Reduction of the interfacial tension between 'immiscible' polymers: to which phase one should add a compatibilizer

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Abstract

The reduction of interfacial tension σ between polyethylene oxide (PEO) and polypropylene oxide (PPO) by either a triblock copolymer EO–PO–EO or a diblock copolymer styrene–EO was studied by means of the pendant drop method from 70 to 120°C. Time independent data correspond to stationary states and do not represent equilibrium information. The addition of the compatibilizer to the PPO phase is approximately twice as efficient as the addition to the PEO phase for both block copolymers. Knowing the concentration dependence of σ for one of the coexisting phases it is possible to forecast the effects resulting from the addition of the other phase by means of model considerations based on the partition coefficient of the additive and the ratio of the viscosities of the coexisting phases. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Compatibilizers are widely used in industry to improve the properties of polymer blends. In most cases there is no choice concerning the phase to which such components should be added, due to their 'insolubility' in one of the blend components. However, for some systems homopolymer A/homopolymer B/compatibilizer, the additive is reasonably soluble in both coexisting phases. For such a situation the maximum reduction of interfacial tension may depend on the site of addition. According to Koberstein and coworkers [1] who studied poly(dimethylsiloxane)/polystyrene blends plus a symmetrical diblock copolymer of the homopolymer units, the addition of the compatibilizer to the PDMS phase reduces the interfacial tension considerably more than the addition to the PS phase. The authors discuss these findings qualitatively in terms of the different solubilities of the block copolymer in the two homopolymers, and of the viscosities of the coexisting phases plus their volumes. Since the observed differences in the efficiency of the compatibilizer indicate beyond doubt that at least one set of data cannot represent equilibrium information they postulate the existence of kinetic traps, which hamper the attainment of the absolute minimum in the Gibbs energy of the system.

In view of temperature jump experiments with polymer solutions [2], which have demonstrated that local equilibria are rapidly achieved at the phase boundaries, another more detailed explanation of the above finding might be possible. One option that came to our mind pertains to the establishment of stationary states which differ depending on the phase to which the compatibilizer is added. The present investigation was undertaken to examine this hypothesis. Blends of polyethylene oxide (PEO) and polypropylene oxide (PPO) have turned out suitable for its implementation. One triblock copolymer (made up of the monomeric units of the blend components) and one diblock copolymer (consisting of ethylene oxide and of styrene units) are sufficiently soluble in both coexisting phases. Furthermore, the latter compatibilizer permits the determination of its partition coefficient between the coexisting phases due to the UV absorption of its aromatic block.

We refrain from presenting a complete list of the work done in the field of compatibilizers and restrict ourselves to papers dealing with questions that are directly relevant for the present work. These topics are above all the thermodynamic situations that are typical for mixtures of two homopolymers A and B plus copolymers, the influences of the molecular architecture of the additive on its efficiency, and its partitioning among the bulk phases and the interphase.

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The thermodynamic conditions that a copolymer must fulfil to act as an efficient compatibilizer for a given blend, have been discussed theoretically in great detail on the basis of phenomenological thermodynamics [3–9]. The influence of the molecular architecture of additives on their activity were also studied extensively by self-consistent-field-methods [10–12] as well as by means of Monte Carlo simulations [13–15]. Considerable experimental information on the above two items (sometimes in contrast with theoretical predictions) has accumulated during the past years also [16–19]. Experiments by means of different methods [20–24] circumstantiate a considerable accumulation of efficient compatibilizers at the interface (i.e. an enrichment in the interphase).

2. Experimental

2.1. Materials

The homopolymer blend components are: PEO 10 with $\bar{M}_w/\bar{M}_n = 1.1$, supplied by Fluka, and PPO 4, $\bar{M}_w/\bar{M}_n = 1.4$, from Aldrich. The numbers in the abbreviations of the homopolymers give the weight average molar mass in kg/mol. The information for PEO is based on gel permeation chromatography (GPC) and an evaluation on the basis of universal calibration. Due to the lack of the Kuhn–Mark–Houwink coefficients, the corresponding data for PPO are estimated only. In both cases toluene was the solvent and polystyrenes were used as standards.

