polymer communications

Phase size/interface relationships in polymer blends: the emulsification curve*

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A detailed study on the dependence of the dispersed phase size *versus* the concentration of interfacial modifier is undertaken for an immiscible blend system, polyamide/polyolefin modified with a polyethylene copolymer ionomer. The resulting curve is known as an emulsification curve, and evidence is presented which indicates that the point of interfacial saturation of an interfacial modifier on the dispersed phase can be estimated from these data. The characteristic shape of the emulsification curve displays an initial rapid drop in phase size, as would be expected for a system experiencing a drop in interfacial tension. A critical concentration value of interfacial modifier (C_{crit}) is subsequently observed, beyond which a quasiequilibrium particle size is obtained. The C_{crit} value is directly related to the interfacial area of the dispersed phase and a lower equilibrium dispersed particle size results in a corresponding shift in C_{crit} for similar systems. The area occupied per molecule, calculated using the C_{crit} value and assuming, as an extreme limit, that all modifier is at the interface, is 5 nm^2 per molecule. The area value is in the appropriate range expected for a system with a saturated interface.

(Keywords: phase size; interface; blends)

Introduction

The interfacial modification of immiscible polymer blends is often necessary in order to obtain desirable physical properties. It is well known, for example, that interfacially modified samples in certain cases show an improvement in impact strength[1], elongation at break[2] and barrier properties[3]. For this reason, significant effort is currently being directed in developing novel modifiers and in reactive processing for the development of interfacial modifiers *in situ* in the extruder. Despite this effort, the efficacy of modifiers for a given interface has not been extensively studied.

It is well known from emulsion studies that the dispersed particle size diminishes when surfactant is added to the mixture[4]. This effect is due to the ability of the surfactant to reduce the interfacial tension between the dispersed phase and the matrix. The quantity of surfactant required to fully cover an interface is related to such variables as the degree and type of mixing, the affinity of the surfactant for the dispersed phase, the size of the dispersed phase, the rate of adsorption and orientation of the surfactant at the interface, and the extent to which the interface is stabilized against flocculation and subsequent coalescence. In classical oil/water emulsions stabilized by surfactants, the efficacy of the interfacial modifier for the interface is often characterized by emulsification curves which essentially follow the evolution of dispersed phase size with modifier concentration[5]. The shape of the emulsification curve is highly dependent on surfactant type and on processing technique and is characterized by an initial rapid drop in phase size followed by the obtention of an equilibrium value at higher concentrations of modifier[6].

In polymer blends, the modification of the interface serves to reduce the interfacial tension between the major components and results, as above, in a significant diminution in the dispersed phase particle size. In previous studies[7-9] the dependence of phase size on modifier concentration has been studied for certain systems, although details concerning their significance and interpretation were not reported. The objective of this paper is to report in a detailed manner on the existence and physical interpretation of emulsification curves for polymer blends and to show their relationship to both interfacial and molecular area.

Experimental

Polyolefin/polyamide system. The polypropylene (PP) resin used in this study was Pro-Fax 6501, obtained from Himont in powder form. The PP resin was compounded with an antioxidant, Irganox 1076, on a twin-screw extruder, and transformed into pellets. The high-density polyethylene (PE) sample, 07055C, was obtained from Dow as pellets. The polyamide-6 (PA) sample was Zytel 211 from Du Pont, obtained in pellet form. The interfacial agent was Surlyn 9020 from Du Pont. This ionomeric resin was a random terpolymer consisting of roughly 80% PE and 20% of a mixture of methacrylic acid, partially neutralized with zinc (approximately 70%), and isobutyl acrylate.

Some properties of these resins are given in *Table 1*. The torques were determined for each of the pure resins by mixing 60 ml of the resin in the Brabender mixing chamber at 250°C for 5 min at 50 rev min^{-1}. The storage modulus of each resin was obtained at 100 rad s^{-1} and 250°C, using a Rheometrics Mechanical Spectrometer (model RMS 605). The instrument was operated in the dynamic mode, with a gap of 1.2 ± 0.2 mm between parallel plates. All experiments were performed under dry nitrogen.

