

Factors influencing structure formation and phase size in an immiscible polymer blend of polycarbonate and polypropylene prepared by twin-screw extrusion

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The modification of the morphology of an immiscible binary blend of polypropylene (PP) and polycarbonate (PC), in a co-rotating, intermeshing, twin-screw extruder has been studied. It was found that the proximity to the die wall, high composition and high viscosity/elasticity ratios resulted in preferential fibre formation for the dispersed phase. The phase size and size distribution increase significantly with composition. The point of phase inversion is difficult to determine precisely due to the presence of extended morphologies over a wide composition range. Composite blend morphologies (occlusion formation) were observed at 60% PC (weight). The influence of the viscosity ratio on phase size was studied over a wide range and was found to be a minor effect at 10% PC (volume) composition. The effect of viscosity ratio becomes more pronounced at 20% PC. Comparison of the viscosity ratio effect on phase size between the twin-screw and an internal mixing chamber indicated a significantly coarser dispersed phase in the latter case at high viscosity ratio. At a lower viscosity ratio the phase size and size distribution were identical in the two processing environments. The minor-phase morphology in the centre of the extruded strand was not found to be highly sensitive to the screw speed and the volumetric flow rate. This indicates that the minor phase in these blends is not highly dependent on the shear stress and energy imposed on the material before the die. The above results are contrasted with previous detailed studies carried out in an internal mixing chamber.

(Keywords: blend; morphology; phase size; twin-screw extrusion; polypropylene; polycarbonate; viscosity ratio; composition)

INTRODUCTION

Physical properties of immiscible polymer blends have been shown to be closely related to the size and shape of the deformable minor phase¹⁻⁷. Such structures are strongly dependent on both the physical properties of the polymers in the molten state and the type of mixing machinery used to process them. Shear stress, shear rate, composition, molecular weight, viscosity ratio, elasticity ratio and interfacial tension play a critical role in microstructure generation of immiscible polymer blends⁸⁻²⁷.

Over the last few years the influence of capillary flow on phase size morphology of immiscible polymer blends has received extensive attention⁸⁻¹². However, large-scale production requires the use of either continuous (extruder) or semi-continuous (internal mixing chamber-extruder) mixing equipment, where die forming and material cooling are actually the last forming steps. In this laboratory a series of studies aimed at understanding how both the size and shape of the minor phase may be controlled during processing have been undertaken.

The use of twin-screw extruders, either co-rotating or counter-rotating, and either intermeshing or non-intermeshing, is gaining in importance for compounding and

blending. A recent paper of White *et al.*¹³ has studied intermeshing counter-rotating and intermeshing co-rotating twin-screw extrusion machinery. The development of the technology is treated simultaneously with the review of basic investigations of flow mechanisms from both the theoretical and experimental points of view. Contrary to single-screw extruders, where material can experience a wide range of mixing history, depending upon its location within the extruder, twin-screw extruders enable a more uniform distribution of shear within the material. Most co-rotating, intermeshing, twin-screw extruders operate on a building-block principle to design the screws. Screw configuration can be changed using positive or negative conveying elements or kneading blocks in order to fit any particular situation. This flexibility, coupled with the fact that twin-screw extruders are operated in a starve-fed mode, makes it very difficult to predict *a priori* the effect of processing parameters on the shape and size of the minor phase of immiscible polymer blends. Most of the difficulties are due to the extremely complex flow patterns existing within these machines, which have to be related to the viscoelastic and interfacial properties of both components of immiscible polymer blends. Although recent advances have been made as far as flow modelling is concerned^{13-17,28,29}, application of these often complex numerical techniques to polymer blends is still difficult and insight into the behaviour of these systems must still rely on experimentation.

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In previous papers the influence of composition^{18,19}, viscosity ratio²⁰ and processing conditions²¹ on the size and shape of the minor phase of an immiscible blend of polypropylene (PP)/polycarbonate (PC) prepared in an internal mixing chamber was examined. The objective of this paper is to consider the influence of the above parameters on the same blends processed in a co-rotating, closely intermeshing, twin-screw extruder.

EXPERIMENTAL

Materials

Three commercial grades of bisphenol-A polycarbonate (PC) and three grades of polypropylene (PP) were used in this study. The polycarbonates were Merlon M-39, M-40 and M-50 obtained from the Mobay Corporation. The polypropylene samples were Pro-Fax 6301, 6501 and 6701 obtained from Himont. Their properties, including the number- and weight-average molecular weights, are summarized in Table 1. Throughout this paper polycarbonates M-39, M-40 and M-50 will be referred to as PC-1, PC-2 and PC-3 respectively, and polypropylenes 6301, 6501 and 6701 will be referred to as PP-1, PP-2 and PP-3. Various combinations of PC in PP allowed the study of the viscosity ratio ($\eta'_a/\eta'_m = p \equiv$ viscosity ratio) in the range of $p > 1$. Unless specified otherwise, all blend concentrations are calculated as per cent by volume.

Mixing

Prior to a typical mixing experiment the sample mixture was dried for 17 h under vacuum at 90°C in order to minimize hydrolytic degradation of the polycarbonate during processing. The polypropylene was stabilized with 0.2% antioxidant. The materials were then blended in a ZSK-30 (Werner-Pfleiderer) intermeshing, co-rotating, twin-screw extruder having a screw length to screw diameter ratio, L/D , of 40. Feeding was performed under dry nitrogen and vacuum was applied in the decompression zone. The die used was a capillary die with an L/D of 2.2 and a 40° angular entry. The dimensions and configuration of the die are shown in Figure 1. Cooling of the extrudates after die exit was performed in water to freeze-in the morphology. Take-up speed was set as low as possible to minimize further modification of morphology due to axial tension.

