Enthalpic interaction of diblock copolymers with immiscible polymer blend components

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SUMMARY

An attempt is made to extend the model of Leibler for the emulsifying activity and interfacial properties of A-b-B diblock copolymers in incompatible blends of the homopolymers A and B - which are identical with the respective copolymer components - to enthalpically interacting C-b-D diblock copolymers, the block C being thermodynamically compatible with A and D with B. Due to the attractive enthalpic interaction the **A/C-b-D/B** compatibilized blends are promising for optimum phase adhesion (bold types for thermodynamically compatible partners). Thus, the extended model for a plane interfacial layer includes the enthalpic interaction of the compatible polymer pairs beside the entropic effects. The approach starts with the equilibrium supposition, not taking into consideration enthalpy driven migration effects of the block copolymer from the bulk to the interface. The model confirms a dominant role of the enthalpic interaction between blocks of the diblock copolymer and the respective homopolymers to the compatibilization of incompatible blend components. It is applicable also for blends compatibilized with block copolymers of unfavourable repulsive type interaction, A/C-b-D/B, and for blend systems with mixed type interactions, e. g. **A/C**-b-B/B or A/C-b-**D/B**.

INTRODUCTION AND PROBLEM

The essential question related with the compatibilization of multiphase polymer blends is how to design the compatibilizing agent for maximal efficiency. In contrast to low molecular weight emulsions, in macromolecular systems not only minimum interfacial energy and maximum dispersion, consequently, has applicational relevance. Efficient adhesion is asked because only in this way energy may be transfered from one phase to the other. This is evident, for instance, for a high impact blend where a thermoplastic glassy polymer is combined with a rubber.

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(I) - The classical way to emulsify the system and to realize an effective adhesion between the two immiscible phases is the use of diblock copolymers - A-*b*-B - with blocks identical with the respective components - A and B - of the blend to be compatibilized [1-4]. Provided the blocks of the copolymer exceed the respective entanglement length, they anchor in 'their' pertaining bulk phase, yielding by compatibilization not only a relatively stable, fine dispersed morphology, but also enhanced mechanical properties due to the effective phase connection [5-6]. The type and the strength of the cohesion of a block in 'its' blend component corresponds to that within the pure blend milieu, which typically may be glassy or semi-crystalline. The synthesis of sufficiently long block copolymers, however, may be crucial in many cases.

(II) - Thus, in order to compensate a lack of entropic by enthalpic interaction, it is attractive to substitute copolymers with blocks identical with the respective blend partners by shorter block copolymers - C-*b*-D - with blocks thermodynamically compatible with the blend components. In spite of some experimental evidence in this field [7-10] the question of the efficiency of this type of compatibilization - **A**/C-*b*-D/**B** (bold types for compatible partners) - is still under discussion. It has been shown, however, that the rheological efficiency in A/A-*b*-**D**/**B** is superior to that of the A/A-*b*-B/B system [11]. It seems plausible that interacting blocks - C or D in C-*b*-D - may be shorter than A or B in A-*b*-B, because their favourable, *attractive interaction* with the blend partners - A and B - is superior.

(III) - Recently, Vilgis et al. reported on a *'universal emulsifier'*, which just inverts the situation concerning enthalpic interaction: They have shown [12] that even unfavourably interacting - *repulsive type* - block partners of a chemical structure, C-*b*-D, different from that of the blend polymers - A and B - are migrating from the bulk phases towards the interface, reducing the interfacial tension and promoting the dispersion degree. Because of lack of attractive interaction with their blend partners, the phase adhesion with such type of blocks should be inferior in the corresponding A/C-*b*-D/B systems than in those discussed before.

It is evident that a more detailed study of the enthalpic type **A**/C-*b*-**D**/**B** compatibilized blends may be useful with respect to the high applicational relevance of phase adhesion. Consequently, an attempt for a phenomenological description of this problem is given in the following, with inclusion of A/C-*b*- D/B systems.

In literature there are essentially two types of approaches to attack the problem of compatibilization of thermodynamically incompatible polymer partners:

(i) - The *'static model'* : One starts with the equilibrium situation, with the block copolymer situated at the interface of the blend components.

(ii) - In the *'dynamic model'* the effect of the enthalpy driven migration of the block copolymer from the bulk phases towards the interface and its consequences to the interfacial tension are taken into account.

Both of the approaches are not elaborated up to now for enthalpically inter-

acting **A/C**-*b*-**D/B** type systems or for those which exhibit different types of inter-actions for both blocks, A/A-*b*-**D/B** or **A/C**-*b*-B/B.