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Table 1 Characterization of the surlyn, polyethylene, polypropylene and nylon-6 resins

Resin	Melt index (g/10 min)	Density at 250°C after 5 min (N m)	Torque at 250°C after 5 min (N m)	Storage modulus at 250°C, 100 rad s^{-1} × 10^{-4} (Pa)	Molecular weight, M_n
Surlyn	1.0	0.74	14.3	4.6	25 000[a]
PE	7.0	0.74	5.9	1.5	16 600[b]
PP	4.0	0.75	8.6	3.6	50 000[b]
PA	–	0.96	8.6	2.6	25 000[a]

[a] Obtained from suppliers
[b] Measured

Compounding. The resins were dry blended and dried under vacuum at 95°C overnight. It should be noted that throughout the text, the blend compositions are given in terms of weight fraction.

The mixed resin pellets were then melt blended in the Brabender mixing chamber using the roller blades recommended for high shear applications. A typical blending experiment consisted of the following steps. With the mixing chamber initially set at 250°C and the blades turning at 50 rev min^{-1}, the resin mixture was fed into the chamber. Once all the resin was added, the blend was allowed to mix for 5 min under a constant flow of dry nitrogen. At the end of 5 min, the melt was rapidly transferred to a mould which was then held in a hydraulic press under 2.5 MPa of pressure until the sample had cooled down to room temperature (approximately 3 min).

Microscopy/image analysis. Plane surfaces were prepared on each specimen using a Reichert Jung Supercut 2050 microtome equipped with a diamond knife. Prior to microtoming, the samples were frozen in liquid nitrogen. While cutting, the surface of the sample was held at approximately −100°C to reduce the degree of surface deformation.

The microtomed samples were then treated with a suitable solvent to dissolve the minor phase present at the surface of the specimen. To dissolve the polyolefin minor phase, the specimens were allowed to sit in decalin at 120°C for 1 h.

The microtomed surfaces were treated with a thin film of Au/Pd and then examined under a Jeol 35-CF scanning electron microscope (SEM) operating at 10–15 kV.

The semiautomatic image analyser used to measure the diameters of the dispersed phase was developed in-house. The operation of this instrument has been described elsewhere[10]. For each sample, six SEM photomicrographs were analysed, and averages then calculated for the number-average diameter, d_n, and the volume-average diameter, d_v. A correction factor was applied to the diameters determined from SEM photomicrographs of microtomed surfaces[11]. On average, 600 diameter measurements were taken per blend preparation.

Results and discussion

Although a drop in phase size with interfacial modifier is well documented, the detailed relationship of this diminution in phase size with interfacial modifier concentration has not been seriously studied for polymer blend systems. *Figure 1* illustrates the dependence of phase size on weight per cent interfacial modifier for PE/nylon blends modified with a PE-*co*-methacrylic acid-*co*-isobutylacrylate ionomer. The interfacial chemistry of PA/ionomer/polyolefin (PO) has previously been examined in our laboratory and has been reported in an earlier paper[12]. The most striking effect in *Figure 1* is a significant drop in size of the dispersed phase with addition of the copolymer. After an initial rapid drop in phase size with addition of interfacial modifier, a critical concentration (C_{crit}) is reached beyond which a quasi-equilibrium particle size is attained. The term quasi-equilibrium is used since immiscible polymer blends are never in a state of true thermodynamic equilibrium. A quasiequilibrium morphology can be obtained as a result of the high viscosities of the individual components of the blend. The basic shape of the curve shown in *Figure 1* appears to be general and has been observed for several systems, as will be discussed below. The theoretical basis for such a dependence can be understood from the often-cited Taylor's theory[12,13]. This theory, derived for Newtonian systems in shear flow, predicts a drop in the dispersed phase size with a lowering of interfacial tension and the subsequent obtention of a limiting diameter due to the balance of viscous forces, tending to disrupt the drop, and interfacial tension forces tending to resist deformation and disintegration. The form of the curve has also been observed by other authors for different systems[9], although in the previous studies the work was presented as support data and detailed morphological analysis was not carried out. The characteristic shape of the curve in *Figure 1* has also been observed in classical emulsion studies, where the curve is referred to as an emulsification curve and the form of the curve can be related to the type of surfactant and processing technique[6]. It should be noted that the emulsification curve has also been studied in this laboratory for polystyrene-*co*-maleic anhydride/bromobutyl rubber blends stabilized with dimethylaminoethanol[8]. The characteristic shape and the presence of a critical concentration is also observed. These results indicate that the form of the curve is of a general nature, as mentioned above.

