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Interfacial modification of polymer blends—the emulsification curve: 2. Predicting the critical concentration of interfacial modifier from geometrical considerations

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Geometrical considerations about macromolecular size have been used in order to make a critical analysis of the minimum amount of block copolymer needed to saturate the interface in the melt mixing of immiscible polymer blends. For the case of dispersed spherical domains an expression has been developed (Equation (8)) which contains only molecular parameters such as the number of bonds, the characteristic ratio and the composition of the block copolymer used to compatibilize the blend. The shell surrounding each particle was divided into small pseudocubical elements: the unperturbed size of the matrix-like blocks of the copolymer was considered as representative of the size of these elements. Comparison has been made with experimental data regarding an ethylene–propylene rubber dispersed in a polystyrene matrix. That blend was compatibilized with styrene-hydrogenated butadiene copolymers with different molecular weights and architecture (diblock and triblock). The experimental data allow a quantitative assessment of the number of compatibilizer chains per unit cubical element corresponding to the onset of interfacial saturation: this value was found to depend on the copolymer architecture but is substantially independent of the copolymer molecular weight. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer; blend; compatibilizer; interface; saturation; model)

INTRODUCTION

It is well known that mixing immiscible polymers often results in a coarse dispersion and poor mechanical properties. A suitable block copolymer (linear or graft) acts as an emulsifier leading to a finer morphology with improved interphase adhesion and mechanical properties[1]. Rather surprisingly there are few detailed studies considering the effect of the quantity of block copolymer on phase size and blend properties. Generally speaking, the blend parameter investigated rapidly changes when small amounts of block copolymer are added and then reaches an approximately constant value. Recently, Fayt *et al.*[2] have reported the effect of the amount of compatibilizer added on some mechanical properties of binary blends. Favis and co-workers[3–5] have shown the dispersed phase size evolution as the compatibilizer content was increased. They reported a critical value of the concentration of the compatibilizer beyond which the particle size was constant. This critical concentration appeared to scale with the interfacial area; therefore, it was suggested to be representative of a saturation effect. One very interesting issue arising from such studies is the possibility to estimate the critical quantity of block copolymer needed to saturate the interfacial area of the blend. For this purpose, in the past years[1], the following formula was proposed:

$$A_{\mathrm{cr}} = \frac{3\phi M}{RaN_{\mathrm{AVO}}} \qquad (1)$$

where A_{cr} is the critical amount of copolymer normalized per unit volume of the blend, ϕ is the volume fraction of dispersed phase, M is the molecular weight of the copolymer, R is the dispersed particle radius, N_{AVO} is Avogadro's constant and a is the 'area' that the copolymer occupies at the interface. This last quantity, however, was not derived from molecular parameters. A semiquantitative estimation of it was obtained by equation (1) from experimental data[6]. It must be pointed out that in carrying out this analysis for a binary blend and a single compatibilizer concentration one has to assume a concentration corresponding to interfacial saturation and that all the compatibilizer is situated at the interface. In this work, starting from the molecular parameter of the copolymer, an expression has been derived to describe the copolymer concentration at interfacial saturation for the case of dispersed spherical particles. Finally, a quantitative comparison has been made with recent experimental data in which detailed data of dispersed phase size *versus* compatibilizer concentration were reported.

The objective of this work is to obtain an expression which can indicate the quantity of modifier necessary to saturate an interface under melt processing conditions. Aspects of the model will be supported by data obtained from experimental emulsification curves.

THEORETICAL FRAMEWORK

Before starting to illustrate the model it is necessary to clarify the use of the term 'interfacial saturation' which is potentially ambiguous. Here we refer to the case of immiscible blends and to the amount of compatibilizer which can be placed at the interface by means of a normal melt mixing process. To obtain an emulsification curve the amount of interfacial agent is varied, keeping constant all the other parameters such as the dispersed phase volume fraction, the viscosity and elasticity ratios of the phases, the mixing history, etc. Under these conditions the dispersed phase size is in principle controlled only by the interfacial tension and (for dispersed phase concentrations larger than about 5%) by the particle coalescence mechanism. The term 'saturation' is used in this paper to refer to the point where the dispersed particle size is no longer significantly dependent on the amount of interfacial agent.

