Interfacial behaviour of compatibilizers in polymer blends

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(Received 15 April 1993)

From an analysis of the literature and our experimental results, we have established that interfacial tension is a function of the concentration of a compatibilizer, and put forward a 'three-stage' physical model to account for the compatibilizing behaviour of polymer blends. The effect of compatibilizer on size of the dispersed phase is studied in binary incompatible blends. The relation between the interfacial area occupied by each compatibilizer molecule and the concentration of the compatibilizer is also studied.

(Keywords: interfacial tension; polymer blends; compatibilizers)

INTRODUCTION

In most cases, polymers are incompatible with each other; their blends are heterogeneous. In incompatible systems, the overall physicomechanical behaviour depends critically on the following two structural parameters: an interfacial tension leading to a phase size small enough to allow the material to be considered as macroscopically 'homogeneous', and an interphase 'adhesion' strong enough to assimilate stresses and strains without disruption of the established morphology. The practical value of these simple blends is very low; compatibilizers are often needed to improve the compatibilization of these materials. There are many studies of compatibilizing incompatible binary blends[1-7]. The common conclusions are: compatibilizers can improve the dispersion of the dispersed phase in the blends; the average radius of the dispersed phase particles decreases with increase in concentration of the compatibilizer within a certain limit. The mechanism of compatibilization and the state of compatibilizer molecules in polymer blends, however, are not well understood.

In this paper, we have studied the interfacial tension and the average radius of the dispersed phase particles as functions of the concentration of compatibilizers and attempted to determine the physical essence of these relations.

THEORY

For incompatible binary polymer blends, the Gibbs free energy of mixing ΔG_m is given by the following equation[8]:

$$\Delta G_m = \Delta H_m - T\Delta S_m + S\cdot\gamma$$

where ΔH_m is the enthalpy of mixing, ΔS_m is the entropy of mixing, T is the temperature, S is the interfacial area and γ is the interfacial tension. When ΔS_m is very small, the above equation becomes:

$$\Delta G_m = \Delta H_m + S\cdot\gamma \tag{1}$$

For incompatible blends, ΔH_m is also very small, hence:

$$\Delta G_m = S\cdot\gamma \tag{2}$$

On the addition of a compatibilizer, γ decreases. If the change in the interfacial tension with the concentration of the compatibilizer is directly proportional to the interfacial tension difference $(\gamma - \gamma_s)$, where the interfacial tension is γ when the concentration of the compatibilizer is C and γ_s when the concentration of the compatibilizer is at saturation (the concentration of the compatibilizer is based on the dispersed phase), then:

$$-\frac{d\gamma}{dC} = K(\gamma - \gamma_s)$$

where K is the rate constant for the change in interfacial tension with concentration of the compatibilizer.

Considering the limiting condition when C is zero, then $\gamma = \gamma_0$, and integration of the above equation yields:

$$\gamma = (\gamma_0 - \gamma_s)e^{-KC} + \gamma_s \tag{3}$$

Figure 1 shows a predicted curve using equation (3).

By means of the revised Taylor equation on the Weber number[9] we get:

$$\frac{G\eta_m A}{\gamma} = F(\eta_r)$$

where γ is the interfacial tension, η_m is the viscosity of the matrix phase, G is the shear rate and $F(\eta_r)$ is the function of the relative viscosity.

Taking $A = 2R$, where R is the average radius of particles of the dispersed phase, results in:

$$\gamma = \frac{2G\eta_m R}{F(\eta_r)} \tag{4}$$

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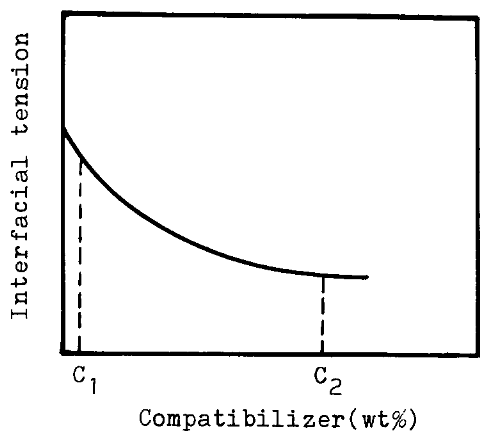

Figure 1 Effect of concentration of the compatibilizer on the interfacial tension of polymer blends