If, as a working hypothesis, the form of the curve shown in *Figure 1* is related to the saturation of the interface, then it should show a dependence on interfacial area. In

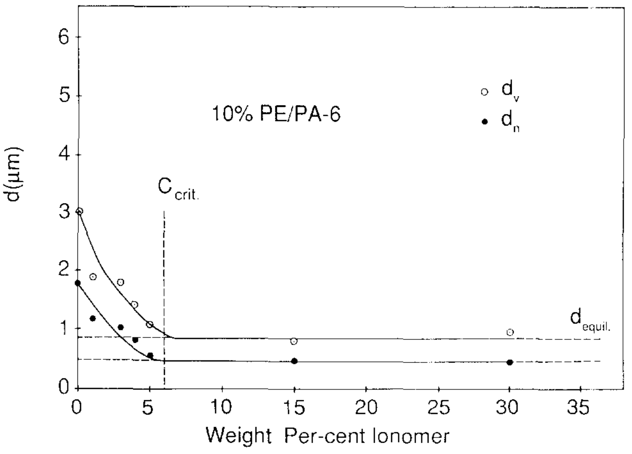

Figure 1 Influence of the interfacial modifier concentration on the dispersed phase size for 10% polyethylene dispersed in polyamide-6. The concentration of ionomer modifier is calculated as weight per cent based on the dispersed phase. Both volume- and number-average diameters are shown

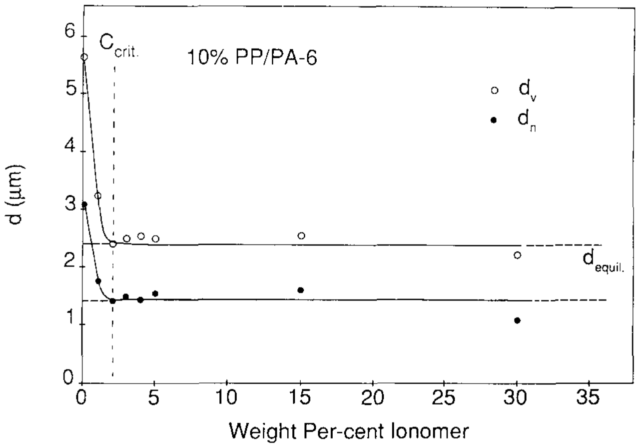

Figure 2 Influence of the interfacial modifier concentration on the dispersed phase size for 10% polypropylene dispersed in polyamide-6. The concentration of ionomer modifier is calculated as weight per cent based on the dispersed phase. Both volume- and number-average diameters are shown. This system has a higher viscosity or torque ratio (see *Table 1*) and hence the particle size diameters are shifted to higher values than in *Figure 1*

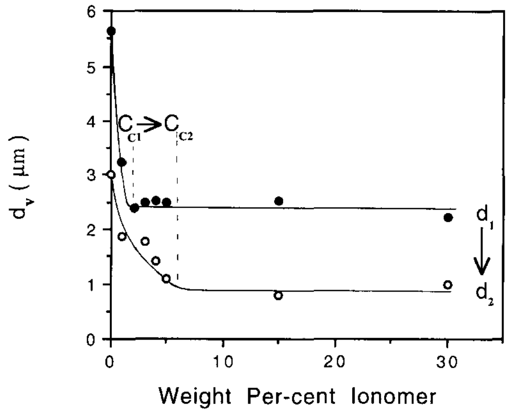

Figure 3 Comparison of the emulsification curves given in *Figures 1* and *2*. Note that a drop in the quasiequilibrium phase size results in a corresponding increase in the critical concentration value

