{bc}R_v N_A} \qquad (8)$$

In eq 8, ϕ_A and ϕ_{bc} are the volume fractions of the minor phase and the block copolymer, respectively, and ρ_{bc} is the density of the block copolymer.

Figure 4 shows the interfacial area per copolymer joint Σ as calculated from eq 7 vs weight fraction of compatibilizers. If the concentration of the block copolymers goes to zero, Σ approaches infinity. For higher concentrations Σ should approach a defined value, the interfacial area per copolymer of a saturated particle, Σ_{cmc}. At this point further accumulation of copolymers at the interface is not possible and leads to the appearance of micelles.

As mentioned above, in a ternary blend system like the one investigated in this paper, micelles are not thermodynamically stable as long as both homopolymers are present. Therefore, the critical micelles concentration (cmc) is reached when the particles have almost the size of micelles. With the blend preparing procedure used in this work (cf. Experimental Section), the free PS as minor phase is vanishing and the onset of cmc is expected to be at a copolymer content of 15 wt %. It should be stressed that in such a system the lowest possible value for the interfacial area per copolymer joint is that for a micelle, Σ_{mic}, and that this value coincides with Σ_{cmc}.

The experimental data for Σ shown in Figure 4 seem to follow a hyperbolic function of the type $\Sigma = a_1 + a_2/w_{bc}$. Such a behavior can be derived from the formulas presented above. Putting eq 5 into eq 7 and assuming $(1 - Kw_{bc})^{-1} \approx (1 + Kw_{bc})$, one gets the following hyperbolic function to describe the experimental results:

$$\Sigma \approx \Sigma_{cmc} + \frac{a_2}{w_{bc}} \quad \text{with} \quad a_2 = \frac{3w_A M_{n\,bc}}{\rho_A R_{v0} N_A} \quad \Sigma_{cmc} = a_2 K \tag{9}$$

Although the condition $(1 - Kw_{bc})^{-1} \approx (1 + Kw_{bc})$ is weak, especially for the cm series, the agreement between experiments and calculations is excellent and the derived constants agree fairly well with literature data. First we will start to discuss the results of the sm series. From the fit displayed by the solid line in Figure 4, one gets $\Sigma_{cmc}^{sm} = 9.7 \pm 1$ nm^2 and with this $K_{sm} = 26.7$ is obtained. The K_{sm} value is very similar to the other K_{sm} values found above. Our result for Σ_{cmc}^{sm} is in good agreement with that estimated for PS/PMMA by Perrin and Prud'homme,[34] $\Sigma_{cmc}^{sm} = 10.6$ nm^2, and the value determined by Russel et al.,[35] $\Sigma_{cmc}^{sm} = 9.95$ nm^2, using neutron reflectivity technique to probe a PS/PMMA interface. In general, it is very difficult to compare values of Σ_{cmc}, because it depends on molecular weight, architecture, and the blend system and should, therefore, be different for each kind of block copolymer and blend system. It should be also noted here, that eqs 6 and 9 are accurate only in the range of low concentrations of block copolymers. Nevertheless, $\Sigma_{cmc}^{cm} = 9.7$ nm^2 seems to be also a reasonable value for the following reasons.

Considering the unperturbed dimensions of the copolymer used in this investigation, one gets an average radius of gyration for the PMMA-block of $R_g = 5.4$ nm and for the PS-block of $R_g = 6.39$ nm.[36] Assuming on the one hand unperturbed dimensions of the block copolymer molecule at the interface, this would lead to a minimum interfacial area per joint of about 91 nm^2. But the presence of many copolymers at the interface leads to more stretched conformations of the blocks, and therefore this number should be smaller. In our case, where the PMMA-blocks build the corona of the micelle and the molecular weight of the block is higher than the matrix material (wet brush case, see Leibler[37]), one can expect a coronal swelling of the block copolymer chains. This leads to an additional extension of the blocks and therefore lowers the Σ_{cmc} value in comparison to that number which is based on the assumption of unperturbed dimensions.

On the other hand Paul[42] suggests a value of $\Sigma = 0.5$ nm^2 for fully-stretched chains. Leibler[37] assumes for a saturated flat interface that Σ_{cmc} is about 8 nm^2. From this point of view, the value we determined seems to be adequate.