In general, two compatibilizer concentration regimes can be observed:

(i) For small concentrations the entropy loss is compensated by enthalpic effects which tend to reduce the number of unfavourable interactions between segments of two immiscible polymers. The copolymer accumulates at the interface, giving rise to a pronounced decrease of the interfacial tension and of the coalescence efficiency: both of these effects contribute to decrease the phase size and to increase the stability of the dispersion.

(ii) At higher concentrations an increase of the compatibilizer content does not lead to a significant decrease of the interfacial tension and/or of the coalescence efficiency: therefore it becomes progressively more difficult for the compatibilizer chains to go to the interface, and it will remain randomly entrapped in one of the phases or it will form micellar structures with other block copolymer chains. This concentration regime is characterized by an approximately constant value ('equilibrium' value) of the dispersed phase size.

The situation is schematically summarized in *Figure 1*. Between the two regimes a critical concentration for the onset of interfacial saturation can be identified. Again we underline that saturation is the point where the interfacial tension and the coalescence inhibition are no longer significantly dependent on the amount of interfacial agent.

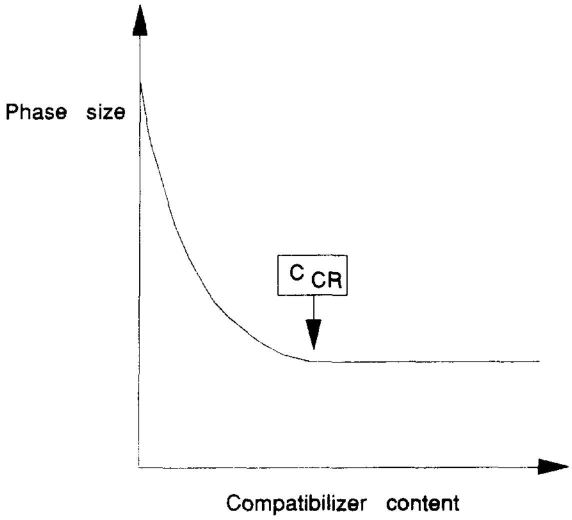

Figure 1 Schematic drawing of a typical emulsification curve where the critical concentration C_{cr} is related to interfacial saturation

Consider now one phase (phase B) dispersed in the continuous matrix of phase A in the form of particles with radius R (the size polydispersity will easily be introduced later) and an A–B block copolymer where A and B denote chemical identity or simply chemical affinity for the two phases and assume a geometrically sharp interface (see *Figure 2*). Here the calculations are done explicitly for the case of a diblock copolymer, but with simple geometrical arguments they are easily extended to the case of multiblocks (see *Figure 2* for the case of an A–B–A triblock copolymer). The case of an A block grafted onto a B backbone is geometrically the same as the linear diblock one. The particle outer shell is divided into small pseudo-cubic elements as shown in *Figure 3*. At interfacial saturation it is reasonable to conceive the particle surface as being homogeneously covered with a given level of A blocks to make a stable colloidal dispersion of B particles in the A matrix. The molecular composition and conformation of the matrix-like blocks in the particle outer shells is known to be very important for the stability of the dispersion[7]. For this reason the role of B blocks, trapped in the inner shells of the B phase spherical particles, will not be considered crucially relevant. One could also speculate on elements with a parallelepiped geometry with the dimension perpendicular to the particle surface having the largest size since chains attached to surfaces are known in some cases to become stretched in the

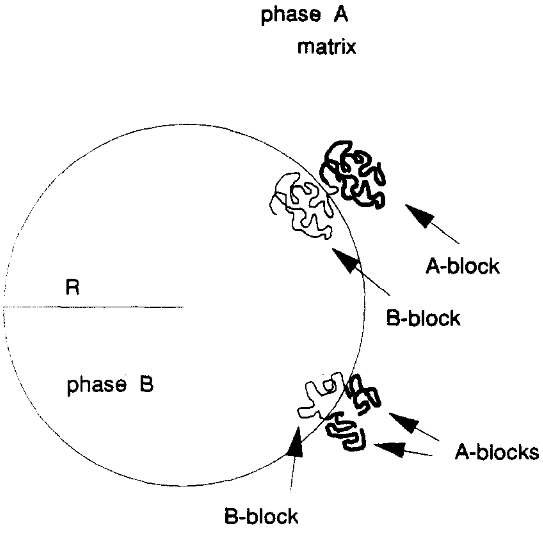

Figure 2 Block copolymer in an immiscible blend with spherical domains: the case of an A–B diblock and an A–B–A triblock located at the interfacial region is shown