Figure 2 an additional system of very similar chemical nature is presented. The system displays all the similar characteristics, a rapid drop in phase size followed by the obtention of a quasiequilibrium value at a critical concentration. The system in *Figure 2* differs in that it has a higher viscosity (torque) ratio than the system in *Figure 1*. For this reason the initial unmodified blend displays a particle size which is higher than that shown in *Figure 1* and subsequently a larger equilibrium particle size beyond C_{crit}. It is quite clearly shown in *Figure 3* that the lower quasiequilibrium particle size results in a corresponding shift in C_{crit}. The C_{crit} values of both systems and their respective interfacial areas are compared in *Table 2*.

In *Figures 1* and *2* the approximate values of C_{crit} were estimated, based on both d_n and d_v values. It can be seen that the increase in critical concentration shown in *Table 2* correlates very well with the change in interfacial area. From the data in *Figure 1* an estimation can be made of the interfacial area occupied per modifier molecule for the PA/PO/ionomer system. Since the average phase size and the total volume of the dispersed phase can be calculated with good precision (the modified dispersed phase shows a narrow particle size distribution), the interfacial area of the dispersed phase can be estimated. The quantity of interfacial modifier used is known as well as its molecular weight (supplied by Du Pont). If, as an extreme limit, it is assumed that all modifier goes to the interface, then the area occupied per molecule can be calculated as 5.3 nm^2 or approximately 5 nm^2 per molecule. The area occupied per molecule was estimated using the data in *Figure 1* and by calculating the interfacial area of the dispersed phase (volume of the dispersed phase = 6 ml; average equilibrium phase size, $d_n = 0.5\,\mu$m) and the number of molecules of ionomer modifier (molecular weight of ionomer, $M_n = 25\,000$; quantity of modifier (C_{crit}) = 6% of dispersed phase or 0.3 g). It should be noted in the above calculation that the molecular weight of the ionomer alone is used. This simplification is explained below. Previous studies[14] indicate that the most likely interaction resulting in copolymer formation is an amidation reaction between the terminal amine of the PA and the carbonyl of the ionomer. No evidence of chemical reaction was found between the ionomer and the PO. If, in light of the above, it is assumed that the overall number of modifier molecules does not change with reaction and since the C_{crit} value is based on the ionomer concentration, the use of the molecular weight of the ionomer alone can be justified.

By way of comparison, classical studies of stearic acid on water, estimated in a Langmuir trough experiment, have shown the molecule to be oriented normal to the water surface and to occupy 0.2 nm^2 per molecule. A branched small molecule, such as triparacresyl phosphate, occupies 0.8 nm^2 per molecule on water[15]. The value of 5 nm^2 per molecule obtained in this study should be taken as a minimum value, since it is unlikely that all the interfacial modifier finds its way to the interface. Nevertheless, the relative magnitude of the interfacial area occupied per modifier molecule falls into the range that would be expected for this type of high molecular weight system. In previous work, Paul[16] suggested an area of 0.5 nm^2 occupied per molecule as a minimum value for a diblock copolymer completely penetrating the two phases. In light of the above work on small molecules, however, it is likely that this estimate is low for high-molecular-weight systems. Fayt *et al.*[17] reported an area value of 2.6 nm^2 for a low-density PE/polystyrene system modified by a poly(hydrogenated butadiene-*b*-styrene) copolymer. In the latter system the authors showed unambiguously, by transmission electron microscopy, that the interface was saturated by the copolymer modifier. Considering that graft copolymer is formed in this case as opposed to a diblock copolymer, which was used in the study by Fayt *et al.*[17], the value of 5 nm^2 per molecule obtained here is quite reasonable. The assumption that all modifier is at the interface is unavoidable, since all attempts to quantify residual modifier in the

Table 2 Relationship of critical concentration and interfacial area ratios for two polyamide/polyolefin systems

C_{crit2}/C_{crit1}	Interfacial area$_2$/interfacial area$_1$
3	2.6
$\left(\frac{6\%}{2\%}\right)$	$\left[\frac{d_n(\text{equil }2)}{d_n(\text{equil }1)} = \frac{0.5\,\mu\text{m}}{1.3\,\mu\text{m}}\right]$

matrix and dispersed phase were unsuccessful. This assumption was also made in the study by Fayt *et al.*[17] and illustrates the need for significant research effort in developing techniques that can quantitatively localize interfacial modifier in a given blend system. If, as a limit, one considers the case where only one-third of the modifier finds its way to the interface, then the area occupied per molecule would increase to $15\,\mathrm{nm}^2$, which is still within a reasonable range for this type of high-molecular-weight system.