For the cm blend series we determined from fit $\Sigma_{cmc}^{cm} = 11.2 \pm 4$ nm^2. Comprising the error bars, this number is equal to that found for the other blend system. Although there are no values available for Σ_{cmc} of this block copolymer system, the value we found seems to be reasonable. Using Σ_{cmc}^{cm} a value of $K_{cm} = 33.6$ is determined. Again, this value agrees fairly well with that found previously.

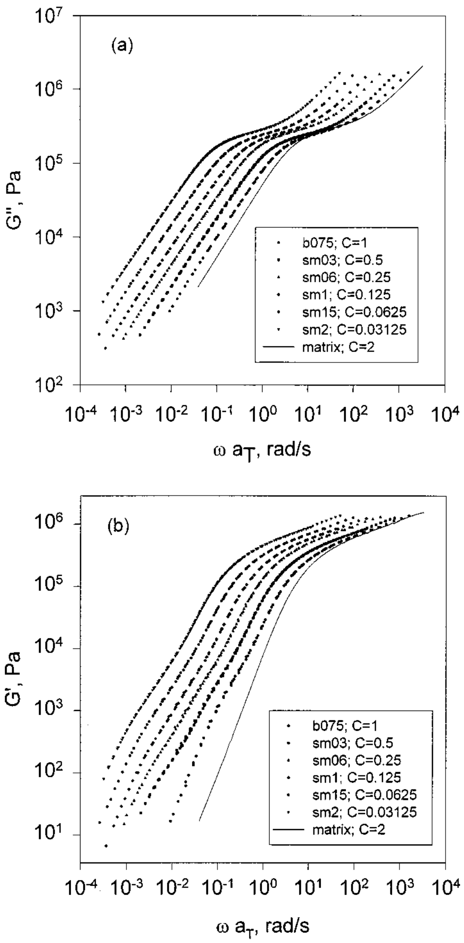

Figure 5. Master curves of the loss modulus G'' (a) and storage modulus G' (b) of the five blends with 0.3, 0.6, 1, 1.5, and 2 wt % of P(S-*b*-MMA) compatibilizer plotted together with the matrix polymer and the uncompatibilized blend b075. The curves are shifted by a factor C to avoid overlap.

Rheology. The loss modulus, G'', and the storage modulus, G', of the matrix polymer, the neat blend, and the five compatibilized blends of the sm series vs the reduced frequency ωa_T are shown in parts a and b of Figure 5, respectively. Due to the similarity of the curves of the cm series with those of the sm series, the corresponding moduli of the cm series are not shown. The master curves of the presented systems are shifted by the factor C to prevent overlapping of data points. The rheological response of the matrix is typical for a linear monodisperse polymer. The blend without any compatibilizer shows an elastic contribution expressed in a shoulder of the storage module, which corresponds to the form relaxation time of the present polymer blend.

Moreover, comparing the not-shifted curves at an identical small frequency, one can observe that with increasing degree of compatibilization the elastic moduli increase. For the not-shown cm blends this increase is a little bit stronger than for the sm blends. In general, the blends become more elastic in the terminal relaxation region while the loss moduli G'' remain unaffected by the process of compatibilization.

To quantify the characteristic times inherent in the observed relaxation behavior, the relaxation time spectra are calculated for the matrix and both blend series. These spectra are presented in parts a and b of Figure 6, respectively. There, the characteristic relaxation times are expressed as maxima which can be easily analyzed quantitatively. In case of some cm blends