The two additives under investigation are the triblock copolymer EO_{92}–PO_{56}–EO_{92} and the diblock copolymer S_9–EO_{22}, where S stands for styrene. The figures of the abbreviations state the numbers of monomer units. The composition of the triblock copolymer (from Polysciences, Inc.) was determined by ^{1}H NMR spectroscopy using literature data [25] for their evaluation. Its polydispersity is $\bar{M}_w/\bar{M}_n = 2.6$ according to GPC experiments. The diblock copolymer was purchased from Goldschmidt AG, Essen, Germany; the characteristic data were supplied by the producer.

The densities of the different polymers, as measured in the temperature range from 70 to 130°C by means of 2 ml pycnometers, are $\rho_{PEO10}/(\text{g cm}^{-3}) = 1.14178$ –0.0006247 t/°C, $\rho_{PPO4}/(\text{g cm}^{-3}) = 1.03465$–0.000123 t/°C, $\rho_{EO92–PO56–EO92}/(\text{g cm}^{-3}) = 1.12602$–0.00102 t/°C and $\rho_{S9–EO22}/(\text{g cm}^{-3}) = 1.15828$–0.00121 t/°C.

2.2. Methods

2.2.1. Interfacial tension measurements

The homopolymers were dried under vacuum at 80°C prior to their use. Blends were prepared by mixing the molten compounds by magnetic stirring for at least 24 h at 80°C. The phase of the higher density (PEO 10) builds the droplet, PPO 4, the compound of lower density, the matrix phase. In case of ternary systems the additive was given to either one of the phases or to both phases.

The interfacial tension $\sigma/\text{mN m}^{-1}$ between the two coexisting liquid phases of the binary or ternary systems was determined by means of the pendant drop method [26–28], the apparatus used for that purpose has already been described in detail [29]. The measurements were carried out from 70 to 120°C in 10°C intervals. For low additive concentrations it was assumed that the density of the homopolymers can be used for the evaluation of the primary data. The typical experimental errors of the interfacial tension measurements are estimated to be 5%.

2.2.2. UV–VIS spectroscopy

The concentrations of the diblock copolymer S_9–EO_{22} in a given polymer mixture were determined by dissolving this blend in a mixed solvent consisting of cyclohexane and ethanol (1:1 w/w) and measuring the peak intensity of the maximum at the wavelength of 259 nm using a ZEISS MCS 320/340 diode-array-spectrometer.

For the determination of the partition coefficient of the diblock copolymer between the coexisting phases of the ternary system we have first established calibration curves for the binary blends PEO/S_9–EO_{22} and PPO/S_9–EO_{22}. Then we have prepared blends of all three components with different amounts of the copolymer up to 10 wt% by stirring for three days at 100°C. After that the coexisting phases were allowed to settle macroscopically at this temperature. In order to detach the coexisting phases, the samples were then cooled to room temperature and their S_9–EO_{22} content was determined by means of the calibration curves.

2.2.3. Viscometry

Shear viscosities, η, of the pure homopolymers were measured with a shear controlled rotational viscometer (Haake CV 100, Karlsruhe, Germany). A coaxial-cylinder geometry (Mooney–Eward ME 15) was used, it has a gap between the static inner cylinder (diameter 13.91 mm, length 12.0 mm) and the rotating outer cup of 0.545 mm. Shear rates up to $\dot{\gamma} = 300 \text{ s}^{-1}$ can be attained. In this range the homopolymers are Newtonian. The measurements were carried out from 65 up to 80°C in intervals of 5°C. The shear viscosities at 80°C are $\eta_{PEO} = 0.153 \text{ Pa s}$ and $\eta_{PPO} = 0.120 \text{ Pa s}$. At 65°C these values read 0.227 and 0.187 Pa s, respectively.

