Effect of interfacial forces on polymer blend morphologies

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In this study, the way in which the components of complex polymer blends (those consisting of more than two resins) are segregated after melt processing is described. Depending on the composition of the blend, the dispersed phases are found to remain separated or form more complicated encapsulated structures. The various morphologies which are formed are shown to be consistent with those predicted from an analysis of spreading coefficients.

(Keywords: interfacial forces; blends; morphology)

INTRODUCTION

The morphologies of two-component polymer blends have been discussed extensively in the literature. Much of this work has been carried out on crystalline or glassy polymers containing rubbery impact modifiers although various blends of glassy and crystalline polymers have also been considered[1]. For the most part, attention has been focused on factors affecting the size, uniformity and stability of the resulting dispersions although a few limited attempts to predict the morphology of two-component blends have appeared[2–4]. Work on blends of greater complexity has been largely limited to systems in which the major components have been 'compatibilized' by the addition of appropriate block or graft copolymers[5–8]. In these cases, there is general agreement that the copolymer resides in the interfacial region and some rather elegant experiments have been carried out to confirm this assumption[9].

In response to commercial pressures and the need for precisely tailored physical properties, more sophisticated blends consisting of multiple components are under active development. In such blends, morphological concerns transcend questions having to do with dispersed phase size, anisotropy, etc., to include more subtle issues such as why one of the dispersed resin phases may spontaneously encapsulate another[10]. It is reasonable to assume that under equilibrium conditions such effects must arise from interfacial energy differences among the blend components. The current study was carried out to more thoroughly investigate the effect of these interfacial forces on the microstructures of complex blends. To satisfy this objective, the morphologies of a number of multicomponent blends were characterized. An attempt was then made to determine if these observations were consistent with those which might be expected from analyses of spreading behaviour.

SPREADING COEFFICIENT CALCULATIONS

The tendency of a liquid to spontaneously spread across a solid or liquid substrate can be expressed in terms of the surface and interfacial tensions of the components using Harkin's equation[11]

$$\lambda_{ij} = \gamma_j - \gamma_i - \gamma_{ij} \tag{1}$$

where γ_j, γ_i and γ_{ij} are the surface and interfacial tensions of the solid, liquid and solid/liquid respectively and λ_{ij} is defined as the spreading coefficient. Spreading is predicted to occur only for positive values of λ (see *Figure 1a*)[12].

Harkin's equation can be rewritten for a system in which two dissimilar phases are dispersed within a third by substituting the appropriate interfacial tensions for the surface tension values in equation (1).

$$\lambda_{31} = \gamma_{12} - \gamma_{32} - \gamma_{13} \tag{2}$$

In this case, λ_{31} is the spreading coefficient for component 3 on component 1 and describes the physical situation shown schematically in *Figure 1b* in which the ability of one dispersed component to displace the matrix from the surface of a second component is considered. In an analogy with equation (1), envelope formation will be observed for positive λ values. When λ_{31} and λ_{13} are both negative the dispersed phases will remain separated.

In order for equation (2) to be useful in characterizing multiphase blends, it is necessary to know the interfacial tensions for the various polymer pairs with considerable

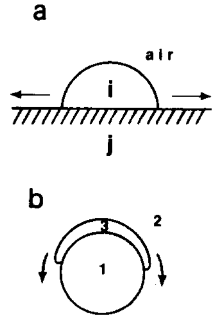

Figure 1 Schematic diagram showing spreading behaviour of liquid on solid substrate (a) and one polymer phase on another within a third (b)

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accuracy. Although some of these data are available, they are lacking for many engineering resins of greatest commercial interest and must be estimated from direct measurements of surface tension[13–15] or from parachor values[16]. To carry out the calculation, these values must be further broken down into dispersive and polar contributions. The best approximation appears to be given by the harmonic mean equation

$$\gamma_{12}=\gamma_1+\gamma_2-4\left[\frac{\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}}}{\gamma_1^{\mathrm{d}}+\gamma_2^{\mathrm{d}}}+\frac{\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}}}{\gamma_1^{\mathrm{p}}+\gamma_2^{\mathrm{p}}}\right] \tag{3}$$

where γ^{d} and γ^{p} are the dispersive and polar terms[14].