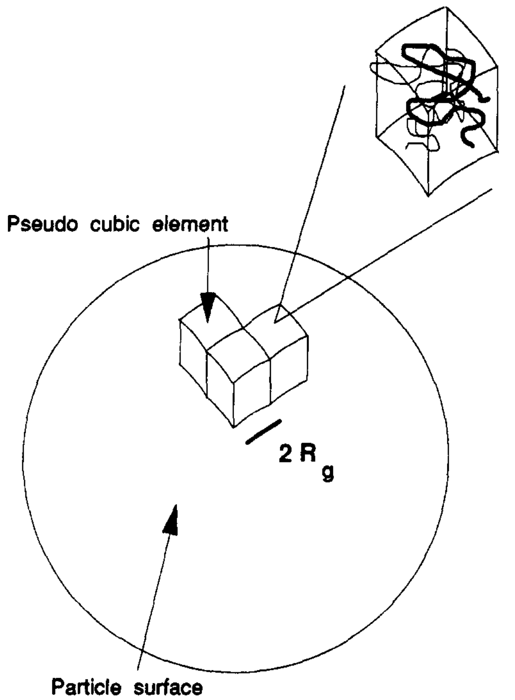

Figure 3 Coverage of a particle with pseudo-cubic elements. The size of each element is related to the macromolecular size of the matrix-like blocks of the interfacial agent. Also shown is an enlarged cubic element containing two matrix-like blocks of the compatibilizer. For clarity the two blocks are drawn with a different thickness

direction perpendicular to the surface[8]. However, this takes place at very high levels of adsorbed or grafted chains, levels which are quite difficult to achieve experimentally[9] due to the very large decrease in entropy resulting both from the placement of a large number of macromolecules in a narrow interfacial region and from the modification of their random coil unperturbed dimensions. The strong stretching of one block surrounded by its melt, due to the screening of the excluded volume effect and to the constraint of constant density, is more difficult than in the case of the same chain diluted in a good solvent. Some experimental work on the rheology of emulsion ABS (acrylonitrile–butadiene–styrene) has shown that too high a surface coverage gives rise to an unstable colloidal dispersion with agglomeration phenomena taking place[10]. That agglomeration was ascribed to the onset of strong stretching of the grafted chains. This reinforces the idea that, when the dispersion is stable, it is reasonable at the onset of surface saturation to consider unstretched A blocks on phase B particle surfaces. Also, some recent data on the sizes of triblock copolymer at interfaces[6] or layered in lamellar structures[11] showed size values practically equal to the unperturbed ones. This also gives further support to the hypothesis of a nearly isotropic (i.e. not strongly stretched) chain conformation.

We also assume no adsorption (i.e. no attraction) of A blocks to the dispersed particle surface. This is a restriction which, however, does not touch most of the practical cases of compatibilized immiscible blends. The only case which could be delicate is the one with strong specific interactions between the A blocks and the B phase.

Another issue is an evaluation of the linear size of the cubic elements. As the A blocks are immersed in the matrix of the phase A melt and within the framework just depicted it is possible to assume that the A block size displays ideal Gaussian behaviour[8,12,13] and is represented by random coils with linear size $2R_g$, where R_g is the radius of gyration of an A block.

The linear size of the cubes should be related to some molecular parameter representative of the size of an A block, and the simplest possible choice is to take it equal to $2R_g$.