3. Results and discussion

In the first two paragraphs we present experimental data for the reduction of the interfacial tension by two types of compatibilizers as a function of temperature, concentration and site of addition. The mathematical representation of the concentration dependence of the interfacial tension σ is performed in terms of the equation of Tang and Huang [30]

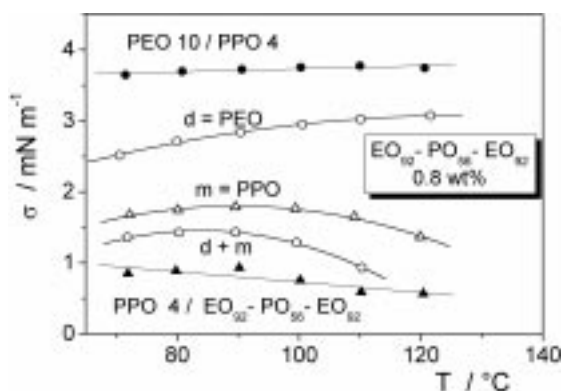$$\sigma = (\sigma_o - \sigma_s)\, e^{-w/w^*} + \sigma_s \tag{1}$$

Fig. 1. Temperature dependence of the interfacial tension σ for the binary polymer blend PEO 10/PPO 4 in the absence and in the presence of the compatibilizer $EO_{92}-PO_{56}-EO_{92}$. Three different situations are distinguished in the latter case: addition of the block copolymer to one phase only or to both phases, where the concentrations were in all cases kept constant at 0.8 wt%. Also shown in this diagram is the interfacial tension for the binary subsystem PPO 4/$EO_{92}-PO_{56}-EO_{92}$.

σ_o is the interfacial tension of the binary system PEO 10/PPO 4 and σ_s is the lowest possible (saturation) value that can be accomplished by the addition of the compatibilizer; w represents the weight fraction of the additive and w^* is a characteristic value quantifying the amount that is required to realize a certain reduction in σ. An evaluation according to Langmuir [31,32] is also possible with comparable accuracy and yields practically identical results.

The different features of the two compatibilizer under consideration are compared and discussed in the third section. In order to rationalize the observed differences in the efficiency of the compatibilizers, depending on the site of addition, we present some model considerations in terms of distribution coefficients and stationary states in the last section.

3.1. PEO/PPO + EO–PO–EO

The interfacial tension between the components of the homopolymer blend is comparatively high, manifesting the pronounced incompatibility of the components, and
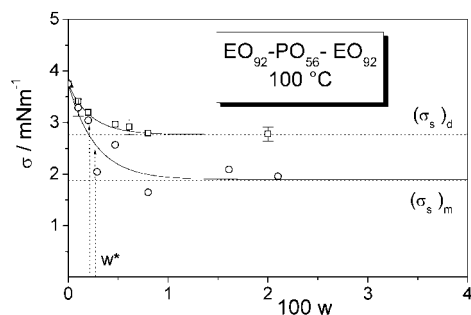

Fig. 2. Interfacial tension between PEO 10 and PPO 4 at 100°C as a function of the concentration of $EO_{92}-PO_{56}-EO_{92}$, where the compatibilizer is either added to the droplet or to the matrix phase only. The lines are drawn according to the relation of Tang and Huang by adjusting the constants.

does within experimental error not depend on temperature. In contrast to that situation σ of the binary subsystem made up of the compatibilizer and PPO decreases markedly as T rises. Although one observes some reduction of the interfacial tension for low concentration of the triblock copolymer in the droplet phase, the effects remain small as compared with its addition to the matrix phase. In that case a concentration of only 0.8 wt% suffices to reduce the interfacial tension of the ternary system to a value which would result from a linear interpolation for more than 60 wt% of the additive. Temperature influences the effects considerably more than if the compatibilizer is added to the droplet.

A direct comparison of the reduction of the interfacial tension associated with a certain constant concentration of the compatibilizer in either of the phases or in both is presented in Fig. 1. According to these data the effect is expectedly largest if the triblock copolymer is added to both phases. However, even this procedure does not guarantee that the interfacial tension measured under such conditions represents an equilibrium quantity.

In order to obtain quantitative information on the efficiency of different additives one normally measures σ as a function of their concentration at constant temperature. The evaluation of these data according to Eq. (1) yields σ_s, the lowest attainable interfacial tension, and w^*, a characteristic weight fraction, which decreases with increasing efficiency of the compatibilizer. Fig. 2 shows this evaluation for the addition of $EO_{92}-PO_{56}-EO_{92}$.