Since melt blending is necessarily carried out at elevated temperatures, the use of equation (2) is justified only if the interfacial tensions are determined at the processing temperature. Thus, the values determined from equation (3) must be extrapolated to a common melt temperature. This correction may be significant since, although the variation in surface tension with temperature ($\mathrm{d}\gamma/\mathrm{d}T$) for most polymers is comparable (0.06–0.08 dyne·cm deg^{-1})[13–15], the extrapolation may cover an extended temperature range. While the need for employing these successive approximations necessarily imposes a limit on the use of spreading coefficient calculations to predict polymer blend morphologies in an a priori sense, the general utility of such an approach is emphasized in the following discussion.

EXPERIMENTAL

A number of three- and four-component blends composed of various combinations of polystyrene (PS), bisphenol-A polycarbonate (PC), poly(butylene terephthalate) (PBT), poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (SAN) were examined in this study. Commercial grades of PBT (Valox 315) and PC (Lexan 141) were obtained from the General Electric Plastics Group. PMMA (Plexiglas 3-1581) was supplied by Rohm and Haas. Polystyrene (Styron 666) as well as several SAN copolymers having different SAN ratios were obtained from the Dow Chemical Company.

All of the blends were compounded on a Welding Engineers 20 mm twin-screw extruder at 270°C. In each case the components were first dry blended and added simultaneously to the hopper. The extruded strand was quenched in a water bath and made into pellets in the usual way. In order to fix the dispersed and continuous phases and permit unambiguous identification of the components, resin ratios of 1/3/7 were maintained for the three-component blends. The ratio of the dispersed phases had no effect on the observed spreading behaviour.

The morphologies of the compounded blends were characterized by transmission electron microscopy (TEM). Thin sections were microtomed from the extruded pellets and stained with ruthenium tetroxide ($\mathrm{RuO_4}$) to enhance contrast between the phases[17]. All observations were carried out on a Hitachi H-600 TEM.

RESULTS AND DISCUSSION

A TEM photograph of a 1/3/7 PMMA/PC/PBT blend is shown in *Figure 2*. In this system the matrix polymer is PBT and the primary dispersed phase is PMMA. Each of the PMMA domains is surrounded by a thick layer of PC. This morphology is preserved when the PMMA/PC ratio is reversed although the thickness of the PC envelopes decreases significantly and few, if any, domains of pure PC remain. This observation emphasizes the fact that the encapsulation process is driven by interfacial effects rather than concentration differences. The behaviour of this system contrasts strongly with that of the 1/3/7 PS/PBT/PMMA blend shown in *Figure 3*. Here PMMA forms the continuous phase and both PBT and PS exist as separate domains. Neither of the dispersed components exhibits any tendency to spread on the other. In the 1/3/7 PS/PC/PBT blend shown in *Figure 4*, envelope formation is again observed with PC encapsulating each of the dispersed PS domains.

The change from envelope formation to separate dispersed phases can be followed in a progressive fashion when SAN copolymers having various S/AN ratios are substituted for the PS homopolymer. The photomicrograph in *Figure 5* shows a 1/3/7 SAN/PC/PBT blend in which the S/AN ratio is 85/15. Although some tendency towards envelope formation is still observed, the polycarbonate layers have become severely broken up and a large fraction of the PC is observed to form independent domains. When the S/AN ratio is lowered to 75/25, envelope formation ceases and the PC and SAN form separate dispersed phases in the PBT matrix (*Figure 6*).