Unless specified otherwise the following conditions were used for blending. Experiments were performed at a constant volumetric flow rate of 350 cm³ min⁻¹. Feeding was calibrated assuming volume additivity of the components at room temperature and 250°C, respectively. Such a procedure allowed extrudates of nearly constant diameter to be obtained for any blend considered. The temperature profile of the barrel was set at 230/236/240/244/244°C from feed hopper to exit. Under these conditions the melt temperature in the die remained constant at 250°C as measured by a thermocouple in direct contact with the melt. The screw speed was maintained at 300 r.p.m. The standard screw configuration used for all experiments is shown in Figure 2.

Morphological analysis

Electron microscopy. A scanning electron microscope (JEOL JSM-T-220) was used to examine the shape and size of the dispersed phase, as well as morphology variations across the diameter of the extrudate. Transverse and longitudinal fracture surfaces were obtained from samples vitrified in liquid nitrogen. No etching was performed. Samples were then coated with a gold/palladium alloy. Unless otherwise indicated, morphological analysis was carried out in the centre of the extrudate strand.

Image analysis. A semi-automatic method of image analysis was used to quantify the size of the minor phase, when applicable. It consisted of a unidirectional digitizing device that works as follows. As the cross-hair of a magnifier connected to the mobile part of a linear variable differential transformer (LVDT) is moved over the photomicrograph, the Ferrets diameter of a domain is recorded and stored in a microcomputer for the calculation of statistical parameters. Two fields of view and 200 diameters are considered for a given sample. The number-average diameter, d_n , and the volume average diameter, d_v , were obtained in this way.

Owing to the difference in shrinkage between the two materials, voids were observed around polypropylene domains in polycarbonate-rich samples. In all these cases the diameter of the voids was considered for the computation of statistical parameters. For the polypropylene-rich samples, both particles and marks left by particles, ejected during the fracture, were measured. No correction factor was applied to the reported diameters. Particle size

Table 1 Characterization of polycarbonate and polypropylene materials

	Melt index (ASTM) (g/10 min) ^a	Density at 250°C (g cm ⁻³) ^a	η'_i at 100 rad s ⁻¹ (Pa s) ^b	M'_n ^a	M'_w ^a
Polycarbonate					
(M-39) PC-1	18	1.08	1.79×10^3	12 300	26 500
(M-40) PC-2	9	1.08	2.19×10^3	13 200	30 300
(M-50) PC-3	4.5	1.08	2.76×10^3	16 500	36 300
Polypropylene					
(6301) PP-1	12	0.75	1.60×10^2	31 300	200 000
(6501) PP-2	4	0.75	2.48×10^2	50 000	325 000
(6701) PP-3	0.8	0.75	3.93×10^2	72 000	470 000