3.2. PEO/PPO + S–EO

How the diblock copolymer reduces the interfacial tension at different concentrations and temperatures if added to either the droplet or the matrix is shown in Fig. 3 and in Fig. 4. From these graphs it becomes obvious that this compatibilizer, containing styrene segments that interacts unfavorably with both blend components, is in its efficiency even superior to the triblock copolymer consisting of EO and PO segments only, despite its considerably lower overall chain length. Again the interfacial tension of the binary subsystem additive/PPO decreases markedly with rising temperature. Except for the lowest concentration in the droplet phase this is also true for the ternary system.

The high efficiency of diblock copolymer manifests itself by the fact that 0.8 wt% of S_9-EO_{22} suffice, if added to the matrix, to reduce the interfacial tension between the coexisting phases almost to the values of the binary system PPO/S–EO, as demonstrated in Fig. 5. This situation is again quantified (cf. Fig. 6) in terms of the concentration dependence of σ measured at 90°C and evaluated according to Eq. (1).

3.3. Comparison of the compatibilizer efficiencies

The characteristic features of the triblock and the diblock copolymers as compatibilizers for PEO and PPO, if added to
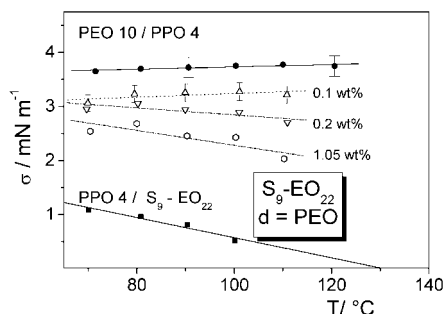
Fig. 3. Temperature dependence of the interfacial tension σ for the binary polymer blends PEO 10/PPO 4 and for different constant concentrations of the compatibilizer $S_9–EO_{22}$, exclusively added to the *droplet phase*.

Fig. 5. Temperature dependence of the interfacial tension σ for the binary polymer blend PEO 10/PPO 4 in the absence and in the presence of the compatibilizer $S_9–EO_{22}$. Two different situations are distinguished in the latter case: addition of the block copolymer to either the droplet phase or to the matrix phase only, where the concentrations were in both cases again kept constant at 0.8 wt%. For comparison the interfacial tension of the binary subsystem PPO $4/S_9–EO_{22}$ is also shown in this diagram.

one of the phases of the blend only, are compared in terms of σ_s, the maximum reduction of the interfacial tension at different temperatures. In principle such a judgment could also be performed on the basis of w^*. This quantity is, however, normally accessible with much less accuracy only because of experimental difficulties in realizing the required low concentrations and the limited numbers of data points in the highly dilute regime. With the present compatibilizer all w^* values lie within the interval 0.001– 0.0025 and scatter considerably.

Fig. 7 illustrates how the lowest interfacial tensions that can be achieved by adding a surplus of the additives exclusively to either the droplet or to the matrix phase changes with temperature. According to this graph the efficiency of $EO_{92}–PO_{56}–EO_{92}$ and of $S_9–EO_{22}$ is practically identical, if added to the PEO phase and the effects do not change noteworthy with temperature. An analogous statement for the addition of the compatibilizers to the PPO phase (where they are considerably more operative) only holds true in the region of low temperatures. Above approximately 80°C the diblock copolymer becomes considerably more efficient than the triblock copolymer. This fact could already be seen very clearly from a comparison of Figs. 1 and 5, where the interfacial tension falls to almost that of the subsystem $PPO/S_9–EO_{22}$ for an additive concentration of only 0.8%, which means that the interface is obviously already completely covered by the compatibilizer under
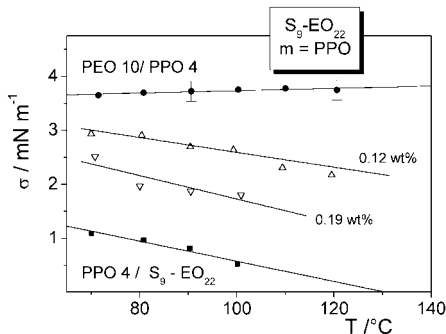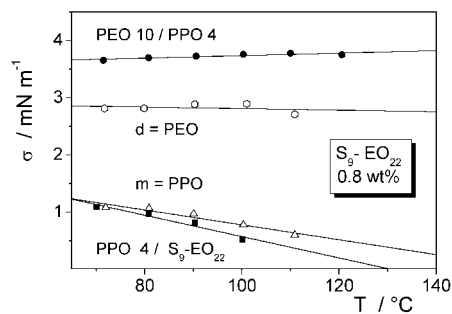
these conditions, in contrast to the situation with $EO_{92}–PO_{56}–EO_{92}$, where the reduction of σ is considerably less pronounced.