The effects of spreading behaviour on blend morphology are illustrated in an even more striking fashion in the 7/3/2/2 PBT/PS/SAN (75/25 S/AN)/PC blend shown in *Figure 7*. Here PBT is the matrix polymer and PS is the primary dispersed component. Neither PC nor SAN form isolated phases but rather combine to form interrupted envelopes around the PS domains. It appears

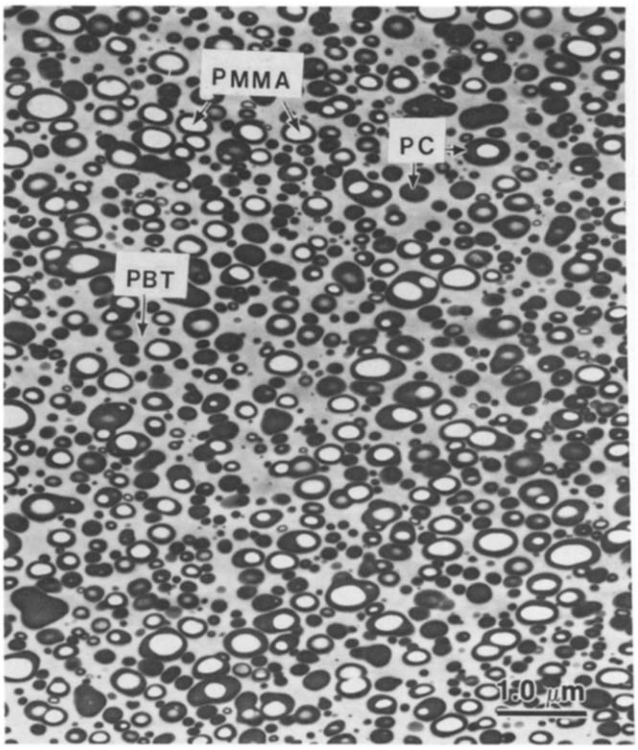

Figure 2 TEM photograph of 1/3/7 PMMA/PC/PBT blend showing PC envelopes around PMMA domains

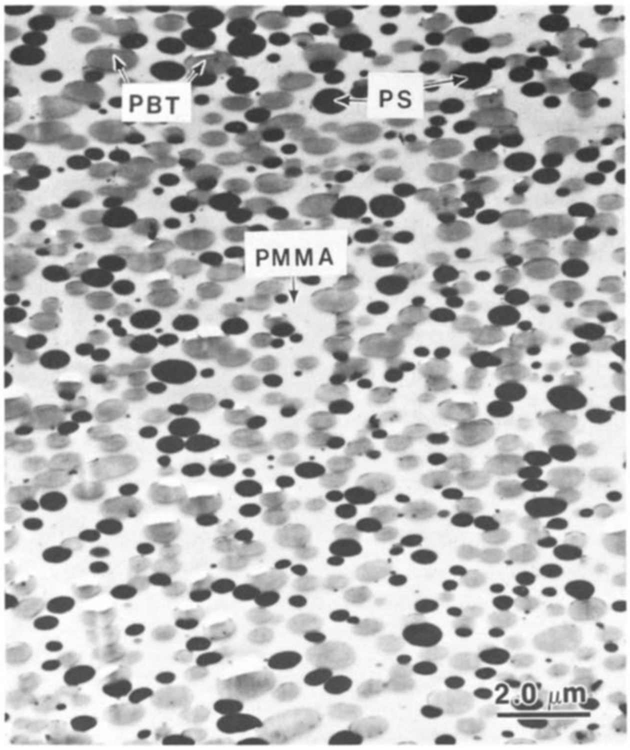

Figure 3 TEM photograph of 1/3/7 PS/PBT/PMMA blend showing separate dispersed phases of PS and PBT