Inserting equation (4) into equation (3), we then have:

$$\frac{2G\eta_m R}{F(\eta_r)} = (\gamma_0 - \gamma_s)e^{-KC} + \gamma_s$$

and

$$R = \frac{F(\eta_r)}{2G\eta_m}((\gamma_0 - \gamma_s)e^{-KC} + \gamma_s)$$
$$= (R_0 - R_s)e^{-KC} + R_s \tag{5}$$

where R_0 and R_s are the average radius of the dispersed phase particles when the concentration of the compatibilizer is zero and at saturation, respectively. Equation (5) predicts the dependence of the average radius of the particles of the dispersed phase on the concentration of the compatibilizer.

Paul and Newman[10] presumed that the interfacial area (a) occupied by each compatibilizer molecule is given by

$$a = \frac{3\phi_d M}{RNW} \tag{6}$$

where N is Avogadro's number, M is the number-average molecular weight of the compatibilizer, R is the average radius of the dispersed phase and W is the weight of the compatibilizer required per unit volume of blend. When ϕ_d, the volume fraction of the dispersed phase, and M are kept constant, a depends mainly on $R \times W$. According to equation (6), R decreases with an increase in the weight fraction of the compatibilizer, and a may either decrease, or not change, or increase. This can influence the state of the compatibilizer molecules in the blend system. We will explain further the change of a with $R \times W$ using experimental data.

RESULTS AND DISCUSSION

The physical model for the behaviour of a compatibilizer in polymer blends

In equation (3), the three parameters γ_0, γ_s and K are dictated by structural parameters of the blend systems.

γ_0, the interfacial tension of a binary incompatible blend, (A/B), is given by the following equation by taking the symmetric case ($Z_A = Z_B = Z$)[11]:

$$\gamma_0 = (2/3)^{1/2}(RT/V)\chi^{1/2}(\chi Z)^{1/2}b(\pi/8 - 0.602/(\chi Z) - 0.459/(\chi Z)^2) \tag{7}$$

where Z is the degree of polymerization, χ is the interaction parameter of the two components, b is the effective length per monomer unit, V is the mean molar volume of the segments and T is the temperature of the polymer blend. From equation (7), it may be deduced that with an increase in χ, Z or b, the interfacial tension of the blend (γ_0) is increased.

The interfacial tension (γ_s) between A and B at the saturated concentration of the compatibilizer is also determined by the structural parameters of the two components of a blend system. When a copolymer C–D is added as a compatibilizer to an A/B blend, where A and C and B and D are miscible, respectively, $\chi_{BC} > \chi_{AC}$ and $\chi_{AD} > \chi_{BD}$; the larger the values of χ_{BC} and χ_{AD} are, the smaller γ_s is, and the larger the polymerization degree Z_k is, the smaller γ_s is[12]. In addition, we think that γ_s is related to the critical micelle concentration (*CMC*) of the compatibilizer; the larger the *CMC* is, the smaller γ_s is.

Finally, the rate constant (K) for the change of interfacial tension with concentration of the compatibilizer is related to the degree of polymerization of the compatibilizer and the interaction parameter. Vilgis and Noolandi[12] found, using statistical thermodynamic theories, that the concentration of the compatibilizer on the interfacial area of A/B blends increases with the degree of polymerization of the compatibilizer and the interaction parameter χ_{BC} (or χ_{AD}). This will lead to an increase in K with the concentration of the compatibilizer.

In the limiting case of $C \to \infty$, then equation (3) becomes:

$$\lim_{C \to \infty} \gamma = \lim_{C \to \infty} ((\gamma_0 - \gamma_s)e^{-KC} + \gamma_s) = \gamma_s$$

Thus, after addition of the compatibilizer, the interfacial tension of the blend system has a minimum of γ_s, which is not often equal to zero. Therefore, the blend is a heterogeneous but not a homogeneous system.