3.4. Model considerations

For the further discussion we require the partition coefficient K of the compatibilizer between the droplet phase (PEO) and the matrix phase (PPO). For simplicity it is defined in terms of weight fractions as

$$K = \frac{w_d^e}{w_m^e} \qquad (2)$$

We have therefore measured the corresponding equilibrium concentrations w^e of $S_9–EO_{22}$ and evaluated these results as shown in Fig. 8. According to these data K amounts to 1.82 at 100°C and signifies a considerable preference of the diblock copolymer for the PEO phase.

Based on this information we can sketch the concentration profiles of the compatibilizer across the phase boundary in case a certain constant concentration ($w \gg w_d^*, w_m^*$) is at time zero either implemented for the droplet phase (left hand side of Fig. 9) or for the matrix phase (right hand
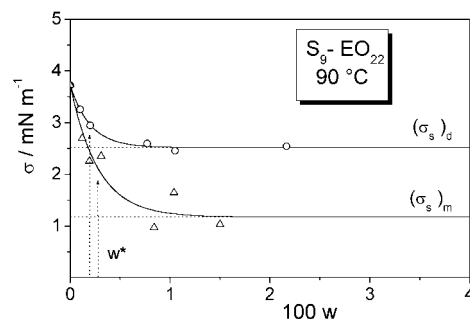

Fig. 4. Like Fig. 3, but for the exclusive addition of the compatibilizer to the *matrix phase*.

Fig. 6. Interfacial tension between PEO 10 and PPO 4 at 100°C as a function of the concentration of $S_9–EO_{22}$, adding the compatibilizer either to the droplet or to the matrix phase. The lines are drawn according to the relation of Tang and Huang by adjusting the constants.
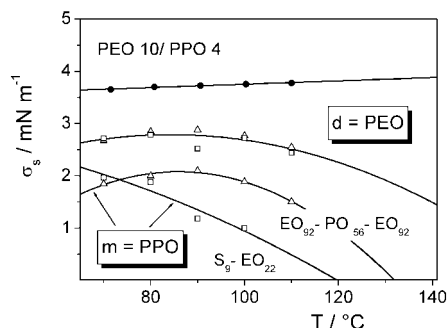
Fig. 7. Temperature dependence of σ_s for the exclusive addition of the compatibilizers to either the droplet or the matrix phase. The triangles stand for $EO_{92}–PO_{56}–EO_{92}$ and the squares for $S_9–EO_{22}$.

side of Fig. 9), keeping the coexisting second phase free of the additive. In this graph the bulk phases are separated by an interphase, designated by τ and the concentrations change abruptly at its interfaces. The dotted lines portray the equilibrium situation for an infinite predominance of the feed phase (copolymer containing phase) as compared with the initially empty receiving phase. According to the partition coefficient of the compatibilizer the equilibrium concentration in the coexisting phase for a given constant starting concentration in the feed phase is higher by a factor of four than in the opposite case. Furthermore the extent of its enrichment in the interphase differs considerably. For the present drawing we have set $w_d/w_m = 2$ and estimated $w_\tau/w_m = 3.15$, where the corresponding partition coefficient w_τ/w_d between the interphase and the droplet phase is given by the condition $K = w_\tau w_d/w_m w_\tau$.

According to the generally accepted correlation between the accumulation of an additive in the interphase and its efficiency, $S_9–EO_{22}$ should be much more helpful for a reduction of σ if added to the matrix phase. For an infinite preponderance of the feed phase these considerations could already explain the present experimental findings. However, in reality we are always dealing with macroscopic receiving phases, which means that the compatibilizer must be transported into the interior of the coexisting second bulk phase
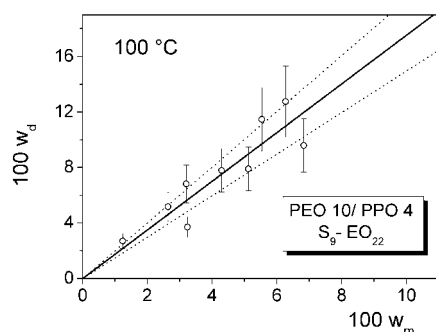

Fig. 8. Equilibrium concentration of $S_9–EO_{22}$ in the PEO-rich phase as a function of its concentration in the PPO-rich phase at 90°C. The experimental errors are estimated to be 20%, the dotted lines show the upper and lower confidence intervals of 95%.

from the micellar reservoir of the feed phase. The attainment of thermodynamic equilibria thus appears extremely unlikely.