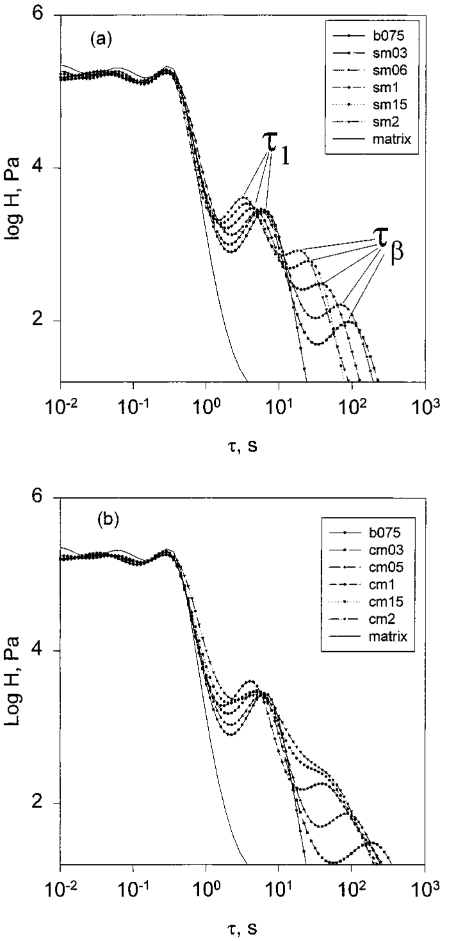

Figure 6. Relaxation time spectra of sm (a) and cm (b) blend series. The lines are drawn to guide the eye.

where no maximum is observed, the relaxation times are derived using a peak fit procedure. The form relaxation process of the neat blend, which is its terminal relaxation process, has a characteristic time $\tau_1 = 6.3$ s. The Palierne model gives an analytical expression for that time τ_1 which depends on the average volume weighted radius of the inclusions, R_v, and the Newtonian viscosity of the matrix material, η_m, and the dispersed material, η_d, and on the interfacial tension, α. With ϕ ($=w_A\rho_A$) the volume fraction of the dispersed phase and k the viscosity ratio η_d/η_m (approximately 0.1 in our case) the following equation holds:[13]

$$\tau_1 = \frac{\eta_m R_v}{4\alpha_0}\,\frac{(19k + 16)(2k + 3 - 2\phi(k - 1))}{10(k + 1) - 2\phi(5k + 2)} \qquad (10)$$

This relation can be used to calculate the form relaxation time. Similar relations have been used by other authors.[9,14,18] With an estimated interfacial tension between PS and PMMA of 2.0 mN/m[5,33] a relaxation time of 6.5 s is calculated for the uncompatibilized blend. This value is in excellent agreement with the relaxation time estimated from the relaxation time spectrum (cf. Table 2). Thus, it can be concluded that this relaxation process is really the form relaxation of the inclusions.

The form relaxation times τ_1 for the compatibilized blends are shifted toward shorter times with increasing copolymer content. Using eq 10 and the form relaxation times determined from the relaxation time spectra, it is possible to calculate the interfacial tension of the compatibilized blends. Contrary to expectations, the interfacial tension increases in this case for both blend series. This result is in contrast to all theoretical findings[37,38] and to the former finding of the dispersing activity of the block copolymer. So, it seems to be that in this case of compatibilization eq 10 is not suitable to describe the influence of block copolymers on the form relaxation process.

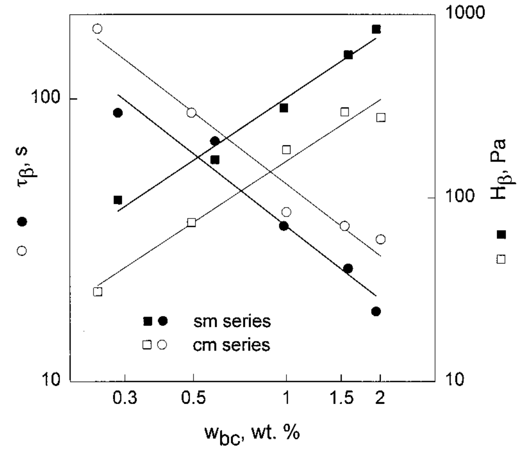

Figure 7. Relaxation time τ_β and relaxation strength H_β of the additional relaxation process as a function of block copolymer concentration for both blend series. The lines correspond to regressions in accordance with eq 11.