Anastasiadis *et al.*[13] have studied the compatibilizing effect of poly(styrene-*b*-1,2-butadiene) on polystyrene/poly(1,2-butadiene) blends. The results showed that the interfacial tension of the blends decreased with an increase in the concentration of the compatibilizer. The experimental data describing the change in interfacial tension of this system with concentration of the compatibilizer fit very well the simulated curve (*Figure 2*) of equation (3) in the following form:

$$\gamma = 0.31e^{-1.0318C} + 0.29 \tag{8}$$

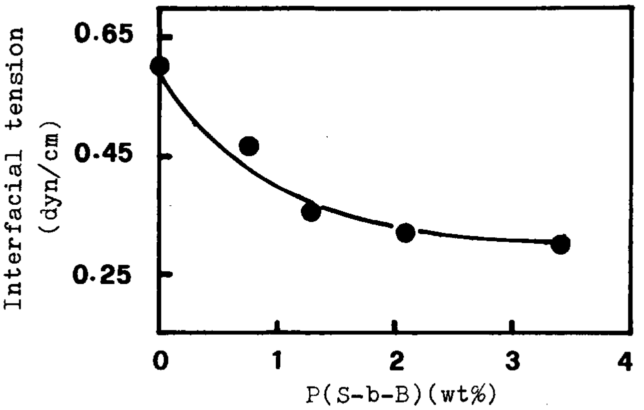

Figure 2 Effect of poly(styrene-*b*-1,2-butadiene) on the interfacial tension of polystyrene/poly(1,2-butadiene): ●, experimental data; ——, the fitting curve from equation (3)

These results show that equation (3) could represent the effect of a compatibilizer on the interfacial tension of binary incompatible blends.

According to the above results, we think that the following physical model explains the change in the behaviour of a compatibilizer in polymer blends:

Stage 1. Linear γ *versus* C (C: 0–C_1)

In this stage, all the compatibilizer molecules exist in the interfacial area between the dispersed phase and the matrix; the compatibilizer molecules do not form micelles.

Stage 2. Non-linear γ *versus* C (C: C_1–C_2)

On addition of more compatibilizer, when block or graft copolymers are used as compatibilizers, only a part of the compatibilizer enters the interfacial area of the blend to complete the compatibilization, the rest forming micelles. For functionalized polymers and random copolymers, each compatibilizer molecule occupies only a smaller interfacial area with further addition of the compatibilizer.

Stage 3. Constant γ *versus* C ($C > C_2$)

When the concentration of the compatibilizer is larger than C_2, further addition of the compatibilizer on the basis of the second stage brings all the excess compatibilizer into micelles. This part of the compatibilizer makes no contribution to the compatibilization of the blends.

This model is different from the two models describing the formation of micelles from small molecular emulsifying agent[14]. Of these two models, one assumes that micelle formation of the emulsifying agent embraces Stages 1 and 3. The other model assumes that micelle formation of the emulsifying agent includes the Stages 2 and 3.

Micelle formation is a common phenomenon in binary blends of homopolymer (A)/block copolymer (A-*b*-B)[15,16]. If the repelling action between B and A segments is large, the block copolymer will form micelles when the concentration of A-*b*-B is above a critical value. Then the B block forms the nucleus and the A block forms the shell of the micelle, in which ΔG_m reaches a minimum. In a three-component blend (A/B/A-*b*-B), however, from a thermodynamical point of view, the micelles of A-*b*-B in bulk A or bulk B are not in a stable state. A-*b*-B will exist only at the interface of A/B, ΔG_m of which is a minimum. When the concentration of A-*b*-B exceeds a critical value, the copolymer also forms micelles.

It is uncertain whether A-*b*-B micelles are formed at the saturated interface of a blend. This needs further experimental study. The following experiments may clarify this problem. Three-component blends A/B/A-*b*-B are usually prepared by one of the following methods: (1) A binary blend of A/B is prepared, and then A-*b*-B is added and mixing continued; (2) A, B and A-*b*-B are blended simultaneously. If the formation of micelles is the result of saturation of the interface, there would be more A-*b*-B molecules in the interfacial area in blends prepared by the first method. Therefore, the size of the dispersed phase of these blends would be smaller than that of the blends prepared by the second method. Otherwise, the micelles would be formed before the interface is saturated by A-*b*-B.

For binary incompatible blends A/B, it is often difficult to synthesize block (A-*b*-B) or graft (A-*g*-B) copolymers to be used as the compatibilizers of A/B blends. However, A-*b*-C or C-*b*-D can be used to replace A-*b*-B if C and D are miscible with A and B, respectively.