From the fact that the measured interfacial tensions become independent of time after typically 12–24 h and that we have never been successful to observe changes thereafter, even when waiting for more than one week, we postulate the attainment of stationary states. How the concentration profiles could look like under these conditions is illustrated in Fig. 9 by full lines. Based on the already mentioned rapid establishment of local equilibria [2], the jumps in the concentration of the compatibilizer at the phase boundaries is again drawn according to the corresponding partition coefficients. Within the interphase and the receiving bulk phase we assume an exponential decay. The basic features discussed for the equilibrium case remain valid: As demonstrated by the shaded areas of the graphs, the average stationary concentration of the compatibilizer within the interphase results considerably higher when initially added to the matrix phase than to the droplet phase.

A rigorous treatment of the stationary accumulation of the compatibilizers in the interphase would require a detailed calculation of the fluxes into the interphase and out of it for both situations. An essential preparatory work for such a modeling has very recently been reported [33] by the group of Koberstein for poly(dimethylsiloxane)/polystyrene blends plus a symmetrical diblock copolymer of the homopolymer units; it studies the segregation dynamics of the additive to the interface. The authors distinguish between three different kinetic processes and report that approximately 4 h are required to reach constant shapes of the droplet phase. This time requirement agrees well with the present findings.

For the time being we restrict ourselves to some preliminary plausible considerations concerning the establishment of different stationary states upon the addition of the compatibilizer to either the PEO or the PPO phase. For the concentration range of the additive in the feed phase i between the critical micelle concentration and the concentration at which σ becomes independent of w_i, we assume that $\langle w_{\tau s}\rangle_i$, the average stationary concentration in the interface, is directly proportional to the corresponding equilibrium concentration w_j^e in the receiving phase j and indirectly proportional to its viscosity η_j. The first assumption rests on the fact that the thermodynamic driving forces and thus the flux increase with an augmentation of the desired concentration in the receiving phase, and the second accounts for the damming back of the compatibilizer in the interphase as the viscosity of the receiving phase increases. We can thus write

$$\langle w_{\tau,s}\rangle_i \propto \frac{w_j^e}{\eta_j} \tag{3}$$

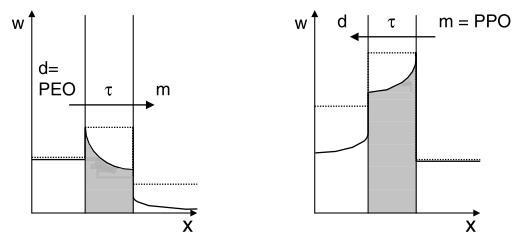Since we have presupposed the following proportionality

Fig. 9. Scheme of the concentration profile of the compatibilizer, added to a binary polymer blend, across the interface under equilibrium conditions (dotted lines) and in the stationary state (full lines). The droplet phase is denoted by d, the interphase by τ and the matrix phase by m. Under equilibrium conditions the compatibilizer distributes between the two coexisting bulk phases according to its equilibrium constant. For the present picture we have set $w_d/w_m = 2$ and $w_\tau/w_m = 3.15$. Furthermore we have simplified the changeover to the higher concentrations in the interior of the interphase by step functions. The two parts of the sketch portray the steady states resulting from the addition of the compatibilizer (identical concentration) to one of the bulk phases only.

for limiting interfacial tension under stationary conditions

$$\sigma_s \propto \frac{1}{\langle w_{\tau,s} \rangle} \qquad (4)$$

we end up with the following expression for ratio of limiting interfacial tension under stationary conditions realized upon the addition of the compatibilizer either to the droplet or to the matrix phase, assuming that the proportionality coefficients are identical for the two cases

$$\frac{(\sigma_s)_d}{(\sigma_s)_m} = \frac{\langle w_{\tau,s} \rangle_m}{\langle w_{\tau,s} \rangle_d} = \frac{w_d^e}{w_m^e} \frac{\eta_d}{\eta_m} = K\lambda \qquad (5)$$

where K is the partition coefficient and λ the viscosity ratio of the coexisting phases.

