Macromol. Symp. ***139****, 87–92 (1999)*

Interfacial Tension Between Polymer-containing Liquids – Predictability and Influences of Additives

B.A. Wolf

Institut für Physikalische Chemie der Universität Mainz
Welder-Weg 13, D-55099 Mainz, Germany

Abstract: The first part of the contribution deals with the interfacial tension, σ, of phase-separated polymer solutions in single or mixed solvents and of binary polymer blends as a function of the relative distance to the critical temperature of the system, special attention being paid to the possibilities of theoretical prediction. Two methods are discussed in more detail. One is based on a realistic description of the Gibbs energy of mixing as a function of composition, the second correlates σ with the length of the measured tie line. The second part is devoted to another aspect, namely the effects of additives on the interfacial tension between the coexisting phases of demixed polymer solutions and between highly incompatible polymers. In the former case, it is demonstrated that an addition of a thermodynamically good solvent is normally associated with a reduction in σ; however, adding a high-molecular-weight compound which is incompatible with the dissolved polymer leads to an increase in σ. The interfacial tension between incompatible homopolymers is efficiently reduced by block copolymers consisting of monomeric units which are either identical with or different from those of the homopolymers; in contrast to theoretical expectation, the molecular architecture of the additives seems to be of minor importance only. Random copolymers which are insoluble in the homopolymers can also efficiently reduce the interfacial tension.

INTRODUCTION

Since approximately five years ago, we have been engaged in the study of interfacial phenomena. The present contribution gives a compilation and analysis of the results obtained in the two areas named in the subtitle. The work of the colleagues who have laid the scientific ground for these investigations is cited in the references, which also name the coworkers who carried out the work reported here. All measurements were performed by means of the spinning, sessile and pendant drop methods.

PREDICTABILITY

In view of the relevance of the interfacial tension σ for technical applications of polymers and the fact that accurate measurements of this quantity require considerable experimental scrutiny, it would be very useful to predict σ either from suitable theories or at least from semiempirical relations. We have therefore tried to find ways for such predictions.

CCC 1022-1360/99/$ 17.50+.50/0

In one approach we have introduced ε, the reduced hump energy, as the area between $\Delta\overline{\overline{G}}/RT$, the reduced segment molar Gibbs energy of mixing as a function of composition and the double tangent to that curve, which fixes the composition of the coexisting phases. According to phenomenological considerations, this quantity should be closely correlated with the interfacial tension[1,2]. The evaluation of the entire accessible experimental material concerning σ and ε of phase-separated polymer solutions indeed results in a scaling law of the form $\sigma = E\varepsilon^F$, where F is close to 0.5 for all systems whereas E varies markedly. Similarly, ε depends on τ, the relative distance from the critical temperature, according to $\varepsilon = A\tau^B$, where B is approximately 2.4 and relatively constant, in contrast to A. According to a more detailed analysis of the situation, the constants A and E of the relations formulated above are not universal[2], contrary to some theoretical expectation.

In spite of this deficiency, the scaling laws provide the means for a rough prediction of σ as a function of temperature from the sole knowledge of the critical point of the system. Using a two-parameter equation to describe the concentration and temperature dependence of the Flory-Huggins interaction parameter, it is possible to calculate the reduced hump energy by means of the critical data. The temperature for which one wants to know σ is then expressed in terms of τ and yields ε, which in turn is converted into σ; notwithstanding the uncertainties in A and E, this prediction is normally better than that based on a direct correlation of (concentration-independent) Flory-Huggins interaction parameters and interfacial tensions.

In an older approach[3,4], we have established a master curve linking σ to $\Delta\varphi$, the length of the corresponding tie line (expressed in terms of volume fractions φ). For phase-separated solutions of polystyrenes and similar macromolecules, the relation reads σ (mN/m) = 0.015 $M^{0.5}\Delta\varphi^{3.85}$, where M is the molar mass of the polymer. The application of the just formulated master curve to molecularly non-uniform polymer samples provides a simple means to grasp the effects of polydispersity[5]. This accounts for the fact that the σ remains finite within a limited interval of negative τ values (i.e., at $T >$ UCST or $T <$ LCST) as a result of the molecular non-uniformity of the polymer. The outlined correlation of σ and $\Delta\varphi$ also works with ternary systems, as demonstrated for solutions of poly(acrylic acid) in mixed solvent consisting of water and propan-2-ol. In this case, a much larger range of σ and lengths of tie lines is experimentally accessible and the resulting exponent of $\Delta\varphi$ is 4.23.