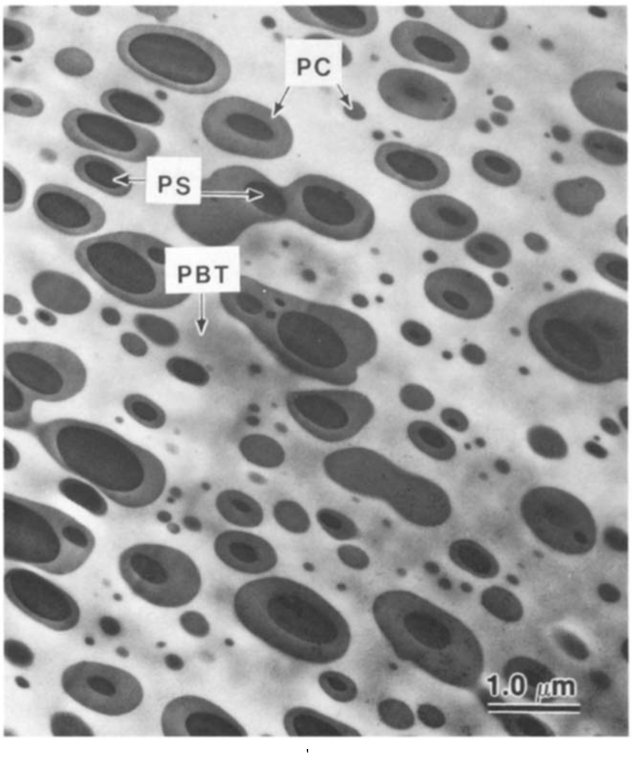

Figure 4 TEM photograph of 1/3/7 PS/PC/PBT blend showing PC envelopes around PS domains

that both PC and SAN complete strongly for the PS substrate with neither polymer being able to displace the other from the surface.

The foregoing observations demonstrate that PC exhibits positive spreading behaviour on both PS and PMMA in a matrix of PBT. They also indicate that neither PBT nor PS spread positively on one another in PMMA. Furthermore, they show that the ability of PC to spread on SAN copolymers declines with increasing AN content. Finally, they indicate that, when several dispersed phases are present, multifaceted envelopes can be generated if two or more of the dispersed components are able to spread on another. From a predictive point of view, it is important that spreading coefficients,

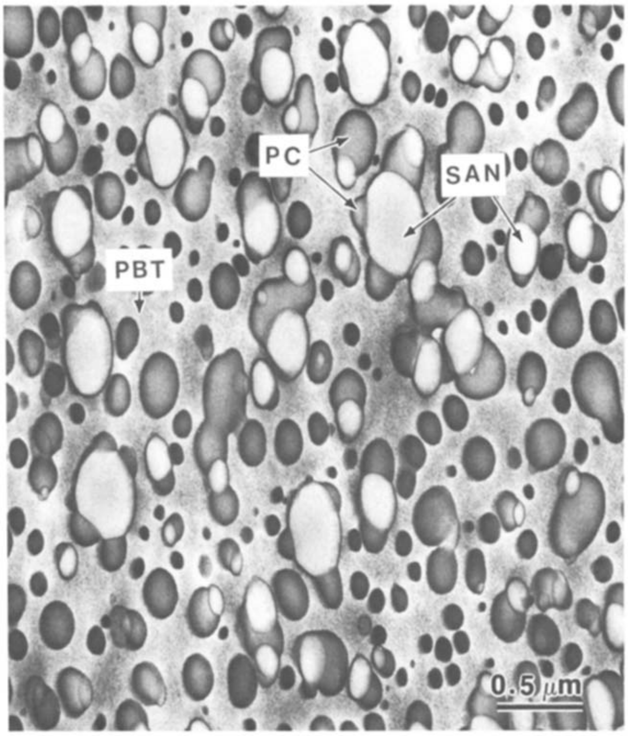

Figure 5 TEM photograph of 1/3/7 SAN (85/15 S/AN)/PC/PBT blend showing interrupted PC envelopes on SAN domains