The analysis of the relaxation time spectra of the compatibilized blends shows that the form relaxation time is no longer the terminal relaxation process. An additional characteristic relaxation time, called τ_β, is the new feature in the spectra of these blends. The appearance of such a process was first described by the authors.[28] Figure 6 clearly demonstrates the systematic change of τ_β with the amount of block copolymer at the interface. This relaxation time decreases with increasing number of block copolymers whereas the strength of that process, characterized by the height of that peak, increases in the range of considered concentrations. This behavior is displayed for sm and cm blend series in Figure 7 where the regression lines indicate that the following relations hold:

$$\begin{aligned} \tau_\beta &\propto {w_{bc}}^{-b} \\ H_\beta &\propto {w_{bc}}^{c} \end{aligned} \qquad (11)$$

Roughly spoken, the product of both terms is the viscosity of that process contributing to the zero shear viscosity of each blend. Knowing that the viscosity remains unchanged during compatibilization the following relationship between b (=0.9) and c(=1.1) can derived: $b \approx c$. From Figure 7 also follows that all relaxation times τ_β are higher for the cm series in comparison to the sm series.

Now the question arises as to how the observed phenomena, constant blend viscosity, slightly shift of form relaxation times, and the appearance and systematic shift of an additional relaxation time can be interpreted quantitatively. It is important for the further discussion to take into account that a interface which is modified by block copolymers should alter its properties. Besides the isotropic interfacial tension such an interface might be characterized by interfacial elasticity. Palierne[12] for example considered emulsions from such a point of view. In his model, which represents a generalization of Oldroyd's former findings,[7] the interfacial stresses may be nonisotropic and depend on deformation-induced variation of interfacial area in the following way:

$$\alpha_{ij} = \alpha_0\delta_{ij} + \beta_{ij} \tag{12}$$

$$\beta_{ij} = \frac{1}{2}\beta'\gamma_{kk} + \beta''\left(\gamma_{ij} - \frac{1}{2}\delta_{ij}\gamma_{kk}\right) \tag{13}$$

α_{ij} are the components of the interfacial stress tensor, $\alpha_0\delta_{ij}$ is the equilibrium tension arising from the coefficient of isotropic interfacial tension α_0, β' is a surface dilatation module, β'' is a surface shear module, and γ_{ij} are the components of a surface strain tensor. Equation 12 shows that, besides the interfacial tension, an additional contribution (β_{ij}) can be found under shear deformation which is proportional to the interface strain γ_{ij}. Consequently, in a dynamic mechanical experiment, one would measure not only the isotropic interfacial tension α_0 but also an apparent interfacial tension α_{ij} composed of α_0 and β_{ij}. From Oldroyd's analysis of emulsions of viscous components, we know that a constant viscosity and an appearing additional relaxation time during the course of enrichment of interface by surfactants is a hint at a largely elastic interface. Moreover, we will assume that the area of the interface remains unchanged during deformation, and this leads us to the following conditions: $\beta' = 0$ and $\beta'' = \beta_{20}$. If we further assume that in the interesting relaxation region the polymers of the matrix and the inclusions are in their relaxed state (τ_1 and $\tau_\beta \gg \tau_m$ and τ_d) we can derive equations for τ_1 and τ_β from Palierne's model:

$$\tau_1 = \frac{t_2}{2}\left[1 - \left(1 - 4\frac{t_1}{t_2}\right)^{1/2}\right] \tag{14}$$

$$\tau_\beta = \frac{t_2}{2}\left[1 + \left(1 - 4\frac{t_1}{t_2}\right)^{1/2}\right] \tag{15}$$

with

$$t_1 = \frac{\eta_m R_v}{4\alpha_0} \times \frac{(19k + 16)(2k + 3 - 2\phi(k - 1))}{10(k + 1) + \frac{\beta_{20}}{\alpha_0}(13k + 12) - \phi\left[2(5k + 2) + \frac{\beta_{20}}{\alpha_0}(13k + 8)\right]}$$

$$t_2 = \frac{\eta_m R_v}{8\beta_{20}} \times \frac{10(k + 1) + \frac{\beta_{20}}{\alpha_0}(13k + 12) - \phi\left[2(5k + 2) + \frac{\beta_{20}}{\alpha_0}(13k + 8)\right]}{(1 - \phi)}$$

Details concerning the derivation of the equations and the analysis of Palierne's model including viscoelastic properties of the interface will be published elsewhere.[39]

For $\beta_{20} \to 0$, i.e. for the uncompatibilized case, eq 14 turns into eq 10, Graeblings result for an interface characterized by only isotropic interfacial tension. The limit for τ_β is infinity, indicating that this time is moving out of the measuring window. With the above derived equations, it is possible to understand the changes in τ_1 and τ_β in the blends investigtated qualitatively as well as quantitatively.