From the above study of the formation of micelles, we naturally associate the *CMC* of A-*b*-B in A/B/A-*b*-B blends with that in A/A-*b*-B and B/A-*b*-B blends. In A/B/A-*b*-B blends, A-*b*-B could exist in three different states: (1) interfacial area; (2) micelles; (3) free state. In binary blends A(or B)/A-*b*-B, A-*b*-B is expected to be in two possible states: (1) micelles; (2) free states. In blends A/A-*b*-B which contain a certain concentration of A-*b*-B, most of the A-*b*-B molecules are in the micelle state and ΔG_m reaches a minimum. In blends A/B/A-*b*-B, however, A-*b*-B of the same concentration must exist mainly in the interfacial area for ΔG_m to reach the minimum. Thus, it can be inferred that the *CMC* of A-*b*-B in blends A/B/A-*b*-B is larger than that of A-*b*-B in A/A-*b*-B (or B/A-*b*-B).

Effect of compatibilizers on the degree of dispersion of polymer blends

Changing the form of equation (5) into

$$R - R_s = (R_0 - R_s)e^{-KC}$$

and taking the natural logarithm on both sides

$$\ln(R - R_s) = \ln(R_0 - R_s) - KC \tag{9}$$

a plot of $\ln(R - R_s)$ against C, can be used to obtain K from the slope.

In the limit $C \to \infty$, then

$$\lim_{C\to\infty} R = \lim_{C\to\infty} ((R_0 - R_s)e^{-KC} + R_s) = R_s$$

shows not only that the average radius of the dispersed phase particles does not tend to zero, but also that it remains constant. The cause of this phenomenon is the effect of the concentration of the compatibilizer on the interfacial tension, illustrating further conformity of the behaviour of the compatibilizer with the physical model we established above.

Equation (5) has been used in studying blends of polypropylene (PP)/nylon-6 (PA)[5]. In blend PP/PA = 90/10, PA is the dispersed phase. On curve fitting, the following equation describes the change in the average particle radius of the dispersed phase with the concentration of the compatibilizer (see *Figure 3a*):

$$R = 0.7121e^{-0.5138C} + 0.3060$$

On treating blends PP/PA = 10/90, PE/PA = 90/10 and PE/PA = 10/90 with equation (5) in the same manner (*Figures 3b–3d*), the parameters in *Table 1* were obtained. Although the same compatibilizer (ethylene–methacrylic acid–isobutyl acrylate terpolymer) was used in the above blends, the characteristic compatibilization parameters are different from each other. Therefore, the compatibilization characters of the blends are closely related to the properties of the systems and the compatibilizer used.

A semi-automatic image analyser was used to measure the radii of the dispersed phase (HDPE) in blend PP/HDPE = 75/25 compatibilized by the ethylene–propylene copolymer EPC-4 (C_2: 40%). The results show that equation (5) describes the effect of a compatibilizer on the average radius of the dispersed phase of blends (*Figure 4*):