(i) - Leibler [13] has discussed some thermodynamic aspects of the interfacial and emulsifying activity of A-*b*-B diblock copolymers in the incompatible blend of the components A and B. He assumed the interlayer between the incompatible polymers as a plane interface (a wall) to which the diblock copolymer is attached, so that each of the two blocks extends into his pertaining bulk phase. Considering only one of the sides of this interface, the picture resembles to the concept of de Gennes' *'polymer brushes'* [14], i. e. a polymer chain grafted with the one end to a rigid wall. Starting with this *static model*, Leibler has calculated the free energy of the A/A-*b*-B/B system, taking into account the contributions of the entropy of mixing, of repulsions and of the elastic stretching of the brushes, which takes place in *wet brushes*.

(ii) - Another more complex *dynamic approach* was derived by Noolandi et al. [12, 15-16] within the framework of statistical thermodynamics. Again for the simple system A/A-*b*-B/B he accounts for the effect of migration of the diblock copolymers from the bulk to the interface and the orientation of the blocks into their respective bulk phases. The migration of the block copolymer itself is enthalpy driven: In the A as well as in the B bulk phase the respective incompatibe block either induces the migration towards the interface, or micelles are built up (self-organization). The effect of the migration is an increasing reduction of the interfacial tension. Also the case of unfavourably interacting *repulsive type* block systems [12] - A/C-*b*-D/B, as cited before - has been studied in the *dynamic approach*. Such 'inert' block copolymers will show a pronounced tendency to self-organisation, to form micelles.

We decided to extend the simple *static model* of Leibler to enthalpically interacting **A/C**-*b*-**D/B** systems not only because of mathematical simplicity. With respect to applicational relevance we argue that for the assumed final situation, i. e. with the block copolymer already at the interface, a contribution due to migration from the bulk to the interface is relevant with respect to dispersion primarily, not to adhesion. The *repulsive type universal emulsifiers*, A/C-*b*-D/B, may give the indication that high dispersion does not mean strong adhesion, the latter being optimized by enthalpic *attractive type* interaction. Thus, our simple approach may contribute to design compatibilized blend systems with optimum adhesion .

Extending, consequently, the model of Leibler for the more general situation of the plane interlayer in the **A/C**-*b*-**D/B** blend, we assume for this system the *wet brushes* as the realistic model. The goal is to estimate how the different parameters influence the interfacial properties and to derive analytical expressions that contain known parameters of the blend system, i. e. the degrees of polymerization and the Flory-Huggins interaction parameters. Using these analytical expressions it should be possible to design the best block copolymer for a given blend. The A/C-*b*-D/B may be treated in parallel, supposing a *dry brush* interface.

DESCRIPTION OF THE MODEL

We assume the immiscible polymer blend comprising the two homopolymers A and B, compatibilized by the diblock copolymer C-*b*-D. A is compatible with C and B with D. Accordingly we have to distinguish between the respective *wet brushes* I (**A/C**) and II (**B/D**). We further assume that the junction between the two blocks is situated at the interface and that each brush is penetrated only by 'its' miscible blend partner. That means the volume fractions of A in brush II and of B in brush I, respectively, are neglected, as well as the corresponding interaction parameters between A/B, A/D, B/C and C/D. Additionally, the interaction between identical blocks at the interface is neglected.

Consequently, only the following contributions to the free energy are accounted for: (i) The mixing entropy between the macromolecules - (ii) enthalpic interactions between the contactic polymers - (iii) repulsion between the immiscible blocks of the block copolymer - (iv) stretching of the copolymer blocks due to excluded volume effects, and - (v) the interfacial energy.

According to the *wet brush* model, the polymers of the bulk phase penetrate only the brushes containing the pertaining compatible block of the block copolymer. The model seems realistic for the supposed *favourable* enthalpic interaction between the components. The *dry brush* model characteristic for negligible polymer penetration is unrealistic for the enthalpic *favourably interacting* system, **A/C**-*b*-**D/B**, but appears applicable for the *unfavourably interacting* A/C-*b*-D/B.

A detailed answer, however, which model represents better a real situation must be given by the experiment. An estimation of the maximum interfacial areal density is possible by considering the blend composition and by using morphological images from electron microscopy. Some of our results [?] support, however, that the wet brush supposition is realistic for **A/C** and for **D/B** brushes, respectively.