The relationship of the critical concentration to (1) interfacial area and (2) a molecular area on the surface in the range expected, strongly suggests that the critical concentration in emulsification diagrams for immiscible polymer blends corresponds to the interfacial saturation of the dispersed phase by the interfacial modifier.

The emulsification curve for polymer blend systems can be potentially very useful in evaluating the overall efficacy of an interfacial modifier for a given blend system. It can indicate the point of interfacial saturation, which is important for estimating the amount of modifier necessary for a given system. Although this type of study has been carried out for classical oil/water-type emulsions, its usefulness has not yet been exploited for polymer blend systems. Future work in our laboratory will focus on the relationship of the shape of the emulsification curve in polymer blends to such parameters as the molecular weight and architecture of the interfacial modifier, the affinity of the modifier for the interface, and the influence of various types of mixing equipment.

Conclusions

A detailed study of dispersed phase size *versus* interfacial modifier concentration for two systems shows that a generalized emulsification curve exists for immiscible polymer blends. The curve is characterized by a rapid drop in dispersed phase size with interfacial modifier concentration followed by the obtention of a quasiequilibrium phase size at a critical concentration (C_{crit}). The shape of the curve is dependent on interfacial area and a corresponding shift in C_{crit} is observed. Using the C_{crit} value, the area occupied at the interface per modifier molecule is calculated to be $5\,\mathrm{nm}^2$ for the PO/PA case, which is in the range expected for these types of systems. Based on the above observations it is believed that the C_{crit} value on the emulsification curve corresponds to the interfacial saturation of the dispersed phase by modifier molecules.

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References

1 Hobbs, S. Y., Bopp, R. C. and Watkins, V. H. *Polym. Eng. Sci.* 1983, **23**, 380
2 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Phys.* 1989, **27**, 775
3 Subramanian, P. M. *Polym. Eng. Sci.* 1985, **25**, 483
4 Walstra, P. in 'Encyclopedia of Emulsion Technology' (Ed. P. Becher), Marcel Dekker, New York, 1983, Vol. 1, Ch. 2
5 Sherman, P. 'Emulsion Science', Academic Press, New York, 1968
6 Djakovic, L., Dokic, P., Radivojevic, P., Sefer, I. and Sovilj, V. *Colloid Polym. Sci.* 1987, **265**, 993
7 Willis, J. M. and Favis, B. D. *Polym. Eng. Sci.* 1988, **28**, 1416
8 Willis, J. M., Favis, B. D. and Lunt, J. *Polym. Eng. Sci.* 1990, **30**, 1073
9 Fayt, R., Jérôme, J. and Teyssié, Ph. *Makromol. Chem.* 1986, **187**, 837
10 Favis, B. D. and Chalifoux, J. P. *Polym. Eng. Sci.* 1987, **27**, 1591
11 Underwood, E. E. 'Quantitative Stereology', Addison-Wesley, 1970
12 Taylor, G. I. *Proc. R. Soc., Ser. A* 1934, **146**, 501
13 Taylor, G. I. *Proc. R. Soc., Ser. A* 1932, **138**, 41
14 Willis, J. M., Favis, B. D. and Lavallée, C. *J. Mater. Sci.* 1993, **28**, 1749
15 Ries, H. E. *Sci. Am.* 1961, **244**(3), 152
16 Paul, D. R. 'Polymer Blends' (Eds D. R. Paul and S. Newman), Academic Press, New York, 1978, Vol. 2, Ch. 12
17 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Lett.* 1986, **24**, 25