Using the time constants as determined from the relaxation time spectra, it is now possible to calculate α_0 and β_{20}. The results are displayed in parts a and b of Figure 8 for the sm and cm series, respectively. The error bars of the presented results are a consequence of the assumed relative errors for the determination of R_v of 10%, for t_1 and t_2 of 15%, and for the matrix viscosity of 3%. It can be seen that the interfacial tension of the sm series is decreasing for the first degrees of compatibilization and then bends up. This increase is a consequence of a jump in t_1 values starting with $w_{bc} = 1\%$. The origin of this jump we do not know. The surface shear module increases, indicating that the rigidity of compatibilized particles is increasing. In the case of the cm series we observe the expected monotonic decrease of interfacial tension with increasing degree of compatibilization. Comparing the first two compatibilized samples of both series, we observe a stronger decrease for the cm blends than for the sm series. This qualitative picture is in accordance with our expectations.

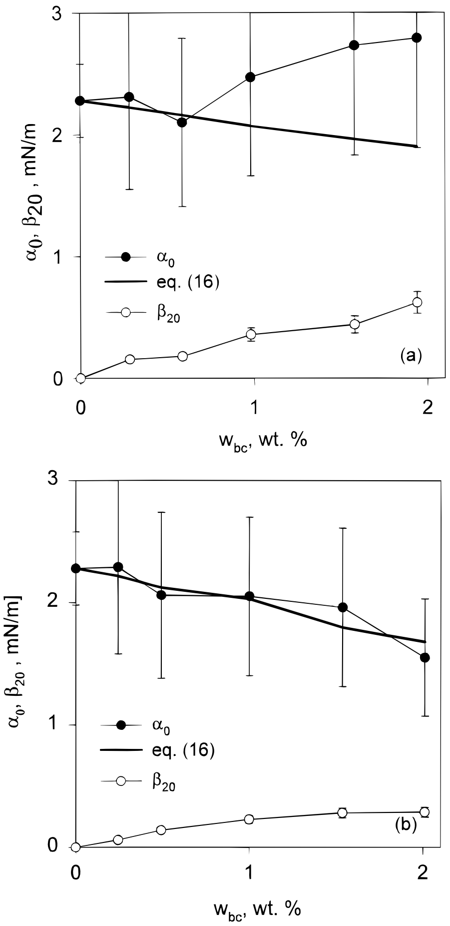

Figure 8. Interfacial tension α_0 and interfacial shear modulus β_{20} in dependence on block copolymer content for sm series (a) and cm series (b). The values are calculated from the extended emulsion model of Palierne. The heavy lines correspond to eq 16.

The appearance of an additional relaxation time and the corresponding surface shear modulus is new, and the dependence of these parameters on molecular characteristics of the block copolymers and block copolymer concentration has been investigated neither experimentally nor theoretically before. Figure 8a shows that β_{20} of the sm series increases from zero to 0.62 mN/m with concentration of compatibilizer and therefore with decrease of the interfacial area per copolymer joint Σ (cf. Figure 4). In the blend with a content of block copolymer of 2 wt % the surface shear modulus reaches nearly 30% of the interfacial tension α_0.

It is obvious that particles in compatibilized blends, if they are deformed by melt blending or other polymer processing techniques, can resist such a deformation better than particles in uncompatibilized blends. This is a consequence of the rigidification of the interface of the dispersed particles. Only if a deformation is applied to the blend and consequently to the interface does the interface shear module come into play and act against the deformation of the interface.