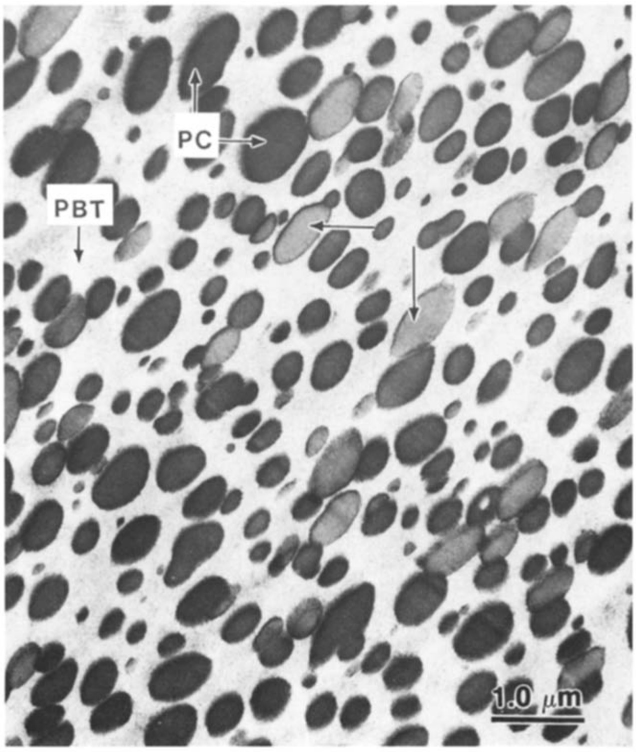

Figure 6 TEM photograph of 1/3/7 SAN (75/25/S/AN)/PC/PBT blend showing separated domains of PC and SAN

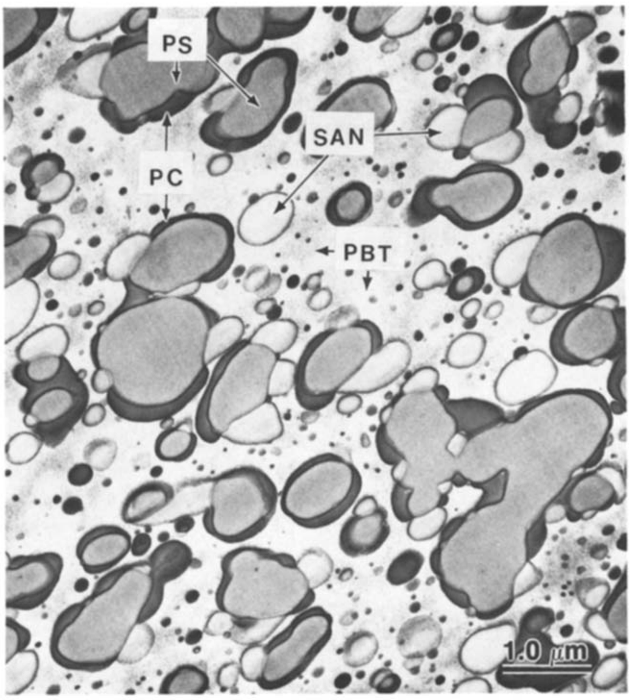

Figure 7 TEM photograph of 7/3/2/2 PBT/PS/SAN (75/25 S/AN)/PC blend showing competition of PC and SAN for PS surface

Table 1 Polymer surface and interfacial tensions

				Calculated 270°C		
Polymer	γ (20°C)	Polarity	$-\mathrm{d}\gamma/\mathrm{d}T$	γ	γ^{d}	γ^{p}
PS	40[a]	0.168[b]	0.072[b]	22	18.3	3.7
PC	40.8[c]	0.267[c]	0.065[d]	24.6	18.0	6.6
PMMA	41.1[b]	0.245[e]	0.076[b]	22.1	16.7	5.4
PBT	52.4[c]	0.236[c]	0.065[d]	36.2	27.6	8.6
PAN	59.8[f]	0.250[d]	0.065[d]	43.6	32.7	10.9
SAN (wt%)						
(75/25)				30.6	24.1	6.5
(50/50)				36.3	27.8	8.5
(25/75)				40.4	30.5	9.9

[a] Average (Wu 40.7[14]; Gaines 39.3[15])
[b] Measured, melt[13]
[c] Measured, contact angle[18]
[d] Estimated
[e] Harmonic mean approximation
[f] Parochor calculation[16]

calculated from available surface tension data, be consistent with these results.