With polymer blends, it is normally impossible to measure σ close to the critical region due to problems in the attainment of equilibria resulting from high viscosity of such mixtures and very similar densities of the coexisting phases. In order to circumvent these difficulties, we have studied blends of different poly(siloxane)s; these substances exhibit very low glass-transition temperatures and are rather fluid. With them, interfacial tensions could be measured for the first time in the vicinity of the critical temperature[6]. It is possible to describe the observed dependence of σ on τ or $\Delta\varphi$ (as shown in Fig. 1), within experimental error, by both the mean field theory and the Ising-3D model.

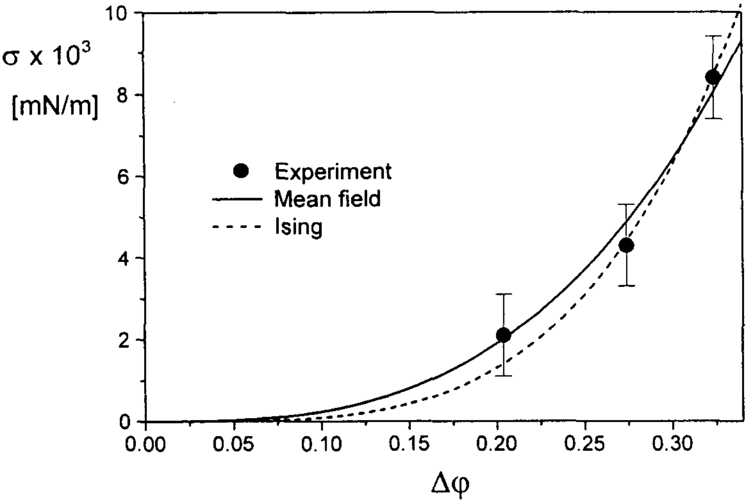

Figure 1: Interfacial tension for mixtures of poly(dimethylsiloxane) (M_w=3 kg/mol) and poly[hexyl(methyl)siloxane] (M_w=113 kg/mol), as obtained by the spinning drop method and theory[7].

ADDITIVES

The sensitivity of the interfacial tension between polymer-containing liquids to small amounts of additives is well established and of technical importance. For a better theoretical understanding of these phenomena, we have studied the effects of low- and high-molecular-weight additives on σ for such binary mixtures of limited mutual solubility.

The effects resulting from an addition of a third component to a phase-separated binary system are normally rather different, depending on its low- or high-molecular-weight nature. An addition of a thermodynamically good (low-molecular-weight) solvent to a demixed polymer solution *reduces* the interfacial tension. Analogously, σ of an incompatible polymer blend becomes smaller as one adds a low-molecular-weight solvent which is completely miscible with both high-molecular-weight components[8]. The situation becomes more complicated if the solvent is good only for one of the polymers but bad for the other; in this case, σ may pass a minimum as the composition of the mixed solvent changes[8].

The addition of a second high-molecular-weight component to a phase-separated polymer solution results in fundamentally different effects. For such systems, it could be shown[9] that the incompatible polymers *increase* the interfacial tension markedly. In terms of the correlation between σ and $\Delta\varphi$ discussed above, this finding can be easily rationalized as an extension of the miscibility gap by the addition of the second polymer, i.e. as a lengthening of the tie line.

As already indicated, measurements with polymer blends are normally possible only far from the region of complete miscibility. We have therefore investigated[10,11] the effects of additives for the system poly(dimethylsiloxane)/poly(ethylene oxide) at temperatures ranging typically from 70 to 150 °C. Two families of block copolymer additives were studied. With type I, the blocks consisted of the monomeric units of the corresponding homopolymers; these additives were varied in their molar mass and molecular architecture. Type II comprised diblock copolymers composed of monomeric units which differ from those of the homopolymers.

In all cases, σ was substantially lowered; for type I additives, the effects range typically from ca. 10 mN/m to 1-4 mN/m when only 0.2 wt.-% is added to the poly(ethylene oxide) phase. The dependence of σ on composition was studied in terms of the x^*_{add}, the base mole fraction of the additive in the droplet phase, i.e. the number of monomeric units contained in the additive divided by the total number of monomeric units. The function $\sigma(x^*_{\mathrm{add}})$ can be well described by two parameters: by σ_s, the saturation value of σ for large amounts of the additive, and x^*_{charact}, measuring its efficiency. The results demonstrate that the total number of dimethylsiloxane units the type I additives contain is more decisive for their efficiency than their architecture (di-, tri- or multiblocks); this finding is in contrast to theoretical expectation.