If M_A is the molecular weight of block A, then the number of main skeletal bonds N_A is

$$N_A = \frac{M_A}{m_A} \tag{2}$$

where m_A is the average mass per main chain skeletal bond (e.g. 14 for polyethylene (PE), 52 for polystyrene (PS), etc.) For ideal chains the mean square end-to-end distance R_{ee}^2 of an A block is

$$R_{ee}^2 = C_\infty N_A L^2 \tag{3}$$

where C_∞ is the characteristic ratio of a chain of type A and L is the length of a skeletal bond (or average length if different kinds of bonds are present). It is useful to remember that for ideal Gaussian chains[13] the equation $6R_g^2 = R_{ee}^2$ holds. The area of each cubic element covering the surface is $4R_g^2$ and thus the number of cubic elements necessary to cover the outer shell of the particle is

$$N_{\text{cub.el.}} = \frac{4\pi R^2}{4R_g^2} \tag{4}$$

The final issue is to estimate an average number of A blocks per cubic element corresponding to the onset of interfacial saturation. Even if one block per cubic element may seem an obvious choice it has to be realized that for polymerically stabilized colloidal dispersions a slightly larger number of chains (at least three or four) per unit mesh of the surface has been suggested[7] to be the minimum level for stabilizing the dispersion. This is probably due to the need of having some overlapping and entanglement of the chains which produce the emulsification effect. At this level of the discussion we leave this number of blocks per cubic element as a parameter, k, which has to be extracted from the experiments. The number of A blocks to cover one dispersed particle of radius R is then given by the expression

$$N_{\text{A-blocks}} = kN_{\text{cub.el.}} = k\frac{\pi R^2}{R_g^2} \tag{5}$$

Thus, one can obtain the weight of the A blocks, needed to saturate the surface of one dispersed particle, which is

$$Wt_{\text{A-blocks}} = k\frac{\pi R^2}{R_g^2} \cdot \frac{M_A}{N_{\text{AVO}}} \tag{6}$$

this weight being expressed in grams if the M_A is in grams per mole as usual. If w_A is the A weight fraction in the copolymer, then the weight of copolymer chains at interfacial saturation is

$$Wt_{\text{copolymer}} = \frac{1}{w_A} Wt_{\text{A-blocks}} \tag{7}$$

From equations (2) and (3) one obtains that R_g^2 of an A block is linearly proportional to its molecular weight through intrinsic chain parameters such as the characteristic ratio, the main chain average bond length and the average mass per main chain bond. In other words this means that the weight of A blocks (equation (6)) needed to saturate the interface does not depend on the molecular weight M_A as long as the parameter k can be considered a geometrical constant which is not dependent on the length of the A blocks. This point will be discussed later in the comparison with the experimental data.

Dividing the quantity in equation (7) by the block copolymer density ρ_{bc} gives the volume of interfacial agent. Dividing further by the volume of a dispersed particle gives the critical saturation concentration value (C_{cr}) of the block copolymer (volume of block copolymer required to saturate the interface per unit volume of dispersed phase):

$$C_{cr} = k\frac{\pi R^2}{R_g^2}\frac{M_A}{N_{AVO}} \cdot \frac{1}{\frac{4}{3}\pi R^3} \cdot \frac{1}{\rho_{bc} w_A} = \frac{3kM_A}{4R_g^2 R N_{AVO}}\frac{1}{\rho_{bc} w_A} \tag{8}$$

Multiplying the quantity in equation (8) by φ (ϕ is the volume fraction of the dispersed phase) gives the critical volume fraction (VF_{cr}) of block copolymer normalized per unit volume of the blend:

$$VF_{cr} = \frac{1}{\rho_{bc} w_A}\frac{3kM_A}{4R_g^2 N_{AVO}}\frac{\varphi}{R} \tag{9}$$

Some consequences of the model just described can now be underlined. The first is that the critical amount of copolymer VF_{cr} needed to saturate the interface scales as ϕ/R (equation (9)); that is, it scales as the interfacial area per unit volume in the blend as would be expected. Another interesting aspect is that the quantity of copolymer required to saturate the interface does not depend on the molecular weight of the copolymer itself, but only on its composition. Changing, for instance, M_A without changing the A/B weight ratio of the block copolymer would not lead to a change in the critical copolymer concentration. If a molecular weight effect is observed experimentally it should not be ascribed directly to a geometrical factor such as the macromolecular size, but more probably to other factors of a dynamic nature. A partial support to this molecular weight independence comes from the recent work of Wagner and Wolf[14] related to the study of polydimethylsiloxane–polyethylene oxide (PDMS/PEO) blends. These authors measured the variation of the interfacial tension upon adding P(DMS–EO–DMS) triblock copolymers and observed no effect of the PDMS block length when it was greater than about 20 monomeric units (i.e. the oligomeric range).