^aObtained from suppliers

^bMeasured

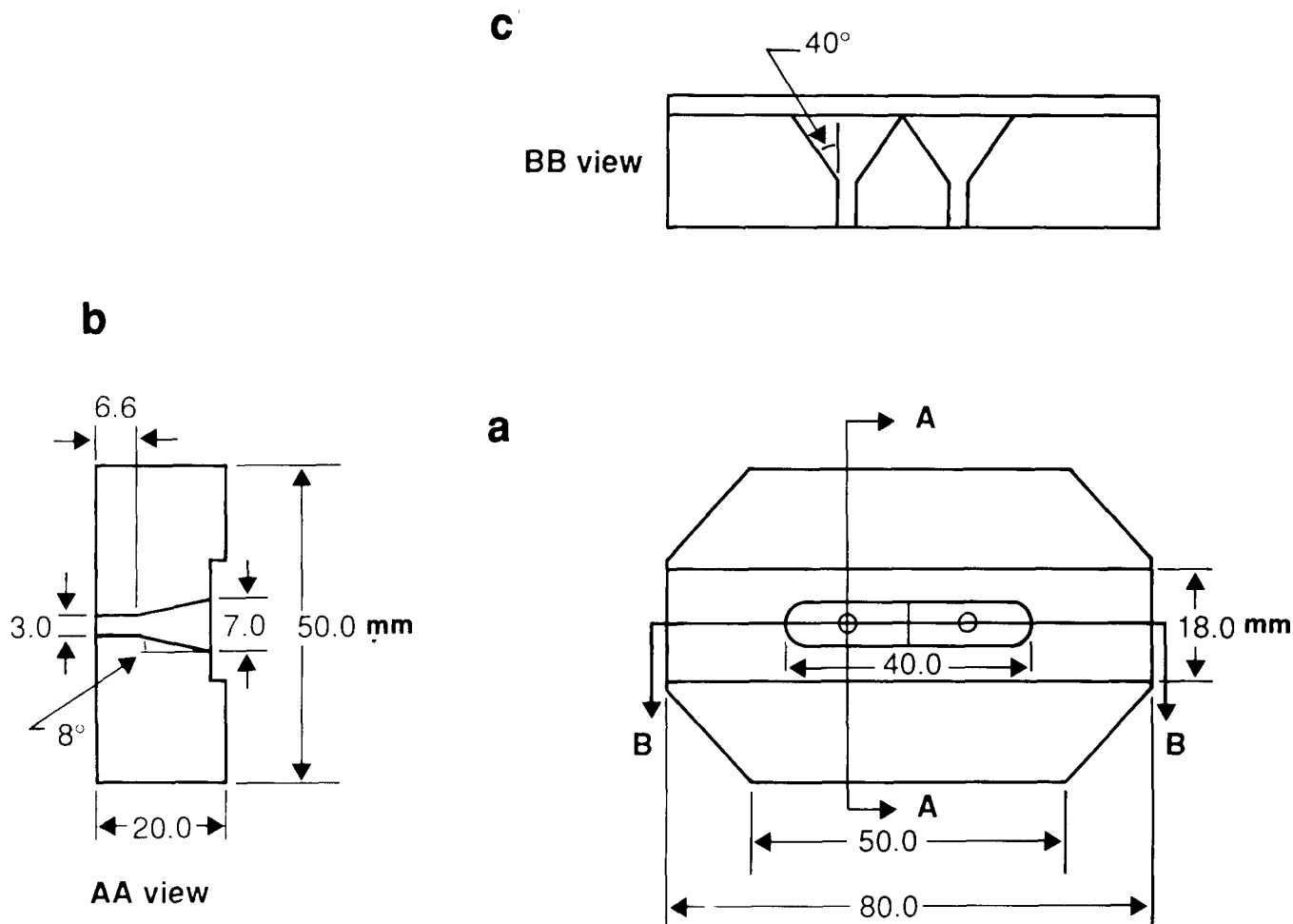


Figure 1 Dimensions and configuration of the die used in this study

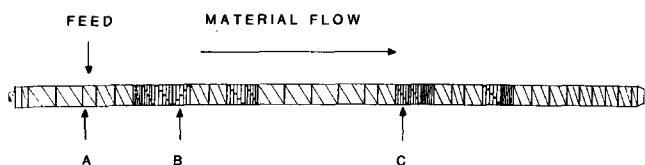


Figure 2 Standard screw configuration used for the ZSK-30 twin-screw extruder (A \equiv transport element, B \equiv left-handed kneading block, C \equiv right-handed kneading block)

corrections account for two phenomena: (a) the fact that the observed diameter of a given particle, after microtoming or fracture, is usually less than the true diameter of the original spherical particle; and (b) materials with large dispersed particle size distributions result in an average diameter value that overestimates the contribution of large particles. In this system, calculations have shown that the particle size distribution is sufficiently low (d_w/d_n is typically 2–2.5) that the two above effects cancel. In other words, despite the fact that mathematical corrections were not applied, the reported diameter in this study should be very close to the true diameter.

Rheological analysis

The Rheometrics Mechanical Spectrometer RMS model 605 was used to measure the dynamic viscosity, η' , and the storage modulus, G' , as a function of frequency at 250°C. The experiments were carried out in the

dynamic mode in parallel-plate geometry at a strain of 10% and gap of 1.2 mm. The experiments were performed in a dry nitrogen atmosphere. The curves representing η' and G' versus frequency for the six neat resins are reported in Figures 3 and 4 respectively.

RESULTS AND DISCUSSION

Droplet/fibre transitions

One of the most striking features of this study is the significant modification of morphology with radial position in the extruded strands. Figure 5 illustrates this effect at two concentrations for PC-2 dispersed in PP-2. It is evident at both concentrations that a fibrous morphology for the dispersed phase is present at the periphery. For 5% PC (by volume) at the periphery, fibre/droplet morphologies coexist whereas only droplet morphologies are observed at the midpoint and centre of the sample. Increasing the concentration to 20% significantly increased the presence of fibres at the periphery and extended structures are also observed at the midpoint. Mostly droplets are observed at the centre of the strand.

These results illustrate the importance of the combined effects of both shear rate and composition on the shape of the minor phase. Shear rate effects are greatest at the wall and least at the centre of the strand. It is also well known¹⁸ that increasing the composition increases the size of the minor phase until particle-particle interactions

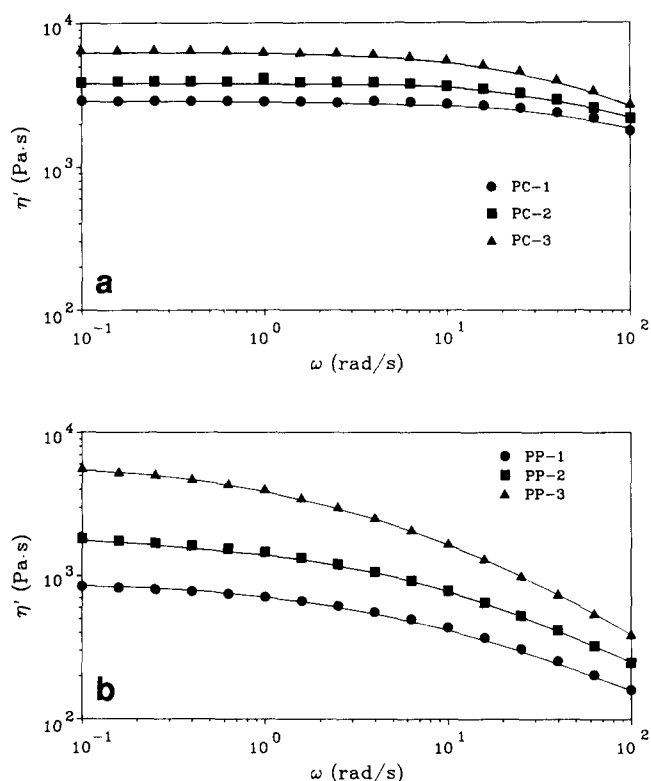


Figure 3 Curves of η' versus ω for (a) three neat polycarbonate samples at 250°C, and (b) three neat polypropylene samples at 250°C