FREE ENERGY OF THE SYSTEM

In order to deduce an expression for the change of the free energy of the interfacial layer by adding the interacting block copolymer, we assume that the molecular weights, the normalized polymerization degrees of the polymers - N_A and N_B - and of the diblock copolymer - $N_{CD} = N_C + N_D$ - are given as well as the respective specific interaction parameters. χ_{AC} and χ_{BD}. χ_{AC} and χ_{BD} have not to be marked with bold or normal types, because this is not relevant for the respective χ's.

In the following, the change of the free energy is evaluated for a *wet brush* I. Introducing the respective volume fractions, Φ_A, Φ_B and Φ_{CD}, the number of polymers, Q'_A and Q'_{CD} and the end-to-end distance of the ideal chain, R_{oc}, the change of the free energy is given by:

$$\frac{\Delta F^{I}}{kT} = \left(Q^{I}_{CD}N_C + Q^{I}_A N_A\right)\left[\frac{\Phi^{I}_{CD}\ln\Phi^{I}_{CD}}{N_{CD}} + \frac{\Phi^{I}_A \ln\Phi^{I}_A}{N_A} + \chi_{AC}\Phi^{I}_A\Phi^{I}_C\right]$$

(1)

$$+ \quad Q^{I}_{CD}\frac{N_C}{N_A}\Phi^{I}_C + \frac{3}{2}Q^{I}_{CD}\left(\frac{L^{I}}{R_{oc}}\right)^2$$

The first two terms represent the entropy of mixing, the 3rd the enthalpic interaction, the fourth the repulsion [14] and the fifth the elastic stretching of the blocks [14].

For *unfavourably interacting dry brushes*, A/C and D/B, the 5th term in (1) $\frac{3}{2}Q^{I}_{CD}\left(\frac{L^{I}}{R_{oc}}\right)^2$ should be omitted because of lack of elastic stretching of the blocks

. We continue with the *wet brush* situation. The dry brush easily can be treated by omitting the relevant stretching terms. Using molecular parameters (segment length, a, degree of polymerization, N) and characteristics of the interfacial geometry (brush thickness, L, interfacial area, A) one can substitute the unknown volume fractions by

(2) $\Phi^{I}_C = \dfrac{N_C a^3}{L^{I}\Sigma}$ $\Phi^{I}_A = \dfrac{Q^{I}_A N_A a^3}{L^{I}A}$ $R_{oc} = \sqrt{N_C}\,a$

Σ is defined by $\Sigma = A/Q_{CD}$. After substitution the change of free energy is given by:

$$\frac{\Delta F^{I}}{Q_{CD}kT} = \frac{N_C}{N_{CD}}\ln\frac{N_C a^3}{L^{I}\Sigma} + \frac{L^{I}\Sigma}{N_A a^3}\left(1 - \frac{N_C a^3}{L^{I}\Sigma}\right)\ln\left(1 - \frac{N_C a^3}{L^{I}\Sigma}\right)$$

(3)

$$+ \quad \chi_{AC}N_C\left(1 - \frac{N_C a^3}{L^{I}\Sigma}\right) + \frac{N_C^2 a^3}{N_A L^{I}\Sigma} + \frac{3}{2}\frac{L^{I^2}}{N_C a^2}$$

Using the last expression (3) it is evident that the decrease of the free energy depends on both, the chain length of the polymers (expressed by the degree of polymerization) and the interaction parameters between the interacting blocks and the corresponding homopolymers. The thickness of the interfacial layer, L, is determined by the minimum condition of the free energy.

The respective expressions for brush II are obtained by appropriate substitution of the indices in equations (1-3).

THICKNESS OF THE INTERFACIAL LAYER

At equilibrium the thickness of the interfacial layer is determined by the condition of minimization of the free energy. Since Eq. (3) depends only on L^{I}, the minimization can be performed for the two brushes separately, the whole thickness of the interfacial layer being given by the sum $L^{I}+L^{II}$ of the two interconnected brushes. For brush I the thickness is obtained from the condition:

(4) $\dfrac{\partial}{\partial L^{I}}\left(\dfrac{\Delta F^{I}}{Q^{I}_{CD}kT}\right) = 0$

Assuming $\Phi^{I}_C \ll 1$, the following cubic equation for L^{I} results:

(5) $L^{I^3} - L^{I}\left(\dfrac{N_C^2 a^2}{3N_{CD}}\right) + \dfrac{N_C^3 a^5}{3\Sigma}\left(\chi_{AC} - \dfrac{1}{N_A}\right) = 0$