The model has just been outlined for a diblock (linear or even graft) copolymer; however, it is quite simple to extend these geometrical considerations to multiblock copolymers. For instance, in the case of a linear triblock copolymer A–B–A, equations (6)–(9) hold with M_A and R_g equal to the molecular weight and the radius of gyration of one A block, respectively. However, it has to be remembered that increasing the complexity of copolymer architecture (multiblocks, star-shaped, etc.) makes it much more difficult for the copolymer chains to be placed at the interface as simply depicted in *Figure 2*. As already mentioned, it may be that the enthalpic gain obtained from a copolymer at the interface is not sufficient to overcome the entropic barrier.

In the most general case the particle outer shell will contain A-type chains due both to matrix chains and to A blocks of the copolymer: it is therefore interesting to estimate the mass density ρ_{OS} of the A blocks in the outer shell of the particle. We already have from equation (6) the mass of the copolymer A blocks needed to saturate the surface of one dispersed particle. This mass is placed in a shell whose area is $4\pi R^2$ and whose thickness is $2R_g$, and thus having a volume V_S:

$$V_S = 8\pi R_g R^2 \tag{10}$$

Therefore, the density ρ_{OS} is given simply by the ratio of the quantities in equations (6) and (10), that is

$$\rho_{OS} = \frac{Wt_{\text{A-blocks}}}{V_S} = k\frac{M_A}{8N_{AVO}R_g^3} \tag{11}$$

As R_g is proportional to the square root of the molecular weight, the following scaling law is immediately derived:

$$\rho_{OS} \propto \frac{1}{M_A^{1/2}} \tag{12}$$

It has to be stressed that this proportionality comes from the assumption that surface saturation is achieved with a given number of compatibilizer chains per cubic element and not with a given level of mass of the compatibilizer.

Therefore, in this framework, the density of A blocks at surface saturation can be too small or too large when they are very long or very short respectively. When M_A is large (ρ_{OS} tends to 0), to keep constant the phase A density, the contribution of matrix chains in the particle outer shell becomes much larger than that of A blocks of the copolymer. In any practical case a numerical calculation of the density is needed in order to check whether the value is realistic or not.

For the case of particle size polydispersity it can be easily shown that equations (8) and (9) are valid by using the so-called surface average radius R_S, given by the ratio of the third to the second moment of the size distribution.

COMPARISON WITH EXPERIMENTAL RESULTS

Recent works[15,16] have reported detailed data regarding the emulsification curves of an EP (ethylene–propylene) rubber dispersed in a PS matrix. For this purpose copolymers of PS and hPB (hydrogenated polybutadiene) were found to be suitable interfacial agents. Different structures and molecular weights of the copolymers were used as reported in *Table 1*. Also reported in *Table 1* are the experimental values of the 'equilibrium' radius (surface average) of the emulsification curve and of the critical concentration C_{cr}. In order to apply the equations formulated in this study, 0.154 nm was taken as the bond length of the PS main chain[17] and $C_\infty = 10.4$ as an average literature value for the characteristic ratio[17–19], and the hypothesis was made that at C_{cr} all the compatibilizer is located at the interface. Therefore it was possible to estimate the k

Table 1 Estimation of the k parameter in equation (8) from experimentally determined C_{cr} values[15,16]. Values are shown for a variety of interfacial modifiers for an EP rubber (dispersed phase)/PS (matrix) system

Copolymer	Molecular weight of the blocks	PS weight fraction	C_{cr}	R_s (μm)	k	ρ_{OS} (g cm^{-3})^a
Triblock PS–hPB–PS	7500–35 000–7500	0.30	0.15	0.16	4.4	0.475
Triblock PS–hPB–PS	10 000–50 000–10 000	0.29	0.15	0.16	4.2	0.393
Triblock PS–hPB–PS	29 000–116 000–29 000	0.33	0.15	0.16	4.9	0.269
Tapered diblock PS–hPB	16 500–17 500	0.49	0.20	0.17	9.5	0.723
Tapered diblock PS–hPB	28 000–36 000	0.44	0.20	0.17	8.6	0.531
Tapered diblock PS–hPB	62 500–73 500	0.46	0.15	0.17	6.7	0.281
Diblock PS–hPB	33 500–29 500	0.53	0.20	0.17	10.2	0.583
Diblock PS–hPB	20 000–47 000	0.30	0.20	0.24	8.1	0.595