The various surface and interfacial tensions used to determine spreading coefficients for the blends investigated in this study are listed in *Table 1*. For two of the resins, PS and PMMA, experimentally measured values for γ and $\mathrm{d}\gamma/\mathrm{d}T$ are available and were extracted directly from the literature[14,15]. For PBT and PC, surface tension and polarity values were determined from room temperature contact angle measurements using water and methylene iodide[18]. The surface tension for PAN (polyacrylonitrile) was calculated from parachor data[16] and $\mathrm{d}\gamma/\mathrm{d}T$ for PBT, PC and AN were estimated based on data available for resins of similar structure (e.g. PET). Using these parameters, and noting that the polarity ($\gamma^{\mathrm{p}}/\gamma$) is independent of temperature, values for γ^{d}, γ^{p} and γ at 270°C were calculated, and are listed in *Table 1*. Values for SAN copolymers having different S/AN ratios were calculated in a similar fashion assuming that the surface tensions varied linearly with the mole fractions of the individual components. Published studies on other random copolymers suggest that this is a valid approximation when no blocking occurs[19].

Spreading coefficients for the various blend components were calculated from the high temperature surface tension data in *Table 1* using equations (2) and (3). The values are listed in *Table 2*. For the SAN blends, the spreading coefficient for PC on SAN in a PBT matrix is plotted as a function of the AN concentration in *Figure 8*. For the systems studied, the results of the calculations are in excellent agreement with the experimental results. The spreading coefficient for PC on PMMA in PBT is +0.96 while that of PMMA on PC in PBT is −1.3. Thus, positive spreading of PC on PMMA is indicated (*Figure 1*). In contrast, the spreading coefficients for both PBT on PS (−6.9) and PS on PBT (−0.81) in PMMA are negative and no spreading is expected. This characteristic inevitably leads to the formation of two dispersed phases

Table 2 Polymer surface and interfacial tensions

Dispersed	Matrix	λ
PC on PMMA	in PBT	+0.96
PMMA on PC	in PBT	−1.3
PBT on PS	in PMMA	−6.9
PS on PBT	in PMMA	−0.81
PS on PC	in PBT	−2.4
PC on PS	in PBT	+0.73
PC on SAN	in PBT (75/25 (S/AN)	−1.4
	(50/50 S/AN)	−3.4
	(25/75 S/AN)	−5.2
	(0/100 S/AN)	−6.9
SAN (75/25) on PS	in PBT	+1.8

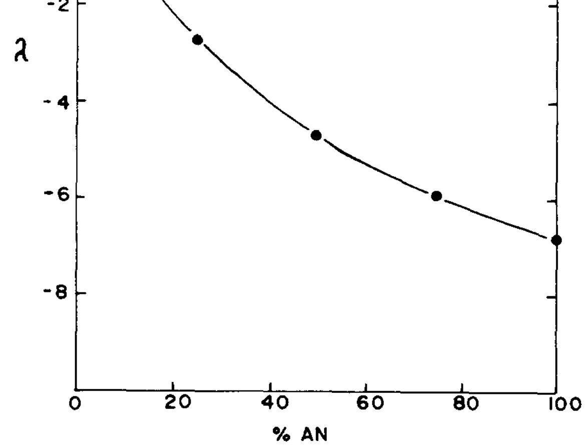

Figure 8 Variation in λ_{PC} on SAN in PBT with S/AN ratio in SAN copolymer

(*Figure 2*). *Figure 8* shows that the spreading coefficient for PC on SAN in PBT is first slightly positive (100% PS) and becomes increasingly negative at higher AN levels. This change is consistent with the observed shift from envelope formation to separate phases in the PC/PS/PBT and PC/SAN/PBT blends (*Figures 3–5*). In the PC/PS/SAN (75/25)/PBT blend, both PC and SAN show positive spreading coefficients on PS in the presence of PBT (+0.73 and +1.8, respectively) while neither will spread on the other. Thus, it is reasonable that both resins should compete to encapsulate the dispersed PS domains as observed experimentally (*Figure 7*).