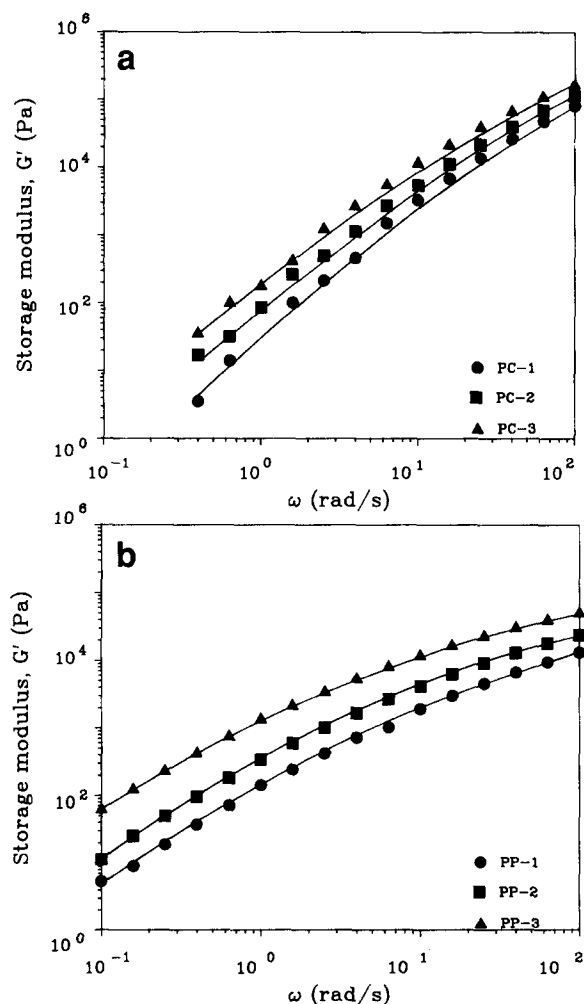


Figure 4 Curves of G' versus ω for (a) three neat polycarbonate samples at 250°C, and (b) three neat polypropylene samples at 250°C

become sufficiently pronounced that extended structures are formed.

The above results are not unexpected for an immiscible binary blend. However, it is interesting to note in Figure 6 that the complementary mixture of PP-2 dispersed in PC-2 results mostly in droplets throughout the strand even at 20% composition. The influence of shear is still evident, with smaller particles at the periphery than at the centre. Preferential droplet formation for PP-2/PC-2 is a highly unexpected result.

In the literature two main mechanisms are postulated for extended morphologies. Van Oene⁹ has shown that, in capillary flow, there are two main modes of dispersion: stratification or droplet formation. These morphologies were shown to be controlled by the particle size, interfacial tension and the differences in the viscoelastic properties of the two phases. In mixtures of polystyrene (PS) and poly(methyl methacrylate) (PMMA), the PMMA, which had the largest second normal stress function, was found to form droplets in the PS matrix. Substitution of a low-molecular-weight PMMA in the same system resulted in stratification. Van Oene noted that when the discrete particles were smaller than 1 μm , the difference in the morphology of complementary mixtures (stratification versus droplets) disappeared, indicating that the elastic term contributing to the interfacial tension was no longer dominant. He developed a theory that considers an elastic contribution to the interfacial tension. This theory would predict a stratified morphology for the least elastic component dispersed in a highly elastic matrix. In Figure 6, however, these experiments show that the less elastic polypropylene dispersed phase is in droplet form.

Tomotika³⁰ has studied the growth of capillary instabilities on a Newtonian fluid thread surrounded by a second Newtonian fluid. In this study it was shown that the time of break-up (t_b) of the thread is proportional to the matrix viscosity and inversely proportional to the viscosity ratio. Elmendorp²² has shown for certain systems that the presence of fibres is more apparent at a lower viscosity ratio. In this study clearly the opposite is observed in these undrawn strands.

Tsebrenko and coworkers⁸ suggest that the main factor governing structure formation processes was the ratio of the melt viscosities, which was varied within very wide limits. It was found that fibre formation is most pronounced at a melt viscosity ratio close to unity. Cox³¹ has reported that at large viscosity ratio values, droplet deformation in the extrudate will be insignificant.

It is interesting to note that none of the above explanations fits the experimental observation of preferential extended structures, or fibre formation, for PC-2 dispersed in PP-2. This effect remains poorly understood. It should be pointed out, however, that Berger and coworkers²³ and Jorgensen and coworkers¹² have also observed preferential fibre formation for a more elastic dispersed phase at higher viscosity ratio values for poly(ethylene terephthalate)/polyamide-6 and poly(methyl methacrylate)/polystyrene blends, respectively.

These results underline the potential of the die in modifying the size and shape of the minor phase. The morphology of the minor phase for these blends appears to be much more sensitive to the die than to phenomena before the die. Factors such as screw speed and volumetric flow rate were found to play only a minor role and are discussed later.