$$R = 1.84e^{-0.02341C} + 1.00$$

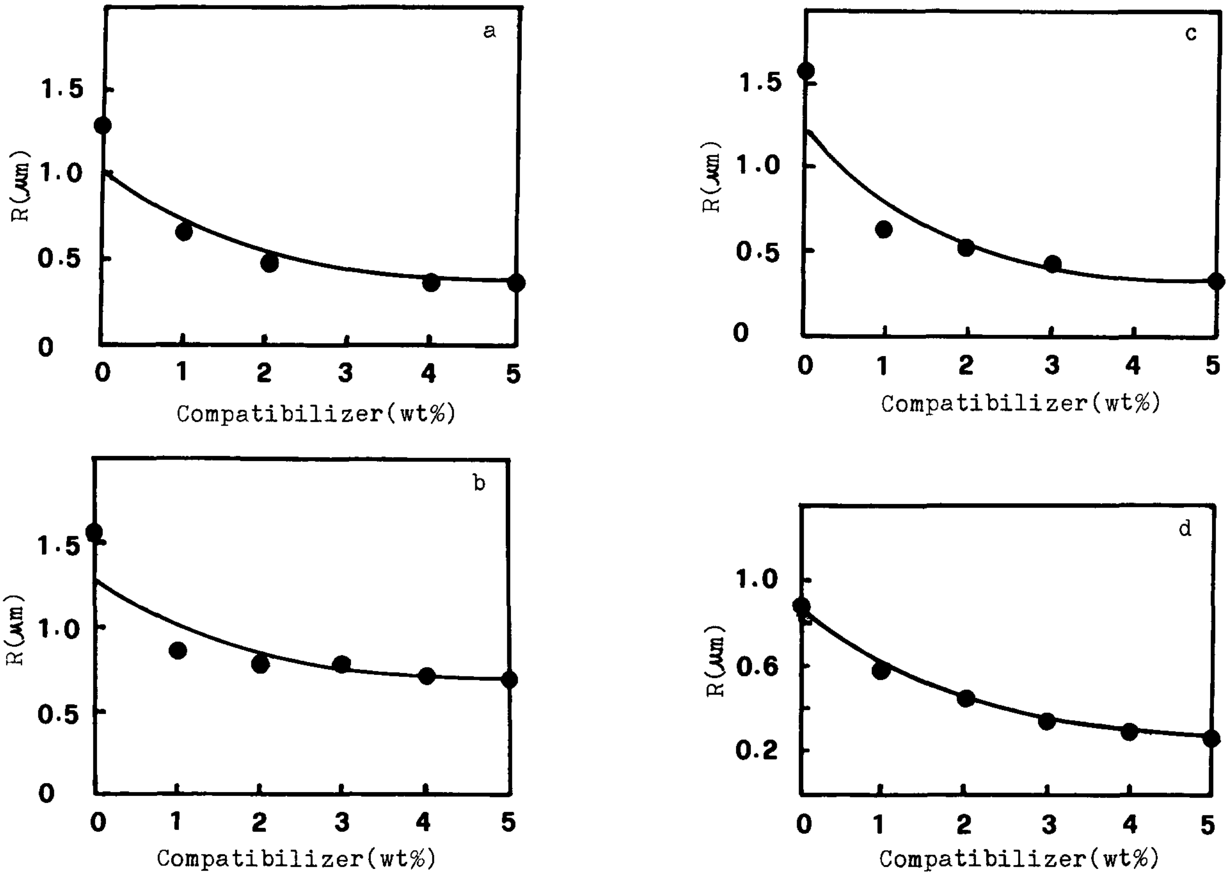

Figure 3 Effect of the compatibilizer on the average radius of the dispersed phase particles in blends PP/PA and PE/PA: ●, experimental data; ——, the fitting curve from equation (3). (a) PP/PA = 90/10; (b) PP/PA = 10/90; (c) PE/PA = 90/10; (d) PE/PA = 10/90

Table 1 Characteristic compatibilization parameters of various blends

	PP/PA		PE/PA	
Parameter	90/10	10/90	90/10	10/90
K	0.5138	0.7550	0.6579	0.4677
R_0	1.0181	1.3239	1.2559	0.8406
R_s	0.3060	0.6530	0.2765	0.2118

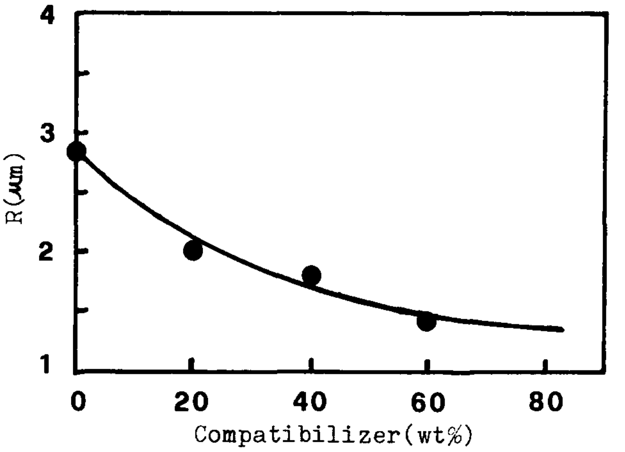

Figure 4 Effect of the compatibilizer on the average radius of the dispersed phase particles in blend PP/HDPE = 75/25: ●, experimental data; ——, the fitting curve from equation (5)

The compatibilizer not only improves the degree of dispersion of the dispersed phase, but also enables the dispersed phase to be better distributed (*Figure 5*), i.e. the size of the dispersed phase is decreased and the size distribution is narrowed after addition of the compatibilizer.