One observation deserves special notice. In the cases in which the additive is markedly soluble in both phases, it can make a big difference for the measured interfacial tension to which the substance is added[12]. We are presently investigating this phenomenon in more detail.

The copolymers of type II we have studied are considerably less effective than those of type I as demonstrated in Fig. 2 for an example.

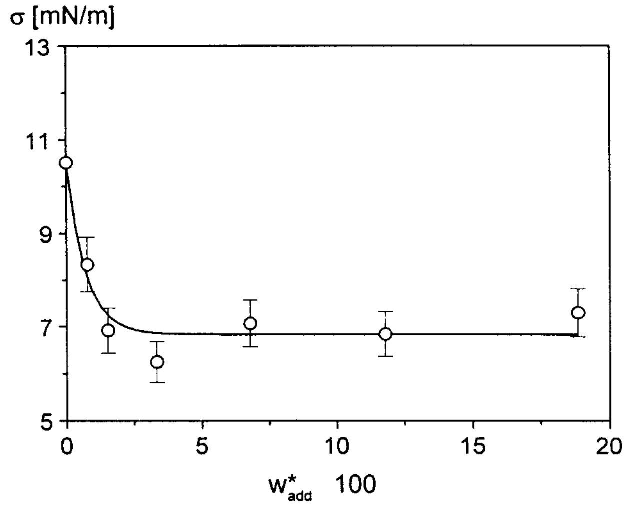

Figure 2: Variation of the interfacial tension at 100 °C between poly-(dimethylsiloxane) (M_w=177 kg/mol) and poly(ethylene oxide) (M_w=41 kg/mol) upon the addition of a diblock copolymer of styrene (75 monomeric units) and methyl methacrylate (110 monomeric units). (w_{add}* is the base mole fraction of the additive in the poly(ethylene oxide) phase).

In view of some drawbacks of block copolymers (like their tendency to form micelles or their slow migration to the interface) and of theoretical interest, we have also begun[13] to study the efficiency of random copolymers. This work was performed with a highly incompatible blend of poly[methyl(phenyl)siloxane] and poly(dimethylsiloxane) where the random copolymer contained 11 mol-% of the former and 89 mol-% of the latter monomeric units. Approximately 1 wt.-% of the additive reduces σ from ca. 2.2. to 1.6 mN/m. It is interesting to note that two different kinetic processes are observed during equilibration of the system. They are tentatively ascribed to the interdiffusion of the components in the vicinity of the phase boundary and to the hydrodynamic relaxation of the droplet. Concerning the efficiency of random copolymers, we conclude that these substances are active exclusively if they are only sparingly soluble in both components of the blend.

ACKNOWLEDGEMENT

We are grateful to the "Materials Science Research Centre of the University Mainz" for financial support.

REFERENCES

1. S. Enders, A. Huber, B.A. Wolf, *Polymer* **35**, 5743 (1994)
2. S. Enders, B.A. Wolf, K. Binder, *J. Chem. Phys.* **103**, 3809 (1995)
3. M. Heinrich, B.A. Wolf, *Polymer* **33**, 1926 (1992)
4. Z. Tong, K. Meissner, B.A. Wolf, *Macromol. Chem. Phys.* **196**, 521 (1995)
5. M. Heinrich, B.A. Wolf, *Macromolecules* **25**, 3817 (1992)
6. A. Stammer, B.A. Wolf, *Polym. Commun.*, submitted.
7. A. Stammer, Ph.D. Thesis, Mainz 1997
8. M. Wagner, B.A. Wolf, *Macromolecules* **26**, 6498 (1993)
9. A. Schneider, B. A. Wolf, *Macromol. Rapid Commun.* **18**, 561 (1997)
10. M. Wagner, B.A. Wolf, *Polymer* **34**, 1460 (1993)
11. U. Jorzik, B.A. Wolf, *Macromolecules* in press
12. I. Welge, M.S. Thesis, Mainz 1997
13. A. Stammer, B.A. Wolf, *Macromol. Rapid Commun.* **19**, 123 (1998)