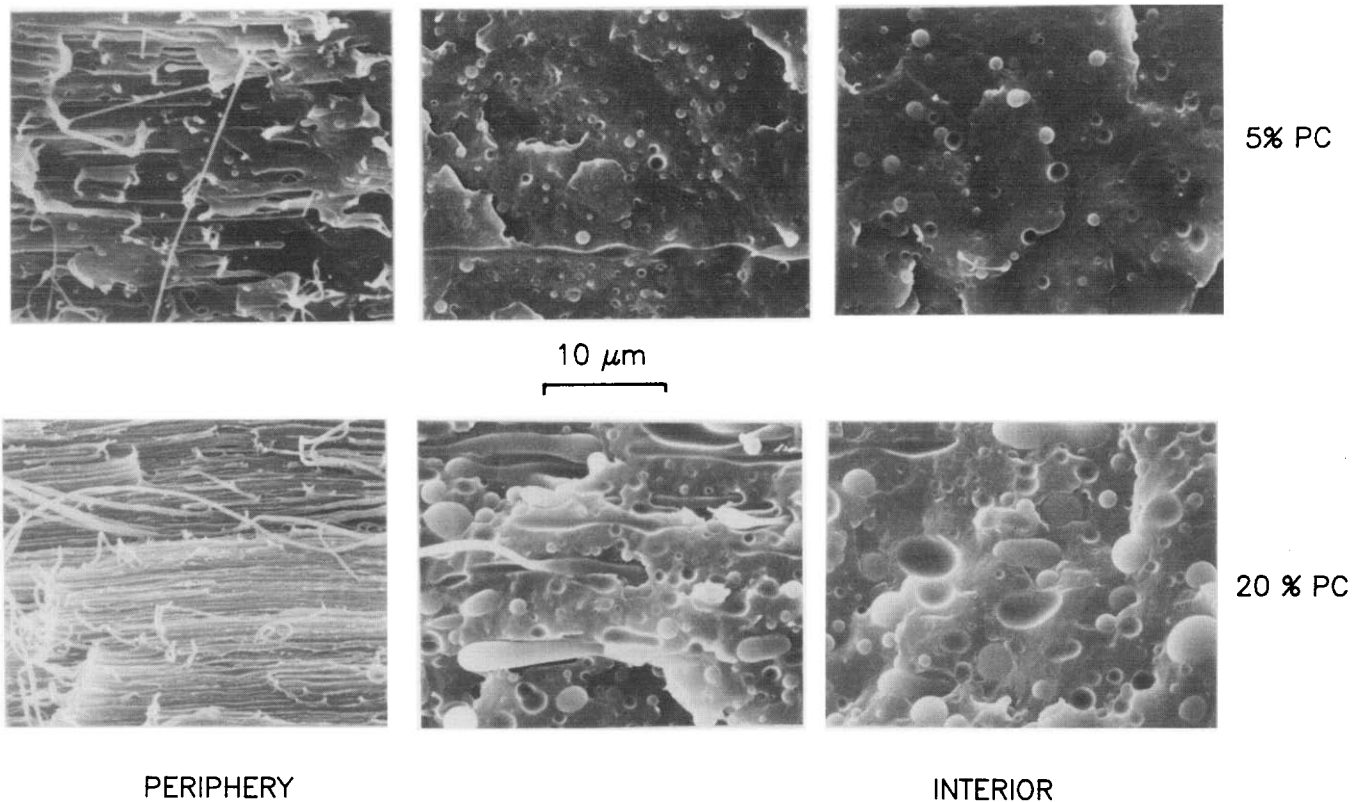


Figure 5 Scanning electron micrographs of fracture surfaces of PC-2 dispersed in PP-2 at three different radial positions for 5% and 20% PC-2 (by volume) samples (Viscosity ratio = 8.83)

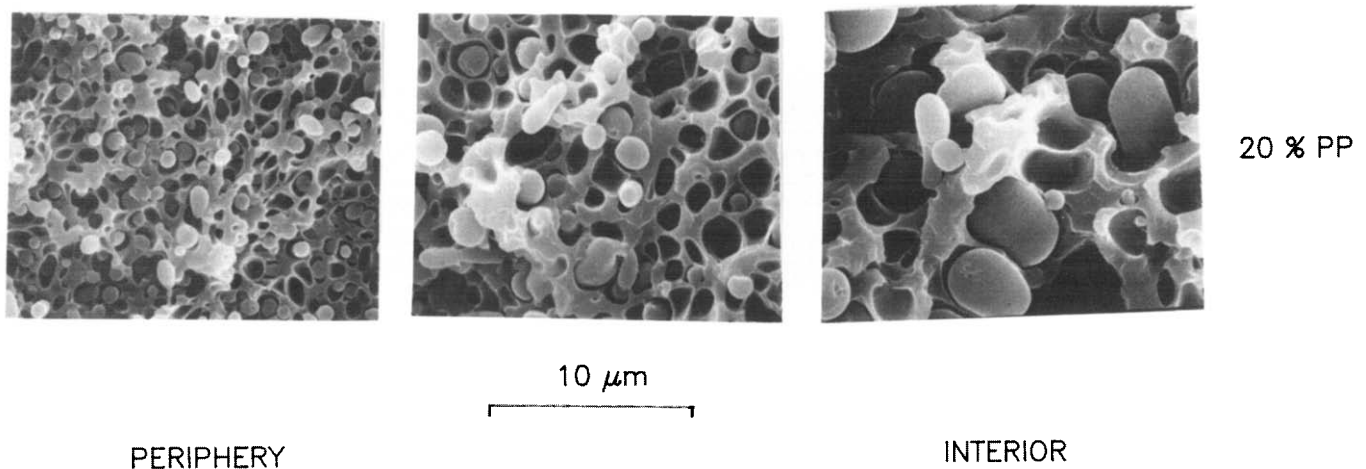


Figure 6 Scanning electron micrographs of fracture surfaces of PP-2 dispersed in PC-2 at three different radial positions for 20% PP-2 (by volume) samples (Viscosity ratio = 0.113)

Influence of composition

Figure 7 shows the phase size/composition dependence of the PC-3/PP-1 blend. The particle size, both d_v and d_n , increases with composition. Although the particle size generated in twin-screw extrusion is smaller, the rate of particle size increase with composition for both d_v and d_n compares well with previous studies in an internal mixing chamber. The dependence of phase size on composition has been treated in detail elsewhere^{18,19}. The particle size distribution (d_v/d_n) also widens with composition as observed previously¹⁸. From Figure 7 it can be determined that the size distribution (d_v/d_n)

increases from 2.5 at 7% to 3.7 at 38% PC (by weight). The location of the region of phase inversion is difficult to determine precisely, but appears to occur between 55 and 65% PC (by weight). This is a somewhat higher concentration compared with that observed for a high viscosity ratio blend in an internal mixing chamber reported previously¹⁸. The observation of composite blend structures consisting of two distinct phases with inclusions present in one of the phases was also observed at a similar composition (60% PC by weight) (see Figure 8).