The state of the compatibilizer molecules in polymer blends

In compatibilization of blends, the relation between the interfacial area occupied by the compatibilizer molecule and the concentration of the compatibilizer is of great interest. Hosoda *et al.*[17] studied blends of maleic anhydride-grafted PP (PP-MA)/PA = 30/70 and found that the product $d_{vs} \times W$ remained constant (d_{vs} is the volume/surface-average diameter of PP and W is the weight fraction of the compatibilizer per volume of blend) and did not change with W. According to equation (6)[10], the interfacial area occupied by each compatibilizer molecule does not change with the concentration of the compatibilizer.

When R in equation (6) is replaced by $d_n/2$ (d_n is the number-average diameter of PP), we find a decrease in a with an increase in concentration of the compatibilizer until saturation (*Table 2*), not constant as claimed by Hosoda *et al.*[17]. Four blends of PP/PA = 10/90, 90/10, PE/PA = 10/90, 90/10 obey the same rule of a decrease in a with an increase in concentration of the compatibilizer (*Table 3*). The decrease in a with an increase in the concentration of the compatibilizer signifies a change in the state of the compatibilizer molecules in the blends. We infer that there are two different mechanisms for the change of state of compatibilizer molecules. When the compatibilizers are block or graft copolymers, they both appear in the interfacial area of the A/B blends and as micelles in the A or B phases. The effective concentration of the compatibilizer used in compatibilization is

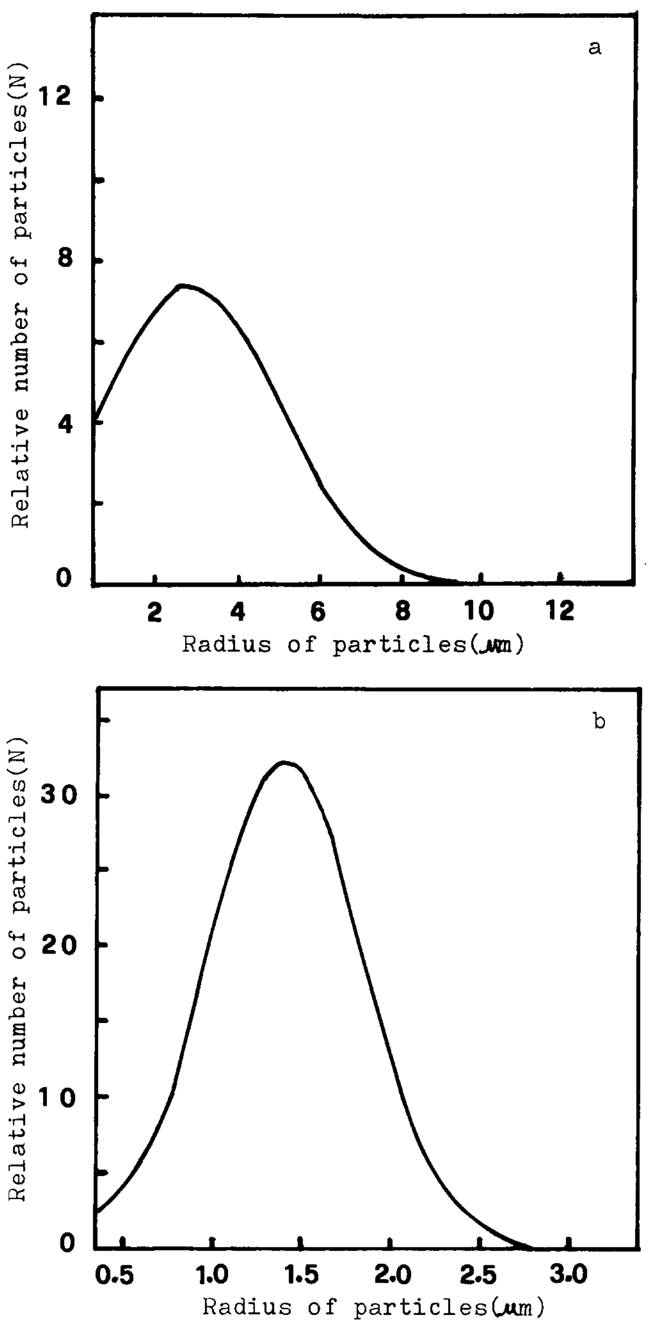

Figure 5 Effect of the compatibilizer on the size distribution of the dispersed phase particles in blend PP/HDPE = 75/25. Concentration of compatibilizer: (a) 0; (b) 60 wt%

Table 2 The effect of concentration of the compatibilizer (C) on a for (PP–MA/PA-6)[a]