Eq.(5) has one real solution if condition (6) of the *wet brush* is satisfied:

(6) $\quad 1 < \dfrac{\Sigma}{a^2} < \sqrt{\dfrac{81}{4}}\, N_C^{3/2}\left(\dfrac{1}{N_A} - \chi_{AC}\right)$

The solution is of the form:

(7) $\quad L^I \approx \dfrac{N_C a}{3^{1/3}}\left(\dfrac{a^2}{\Sigma}\right)^{1/3}\left(\dfrac{1}{N_A} - \chi_{AC}\right)^{1/3}$

Since Eq. (7) contains both, the degrees of polymerization and the interaction parameter of the interacting pair, it is possible to compare the magnitudes of the respective contributions. The degree of polymerization of the blocks is usually of the order of 10^2 to 10^4. As a consequence the compatibilizing effect will be dominated by the enthalpic interaction. This is the main difference to the A/A-b-B/B system, where the block length governs the behaviour.

Eq. (7) shows, that the brush thickness depends linearly on the copolymer block length, on the 1/3 power of the copolymer areal density, and (for $-\chi >> 1/N_A$) on the interaction parameter. The dependence on the block length (for $\chi \approx 0$) is of -1/3 power. A similar expression for infinite homopolymer length has been deduced before by Brown et al. [17]. According to the authors the expansion of the interface with decreasing χ is the enthalpy-driven brush swelling.

REDUCTION OF THE INTERFACIAL TENSION

The change of the interfacial tension, $\Delta\gamma$, is defined by the derivative of the free energy, ΔF^{I+II}, with respect to the interfacial area [18]:

(8) $\quad \Delta\gamma = \dfrac{\partial}{\partial A}\left(\dfrac{\Delta F^{I+II}}{Q_{CD}kT}\right) = \dfrac{\partial}{\partial\Sigma}\left(\dfrac{\Delta F^I}{Q_{CD}kT} + \dfrac{\Delta F^{II}}{Q_{CD}kT}\right)\dfrac{d\Sigma}{dA}$

Introducing Eq. (7) one obtains:

(9) $\quad \dfrac{a^2\Delta\gamma}{kT} = -3^{1/3}\left(\dfrac{a^2}{\Sigma}\right)^{5/3}\left[\dfrac{N_C/N_A - \chi_{AC}}{(1/N_A - \chi_{AC})^{1/3}} + \dfrac{N_D/N_B - \chi_{BD}}{(1/N_B - \chi_{BD})^{1/3}}\right] - \left(\dfrac{a^2}{\Sigma}\right)$

From Eq. (9) it results that the interfacial tension is strongly influenced by the copolymer density at the interface, a^2/Σ. For predominant enthalpic interaction the following approximations are reasonable:

(10) $\quad \dfrac{N_C}{N_A} - \chi_{AC} \approx \dfrac{N_C}{N_A} \qquad \dfrac{1}{N_A} - \chi_{AC} \approx -\chi_{AC}$

Thus, Eq. (9) may be simplified according to

(11) $\quad \dfrac{a^2\Delta\gamma}{kT} \approx -3^{1/3}\left(\dfrac{a^2}{\Sigma}\right)^{5/3}\left[\dfrac{N_C}{N_A}\chi_{AC}^{-1/3} + \dfrac{N_D}{N_B}\chi_{BD}^{-1/3}\right] - \left(\dfrac{a^2}{\Sigma}\right)$

It results that the reduction of the interfacial tension depends on the ratio between the chain lengths of the interacting block and the corresponding homopolymer.

DISCUSSION

The presented analysis concerns only a plane interface. For curved interfaces some corrections are necessary [13]. Additionally, the possibility of fluctuations of the copolymer concentration at the interface and micelle formation in bulk have been neglected. Due to micelle formation, the concentration of the compatibilization relevant copolymer at the interfaces is decreased.

In the model is included the unknown areal density of the block copolymer at the interface, a^2/Σ, which contributes to both L^I and $\Delta\gamma$. The areal density is influenced by the attraction between the interacting pairs A/C and B/D as well as by the repulsion between A/D and B/C, respectively. The stronger these interactions, the more copolymer will accumulate in the interface. The corresponding influences on L^I and $\Delta\gamma$ are shown in Eqs. (7) and (9).