From the excellent correlations obtained in this investigation, it is tempting to speculate that the morphologies of other multiphase polymer blends may be consistently predicted from spreading coefficient computations. However, it is important that such optimism be tempered with the knowledge that a number of successive approximations are involved in the preceding calculations and the current results must be treated with considerable caution. Some of these deficiencies, including the inaccuracies in surface tension and polarity values, the long temperature extrapolations, and the method of approximating interfacial tensions from surface tensions, have been noted. Others, such as neglect of the effects of partial miscibility[20], must also be considered. All of these factors emphasize the importance of carrying out direct interfacial tension measurements at the temperatures of interest. By doing this, equation (2) may be applied directly and reliable spreading coefficient values may be expected. The current studies suggest that the results will have considerable predictive value.

CONCLUSIONS

(1) TEM studies of a number of three- and four-component polymer blends indicate that their morphologies are dominated by the relative abilities of the blend components to spread on one another.

(2) Single-phase envelopes, multi-faceted envelopes and completely phase-separated structures have been observed. The evolution from one microstructure to another can be conveniently followed by employing random copolymers (e.g. SAN) of varying composition as one of the blend components.

(3) Spreading coefficient calculations based on experimental and calculated surface tension data are in excellent agreement with the observed experimental results from the blends examined in the current study.

(4) The results presented in this paper suggest that spreading coefficient computations may offer a promising route for predicting the morphologies of complex polymer blends. The general use of this method, however, is predicated on the acquisition of more precise interfacial tension values.

REFERENCES

1 Hobbs, S. Y. in 'Plastics Polymer Science and Technology' (Ed. M. D. Baijal) Wiley Interscience, New York, 1982, Ch. 6
2 Jordhamo, G. M., Mason, J. A. and Sperling, L. H. *Polym. Eng. Sci.* 1986, **26** (8), 517
3 Starita, J. M. *Trans. Soc. Rheol.* 1972, **16**, 339
4 VanOene, H. *J. Colloid Interface Sci.* 1972, **40**, 448
5 Rudin, A. *J. Macromol. Sci., Rev. Macromol. Chem.* 1980, **C19** (2), 267
6 Cavanaugh, D. B. and Wang, C. H. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1269
7 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Lett.* 1981, **19**, 79
8 Heikens, D., Hoen, N., Barentsen, W., Piet, P. and Landan, H. *J. Polym. Sci., Polym. Symp.* 1978, **62**, 309
9 Fayt, R., Jérôme, R. and Teyssié, Ph. 'Characterization and Control of Interfaces in Emulsified Incompatible Polymer Blends', presented at the WRCC/IMRI Polymer Symposium Series, Polyblend-86, Montreal, April 1986
10 Hobbs, S. Y., Dekkers, M. E. J. and Watkins, V. H. *Polym. Bull.* 1987, **17**, 341
11 Harkins, W. D. 'The Physical Chemistry of Surface Films', Reinhold Pub. Co., New York, 1952, p. 23
12 Becher, P. 'Emulsions Theory and Practice', ACS Monograph no. 162, Reinhold Pub. Co., New York, 1957, p. 15
13 Wu, S. 'Polymer Interface and Adhesion', Marcel Dekker, New York, 1982, Ch. 3
14 Wu, S. *J. Polym. Sci. C*, 1971, **34**, 19
15 Gaines, G. L. *Polym. Eng. Sci.* 1972, **12** (1), 1
16 VanKrevelen, D. W. 'Properties of Polymers', Elsevier, Amsterdam, 1976, Ch. 4 and 5
17 Trent, J. S., Scheinbeim, J. I. and Couchman, P. R. *Macromolecules* 1983, **16**, 589
18 LeGrand, D. G., personal communication
19 Rastogi, A. K. and St. Pierre, L. E. *J. Colloid Interface Sci.* 1969, **31**, 168
20 Hobbs, S. Y., Groshans, V. L., Dekkers, M. E. J. and Shultz, A. R. *Polym. Bull.* 1987, **17**, 335