C^b (wt%)	6.5	12.5	17.8
a (Å^2)	565	512	450

[a] Data from ref. 17
[b] Based on the dispersed phase

Table 3 The effect of concentration of the compatibilizer (C) on a (Å^2)[a]

C^b (wt%)	1	2	3	4	5	15	30
PP/PA = 90/10	749	509	–	313	269	97.4	54.3
PP/PA = 10/90	580	314	226	175	142	–	–
PE/PA = 90/10	814	466	383	278	103	–	–
PE/PA = 10/90	655	543	463	407	360	–	–

[a] Data from ref. 5
[b] Based on the dispersed phase

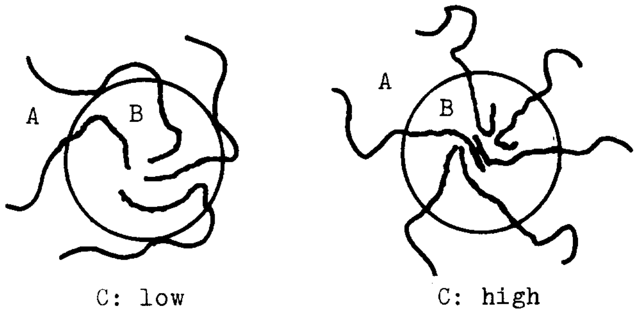

Figure 6 Effect of concentration (C) of the compatibilizer on states of compatibilizer molecules: 〰, compatibilizer molecule; A, matrix phase; B, dispersed phase

less than the quantity added. A greater quantity added only leads to its less effective participation as a compatibilizer. In the case of functionalized copolymers or random copolymers, they do not tend to form micelles; thus most of the compatibilizer molecules are in the interfacial area with a small amount distributed in bulk A or B. At a low concentration of the compatibilizer, each molecule occupies more interfacial area than when the concentration is high, where the molecules arrange themselves compactly in the interfacial area, so as to occupy a smaller interfacial area per compatibilizer molecule as depicted in *Figure 6*.

CONCLUSION

This paper examines interfacial tension (γ) as a function of the concentration of a compatibilizer (C). A 'three-stage' physical model is put forward to account for the compatibilizing behaviour of polymer blends. On this basis, a relation between the average radius (R) of the dispersed phase particles and C is given. The theoretical prediction conforms well with the literature data. The interfacial area (a) occupied by each compatibilizer molecule is not constant; therefore the molecular state of the compatibilizers changes with the concentration of the compatibilizer in the polymer blends.

REFERENCES

1 Heikens, D., Hoen, N., Barentsen, W., Piet, P. and Ladan, H. *J. Polym. Sci., Polym. Symp.* 1978, **62**, 309
2 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Ed.* 1981, **19**, 79
3 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Ed.* 1981, **19**, 1269
4 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Ed.* 1982, **20**, 2209
5 Willis, J. M. and Favis, B. D. *Polym. Eng. Sci.* 1988, **28**, 1416
6 Qin, C., Yin, J. H. and Huang, B. T. *Polymer* 1990, **31**, 663
7 Serpe, G., Jarrin, J. and Dawans, F. *Polym. Eng. Sci.* 1990, **30**, 553
8 Wu, S. 'Polymer Interface and Adhesion', Marcel Dekker, New York, 1982
9 Wu, S. *Polym. Eng. Sci.* 1987, **27**, 335
10 Paul, D. R. and Newman, S. 'Polymer Blends', Vol. 2, Academic Press, New York, 1976, Ch. 12
11 Kammer, H.-W. *Z. Phys. Chem., Leipzig* 1977, **258** (6), 1149
12 Vilgis, T. A. and Noolandi, J. *Macromolecules* 1990, **23**, 2941
13 Anastasiadis, S. H., Gancarz, I. and Koberstein, J. T. *Macromolecules* 1989, **22**, 1449
14 Blackley, D. C. 'Emulsion Polymerization, Theory and Practice', Applied Science Publisher, London, 1975
15 Leibler, L., Orland, H. and Wheeler, J. C. *J. Chem. Phys.* 1983, **79**, 3550
16 Whitmore, M. D. and Noolandi, J. *Macromolecules* 1985, **18**, 657
17 Hosoda, S., Kojima, K., Kanda, Y. and Aoyagi, M. *Polym. Network Blends* 1991, **1**, 51