[a] Density of interfacial modifier in the outer shell

parameter (and the density in the outer shell ρ_{OS}) corresponding to the onset of interfacial saturation (see *Table 1*) from which the following conclusions can be drawn:

- The number of blocks at interfacial saturation depends on the copolymer architecture (diblock *versus* triblock) but, at a fixed architecture, does not depend significantly on molecular weight.
- Diblock copolymers are packed at the interface more easily than triblocks as reasonably expected.
- The k parameter is consistent with the indications coming from polymerically stabilized colloidal dispersions[7]. In this case the minimum value of chains per unit molecular mesh of the particle surface was suggested to be approximately three.
- The density of styrenic blocks in the particle outer shell is molecular weight dependent; however, the values obtained are always reasonable in the sense that they are not too small and they are appreciably less than the pure PS density, which is about 1 g cm^{-3} in the melt.

The last point assures that the compatibilizer styrenic blocks are overlapped and entangled with PS matrix chains: this is needed in order to have a good and stable dispersion of the minor phase particles[10].

It should be underlined that, due to the statistical nature of polymeric chains, it is possible to make different choices for the unit mesh of the particle surface (*Figure 3*). For instance, one can consider the magnitude of the end-to-end vector, R_{ee}. As this vector is randomly oriented in space another possibility is to consider its average projection along one of the three Cartesian axes, namely $R_{ee}/\sqrt{3}$. This would lead to a correction by a numerical factor to the k values obtained with $2R_g$ and reported in *Table 1*. Those values need to be multiplied by 1.5 if the unit mesh is chosen as R_{ee} and divided by 2 if it is chosen as $R_{ee}/\sqrt{3}$.

Therefore changing the unit mesh gives rise to different results for the k parameter; however, if a 'reasonable' quantity is considered as representative of the molecular size, the k parameter varies only by a small numerical factor. In other words, one makes an evaluation which is semiquantitatively correct although not 'exact'.

Last but not least, the experimental data together with the model equations support the original assumption of not being in the stretched chain regime. Conformational stretching is observed when the density of chains anchored to the surface is higher than some critical level. Theoretical estimates of this critical density have been proposed, for instance, by deGennes[8] and by Leibler[20]: these theoretical values are approximately an order of magnitude larger than the chain density of the block copolymer at the particle surface in our case. An even more direct comparison can be made with the recent experimental data of Zhao *et al.*[21]. These authors measured the concentration profiles of carboxyl-terminated PS chains in the melt, grafted onto oxide-covered silicon substrates. They observed stretching of the grafted chains only when the grafting density was higher than 10 mg m^{-2}. For this system it is possible to compute the grafting density by dividing the quantity in equation (6) by the particle surface. For the experimental cases summarized in *Table 1* we obtain that the styrenic blocks of the compatibilizer are anchored to the particle surface with a density ranging from about 2 to 6 mg m^{-2}. Again we find a concentration which is definitely smaller than the one experimentally found to give rise to chain stretching. Hence the assumption concerning the use of a random coil configuration and unperturbed dimensions at the interface appears to be justified.

CONCLUSIONS

A promising approach to describe block copolymers in melt mixed immiscible blends has been reported. The model can be applied to two-phase systems in which one phase is dispersed in the form of spherical domains. In the model, each particle outer shell has been divided into small pseudo-cubic elements whose linear size is related to the unperturbed coil dimensions of the matrix-like blocks of the compatibilizer. In this framework it is possible to make a critical analysis, based on molecular parameters, of the block copolymer critical concentration required to saturate the interface, C_{cr}. From the experimental data coming from emulsification curves it is possible to estimate the number of block copolymer chains per cubic element corresponding to the interfacial saturation.

The comparison with experiments suggests that this value depends on the copolymer architecture (diblock versus triblock) but is substantially independent of the copolymer molecular weight.

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