The unknown areal density, a^2/Σ, has to be substituted, however, by measurable quantities. Two ways are possible. First to measure directly the copolymer concentration profile at the interface, $\Phi_{CD}(x)$, in order to be able to determine Φ_{CD}^{exp}. The mean value can be calculated by using Eq. (12):

$$(12) \quad \Phi_{CD}^{exp} = \frac{\int_{\beta}^{\alpha} \Phi_{CD}(x)dx}{\alpha - \beta}$$

α and β are the x-coordinates of the interfacial layer.

The mean copolymer concentration is given by:

$$(13) \quad \Phi_{CD} = \frac{\Sigma(L^I\Phi_C + L^{II}\Phi_D)}{L\Sigma}$$

Considering Eq.(7) one obtains:

$$(14) \quad \frac{a^2}{\Sigma} = \left[\Phi_{CD}^{exp} 3^{-1/3}\left\{\frac{N_C}{N_{CD}}\left(\frac{1}{N_A} - \chi_{AC}\right)^{1/3} + \frac{N_D}{N_{CD}}\left(\frac{1}{N_B} - \chi_{BD}\right)^{1/3}\right\}\right]^{3/2}$$

Concentration profiles of the copolymer have been measured by Brown et al. [17] and Dai et al. [19]. Neuber [20] has demonstrated the possibility to measure such profiles at the interface by FTIR during interdiffusion of compatible polymers.

The second method requires the knowledge of the copolymer concentration in the bulk. Supposing equilibrium, the chemical potential of the copolymer in the interfacial layer and in the bulk are identical. The potential of the copolymer in the interfacial layer can be calculated by using the corresponding expression of the free energy. Using the two relations for the chemical potential in bulk and in the interface, one can eliminate the chemical potential and derive an expression for the (numerical) evaluation of a^2/Σ.

The last term in Eq. (9) represents in fact the combinatorial entropy of the block copolymer. This entropy is, however, strongly reduced due to the accumulation of the block copolymer at the interface. It depends not only on the chain

stiffness, but also on the interaction between the polymers. Thus, for enthalpically interacting systems its contribution to the interfacial tension probably is overestimated. However, the assumed equilibrium condition may be questionable, because polymer blend morphologies may be far from equilibrium. One of the reasons may be the very slow diffusion of the block copolymer in the blend to be compatibilized.

In conclusion, a simple approach has been tried to describe the interfacial consequences of compatibilizing incompatible blends - **A/C**-*b*-**D/B**- and A/C-*b*-D/B-type - by block copolymers interacting with the blend partners favourably or unfavourably.

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REFERENCES

1   Wippler C (1991) Polym Bull 25: 357
2   Valenza A, La Mantia FP, Demma GB, Romano V, Acierno D
    (1991) Polym Networks Blends 1: 71
3   Utracki LA, Sammut P (1988) Polym Eng Sci 28: 1405
4   Löwenhaupt B, Hellmann GP (1990) Colloid Polym Sci 268: 885
5   Andradi LN, Löwenhaupt B, Haufe A, Hellmann GP
    (1991) Angew Makromol Chem 185/86: 87
6   Fayt R, Jérôme R, Teysslé P, Interface Modification in Polymer Blends In:
    Utracki LA, Weiss RA (Eds.), Multiphase Polymers: Blends and Ionomers
    (1989) ACS Symp Ser 395, Am Chem Soc, Washington, p. 38
7   Chen CC, Fontan E, Min K, White JL (1988) Polym Eng Sci 28: 69
8   Jo WH, Kim HC, Baik DH (1991) Macromolecules 24: 2231
9   Gleinser W, Braun H, Friedrich Chr, Cantow H-J (1994) Polymer in print
10 Auschra C, Stadler R, Voigt-Martin I (1993) Polymer 34: 2081
11 Riemann R-E, Braun H, Weese J, Schneider HA (1994) New Polym Mat in print
12 Vilgis TA, Noolandi J (1990) Macromolecules 23: 2941
13 Leibler L (1988) Makromol Chem Macromol Symp 16: 1
14 de Gennes PG (1980) Macromolecules 13: 1069
15 Noolandi J, Hong KM (1982) Macromolecules 15: 482
16 Noolandi J, Hong KM (1984) Macromolecules 17: 1531
17 Brown HR, Char K, Deline VR (1990) Macromolecules 23: 3383
18 de Gennes PG, Taupin C (1982) J Phys Chem 86: 2294
19 Dai KH, Kramer EJ, Shull KR (1992) Macromolecules 25: 220
20 Neuber R (1992) Diploma Thesis Freiburg