In order to check the validity of Eq. (5) for the description of the experimental results presented in Fig. 6, we have inserted $(\sigma_s)_m$, the saturation interfacial tension for the addition of the compatibilizer to the matrix phase, and calculated $(\sigma_s)_d$ by means of the measured partition coefficient and viscosity ratio. For λ we have used an extrapolated value
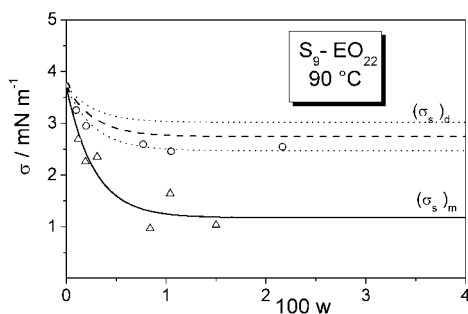

Fig. 10. Forecast of the reduction of the interfacial tension between PEO 10 and PPO 4 at 90°C as a function of the concentration of the compatibilizer in the droplet phase (no additive in the matrix phase) by means of measurements for the inverse situation (additive in the matrix phase only) plus the knowledge of the partition coefficient of S_9–EO_{22} according to Eq. (1). The two thin lines result if $K\lambda$ is varied by $\pm 10\%$.

of 1.257 at 100°C. Inserting this value into Eq. (1) and neglecting possible differences in x^* for the two types of experiments yields the prediction for the concentration dependence of σ in case the compatibilizer is exclusively added to the droplet phase shown in Fig. 10. In view of the theoretical simplifications and experimental uncertainties in the determination of K and λ, the agreement appears surprisingly good.

4. Conclusions

The present experimental results confirm earlier literature report [1] according to which the time independent interfacial tensions of a polymer blend plus a compatibilizer (both components are to a certain extent miscible with the additive) differ considerably depending on the phase to which the compatibilizer is added. Only one of them can possibly represent an equilibrium. With the present system this is very likely true for some of the lower interfacial tensions realized upon the addition of S_9–EO_{22} to the matrix phase of PPO. An example for that situation is given in Fig. 5, where only 0.8 wt% suffice to lower σ down to approximately the value of the binary subsystem S_9–EO_{22}/PPO. In molecular terms this finding can be interpreted as a total disguise of the interphase by the compatibilizer, which cannot be surpassed, and which should therefore represent an equilibrium.

According to the model considerations outlined in the last section, the considerably more prominent enrichment of the compatibilizer in the interphase, i.e. its higher efficiency, when added to the matrix phase of PPO, reflects the larger additive concentrations in the interphase, which in turn result from larger thermodynamic driving forces and more pronounced back-damming. The conclusion that can be drawn from the present findings for industrial processes (disregarding effects of largely different phase volumes for the time being) is the following: in order to achieve the highest possible reduction of the interfacial tension by means of a given amount of compatibilizer, it should be added to the phase with the lower affinity to this component. In that manner the stationary interfacial tension becomes minimum. In line with these ideas it would appear worthwhile to investigate, whether compatibilizers that are soluble in one of the phases only could be more efficiently applied in form of their (two phase) suspension in the other coexisting phase.

Although the present considerations cannot be applied to polymer blends plus a compatibilizer that dissolves in one of the coexisting phases only (a comparison of σ for equal starting concentrations in the coexisting phases is impossible), it appears justified to ask, whether the wealth of data reported for such systems represents equilibrium information or corresponds to stationary conditions only. Although this question cannot be answered rigorously at the moment, it appears reasonable to assume that the differences between the

stationary states preceding the achievement of equilibria and the equilibrium itself should remain within experimental uncertainty, due to the extremely low equilibrium concentration in the receiving phase in combination with a pronounced preference of the compatibilizer for the interphase.

Acknowledgements

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