Due to the lack of values of the coefficient of interfacial tension of compatibilized PS−PMMA blends we will compare the experimental values with model predictions. Statistical thermodynamic theories considering the reduction of interfacial tension with copolymer addition have been proposed by Noolandi and Hong[38] and Leibler.[37] Noolandi and Hong found for a symmetric diblock copolymer that the reduction of interfacial tension, $\Delta\alpha = \alpha_0^0 - \alpha_0$, with increasing copolymer molecular weight and concentration, arose mainly from the energetically preferred orientation of the blocks at the interface in order to extend themselves into their respective compatible homopolymers. Leibler suggested a theory of interfacial copolymer segregation where two regimes are defined. Depending on the extent of penetration of homopolymer chains into the copolymer brush at the interface, there may be a dry brush and/or wet brushes. The asymmetric case in which the brush is wet ($P_a < N_a$) on one side of the interface and the brush on the other side is dry ($P_b > N_b$) is called the wet−dry brush case and was analyzed by Dai et al.[40] on the basis of Leibler's brush model. P_{wet} and N_{wet} are the degrees of polymerization of the homopolymer and the corresponding block respectively on the "wet side". All these models do not take into consideration possible enthalpic interactions as is the case for cm series blends. Here we will neglect such effects too and consider the interaction between the PCHMA block and the PS of the inclusions as purely entropic. In this case, all blends introduced belong to the wet−dry brush case with the wet brush located at the outer side of the inclusions. The matrix material, PMMA, has a lower molecular weight than the corresponding block of the diblock copolymer whereas the minor phase material PS has a higher molecular weight than the corresponding PS- and PCHMA- blocks of the copolymers (cf. Table 1). According to Dai et al. and with the notation used in this paper, one derives for the change of the coefficient of interfacial tension the following formula:

$$\alpha_0 = \alpha_0^0 - \frac{k_B T}{a^2}\left[\left(\frac{a^2}{\Sigma}\right)^3 + \left(\frac{a^2}{\Sigma}\right) + \left(\frac{3}{4}\right)^{1/3} \frac{N_{wet}}{(P_{wet})^{2/3}}\left(\frac{a^2}{\Sigma}\right)^{5/3}\right] \tag{16}$$

α_0^0 is the isotropic interfacial tension of the uncompatibilized blend, a is the statistical segment length of the wet brush case polymer (PMMA), and k_B is the Boltzmann constant. Figure 8 displays the fit of eq 16 to the data of α_0 found above. Σ was computed from eq 8 and is displayed in Tables 2 and 3 as well as in Figure 4. The only free parameter in this equation is the segment length, which is found to be 0.8 nm for the sm series and 0.9 nm for the cm series. These values correspond surprisingly well with the value given in the literature for poly(methyl methacrylate),[41] $a = 0.74$ nm, if one takes into account that the experimental results are received from morphological and rheological experiments. Although it was not the aim of this paper to determine the segment length of block copolymers, these results demonstrate the potential of rheological and morphological investigations on these systems. Mainly the results show that the calculation of interfacial tension α_0 of compatibilized blends using eqs 14 and 15 is possible and that the observed numbers are reasonable. We conclude that the values for the interfacial shear modulus β_{20} are reasonable too.

Conclusions

We have shown how the addition of P(S-*b*-MMA) and P(CHMA-*b*-MMA) block copolymers alters the morphological as well as the rheological properties of a PS/PMMA blend whose viscosity ratio (inclusion to matrix) is about 0.1. The morphological analysis gives evidence that with addition of compatibilizers the number concentration of block copolymer molecules at the interface increases from zero for the neat blend up to 0.07 nm^{-2} for the highest degree of compatibilization in case of both blend series. The rheological measurements reveal that besides the form relaxation process characterized by the form relaxation time τ_1, a new, additional relaxation process appears. This process is characterized by the characteristic relaxation time τ_β and is associated with changes of the interfacial properties during compatibilization. In particular, we have shown that this time corresponds to the interfacial shear modulus β_{20}, for which a first estimation is given.

Knowing both relaxation times, it is possible to calculate the interfacial tension and the surface shearing modulus for the compatibilized blends on the basis of Palierne's emulsion model. The observed decrease of interfacial tension and increase of interfacial shear modulus is in qualitative agreement with basic physical principles. Calculated values of interfacial tension from thermodynamical theories are in good quantitative agreement with our findings.

From the experimental observations made, we conclude that the appearance of the additional relaxation time depends first on a sufficient deformability of inclusions and second on entanglement interactions of the outer block of the compatibilizers with the matrix. To verify this hypothesis, experiments with varying molecular weights of the outer block shall be performed. A transition from an elastic interface to a viscoelastic interface should be observable.

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