The main difference observed in the phase size/com-

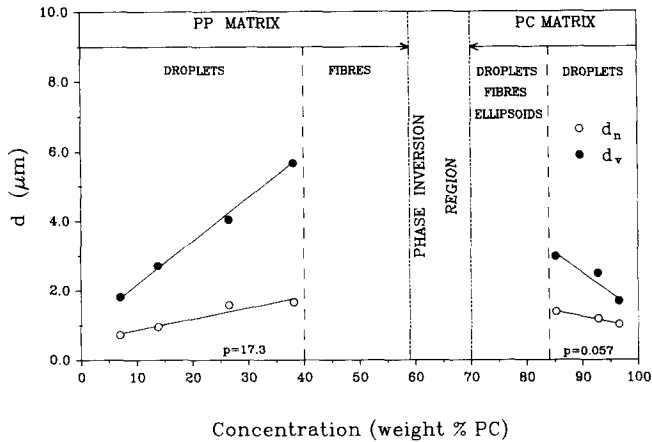


Figure 7 Dependence of phase size (d_v and d_n) on composition (wt%) for blend of PC-3 and PP-1 ($p \equiv$ viscosity ratio)

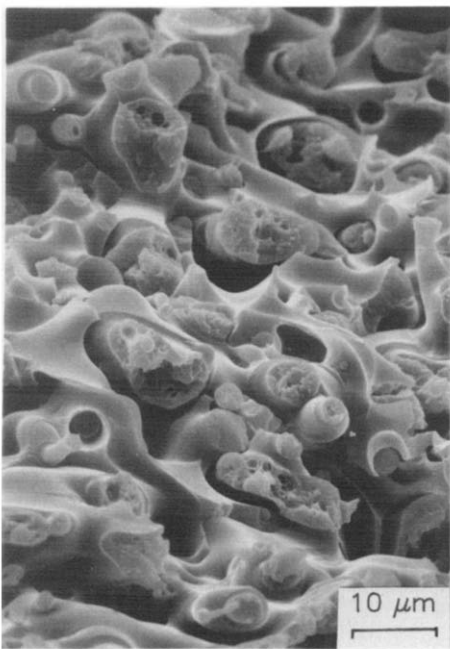


Figure 8 Scanning electron micrographs of composite structures for PC-3 and PP-1 blend at 60% PC (by weight)

position dependence during twin-screw extrusion is the presence of a large region bounding the phase inversion zone where extended structures/matrix morphology is observed. Fibres were observed between 45 and 55% PC, and a combination of droplets, fibres and ellipsoids were observed for the complementary mixture between 65 and 80% PC. This was the main reason why the precise point of phase inversion is difficult to determine.

Influence of viscosity ratio and processing environment

The influence of viscosity ratio p for $p > 1$ is shown in Figure 9. Since it is difficult to estimate the shear rate for mixing in a twin-screw extruder, the viscosity ratio presented in Figure 9 is obtained from the viscosities of the pure resins obtained at 100 s^{-1} on the Rheometrics Mechanical Spectrometer (see Figures 3a and 3b). The difficulty in estimating the shear rate is due to the fact that in the twin-screw extruder the material is modified progressively from solid to liquid form and experiences a range of temperatures in a limited timescale. It can be

seen from Figure 9 that phase size increases with viscosity ratio, although the effect is small for the number-average diameter at low composition. The effect of viscosity ratio is more pronounced at higher composition and for the volume-average diameter. The latter point indicates that the particle size distribution increases

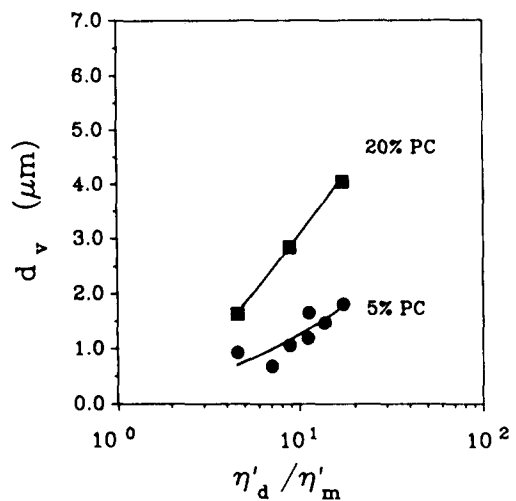
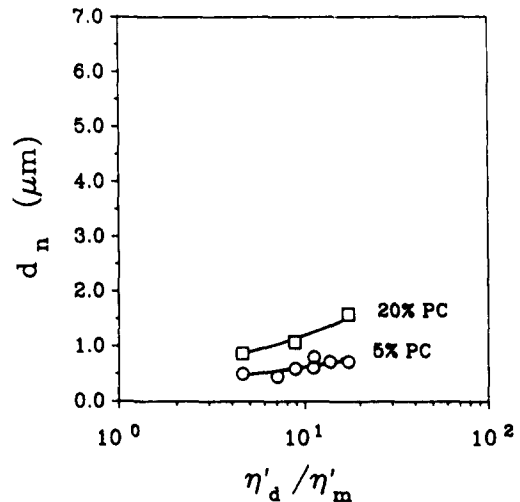


Figure 9 Volume- and number-average diameters of minor phase versus viscosity ratio, η'_d/η'_m , for 5% and 20% PC (by volume) samples

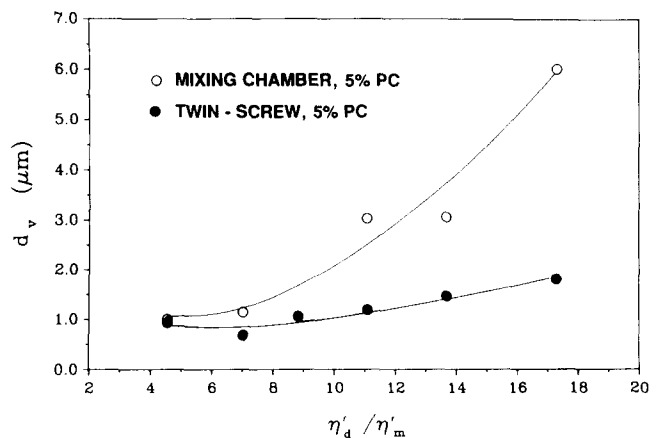


Figure 10 Effect of viscosity ratio for samples prepared in two different processing environments: internal mixing chamber and twin-screw extruder (composition of minor phase is 5% PC by volume)

significantly with phase size; d_v/d_n increases from 1.9 to 2.6 over a four-fold range of viscosity ratio for the 20% samples.

In Figure 10 the effect of the processing environment is shown. The phase size/viscosity ratio relationship in an internal mixing chamber, as studied previously²⁰, is compared to that in the twin-screw extruder. The viscosity ratio reported here is calculated from the η' values of the RMS at 100 s^{-1} . As mentioned earlier, although the shear rate in the mixing chamber can be estimated empirically as 185 s^{-1} , it is virtually impossible to estimate the shear rate reliably in the twin-screw extruder. A study of the viscosity ratio at various shear rates shows that a systematic error is introduced, but that the ordering of change is not affected. The data presented in Figures 9 and 10 should therefore be considered as an apparent viscosity ratio. Figure 10 shows how the same sample characterized on separate rheological equipment behaves in two very different processing environments.

Figure 10 shows that the difference in processing environments is very pronounced at high viscosity ratio. The difference in the phase size at $\eta'_d/\eta'_m = 17.3$ differs by a factor of 4. It is interesting to note that the difference in phase size is virtually eliminated at low viscosity ratio. Both the phase size and polydispersity of the samples produced at $\eta'_d/\eta'_m = 4.5$ are identical. It is also interesting that, despite the differences in phase size with viscosity ratio for the internal mixer and twin-screw extruder, the particle size distributions are similar over the entire viscosity ratio range: (d_v/d_n) varies from ~ 1.3 at $\eta'_d/\eta'_m = 4.5$ to 2.8 at $\eta'_d/\eta'_m = 17.3$ in both cases.

Overall the influence of viscosity ratio is more pronounced in an internal mixer than in the twin-screw extruder. It should also be re-emphasized that the influence of viscosity ratio becomes more pronounced at higher composition in the twin-screw extruder, as shown in Figure 9.

The phase size/viscosity ratio dependencies for the processing environments shown in Figure 10 bear a striking similarity to classical studies carried out by Taylor³². In those studies he considered the energy required to disintegrate the dispersed particle (E_d) as a function of viscosity ratio (p) for Newtonian fluids in shear and elongational flow fields. The results for shear flow indicate that it was difficult to break the droplet at high viscosity ratios. In an elongational flow field, however, it was observed that droplet break-up was relatively easy over a wide range of viscosity ratios. Since the final phase size gives an indication of the extent of droplet break-up, in an oversimplified manner the results in Figure 10 suggest that the mechanism for deformation/breakdown is predominantly shear flow in the internal mixer, whereas that for the twin-screw extruder is extensional flow. This may not be unexpected when considering the influence of mixing elements in the twin-screw extruder, which force melt through narrow orifices, and the convergence ratio from the barrel to the die.

Influence of processing parameters

In Figures 11 and 12 the influence of screw speed at constant volumetric flow rate, and the influence of volumetric flow rate at constant screw speed (r.p.m.), are shown. Over a wide range, these processing parameters have no significant effect on phase size in the centre of

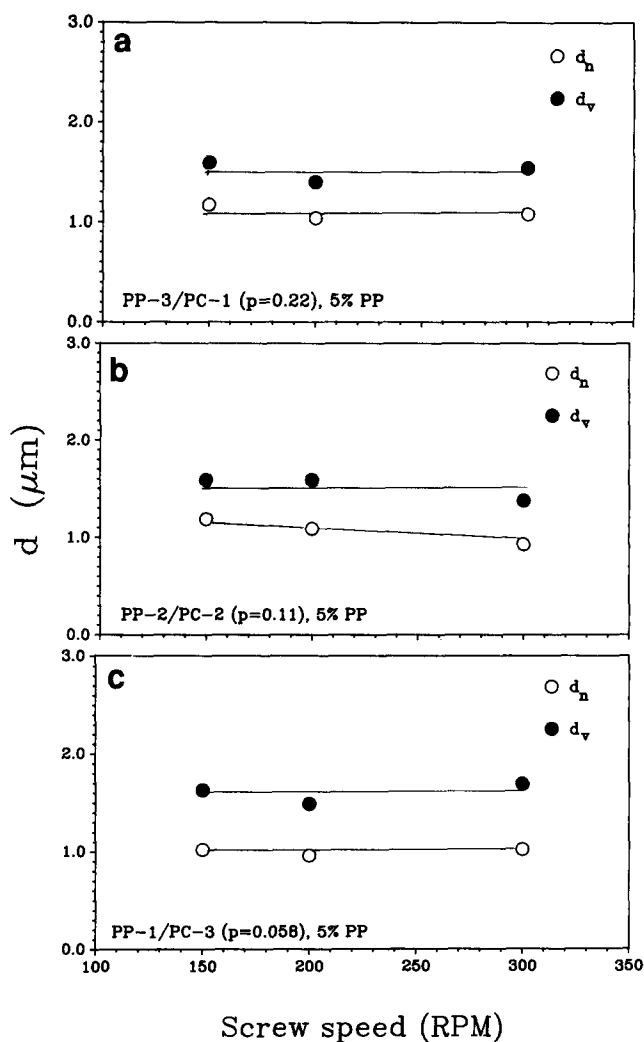


Figure 11 Effect of screw speed for 5% PP (by volume) samples at constant volumetric flow rate: (a) PP-3/PC-1, (b) PP-2/PC-2, (c) PP-1/PC-3

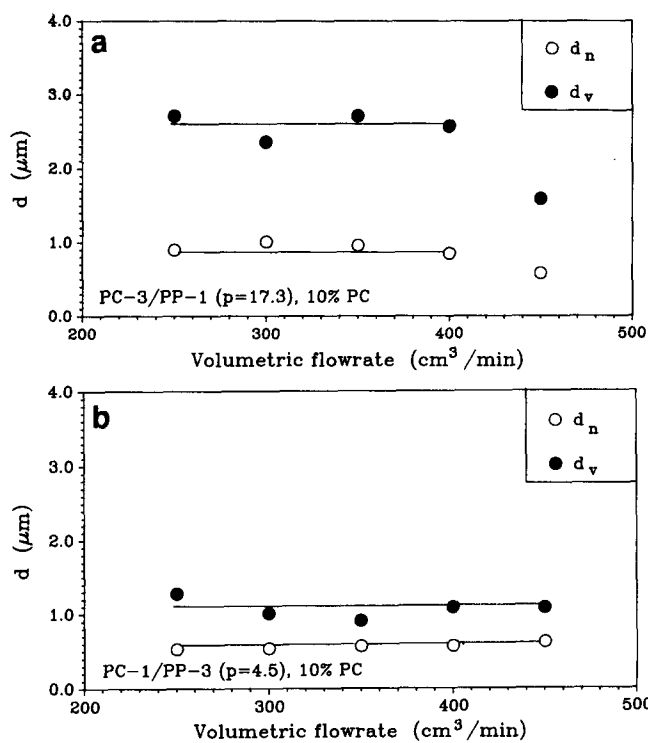


Figure 12 Effect of volumetric flow rate for 10% PC (by volume) samples at constant screw speed: (a) PC-3/PP-1, (b) PC-1/PP-3

the extruded strand for a 10% blend of both PP-1 and PC-1 dispersions in one another. Therefore, the morphology is not sensitive to the influence of energy and shear stress imposed on the material before the die. This conclusion confirms data observed previously in an internal mixing chamber²¹. It thus seems clear that further modification of morphology for polycarbonate/polypropylene blends must be achieved through compatibilization or by die land modification, since this seems to have the most profound effect on the dispersed phase morphology.

Eise *et al.*²⁴ report that homogenization/mixing of polymer blends on the twin-screw extruder are enhanced by high screw speeds, reduced rates of feeding (low degree of fill) and the use of many kneading blocks. Bartilla *et al.*²⁵ have studied the effect of processing variables in 70:30 (by weight) polypropylene/ethylene-propylene-diene terpolymer (PP-EPDM) blends extruded on a twin-screw machine. These authors found that the presence of built-in baffles (left-handed elements located downstream of the kneading blocks of the plastification zone) resulted in considerably more uniform and finer blends of EPDM in PP. Increasing the screw speed resulted in more uniform EPDM distribution, while increasing the material throughput produced a coarsening of the dispersed phase. Different metering zone geometries showed a perceptible, but only minor, effect on EPDM distribution. Narrow tapered discs brought about a narrower elastomer particle size distribution, whereas the geometry involving a few side-tapered discs produced numerous large EPDM particles. Compared to the melting zone, the differences achieved in the metering zone were slight. A trend was observed, however, in the sense that narrow kneading discs were more likely to produce a narrow particle size distribution. Plochocki *et al.*²⁶ noted that the melting section had an important effect when mixing a 70:30 high-density polyethylene/polystyrene uncompatibilized blend on a twin-screw co-rotating extruder. The compatibilized blend was unaffected by the same changes in screw configuration.

Recent studies²⁷ have shown that processing parameters such as screwspeed and volumetric flow rate have more of an effect on highly elastic dispersed phases such as elastomers.

CONCLUSIONS

The morphology of the minor phase in PP/PC blends processed on a twin-screw extruder appears to be significantly more influenced by the die than by phenomena before the die. The presence of extended structures is favoured by higher shear rate (proximity to the die wall) and composition. Viscosity and/or elasticity ratios also appear to influence significantly the shape of the dispersed phase. Fibre formation was observed at high viscosity and elasticity ratios.

The particle size increases and particle size distribution widens as composition is increased. The observation of composite droplets occur at similar compositions, as in previous studies using an internal mixer.

The phase size, particularly the volume-average diameter, increases with viscosity ratio. The effect is more pronounced at higher composition. At a high viscosity ratio, the phase size was found to be four times larger in

an internal mixer as compared to that generated in a twin-screw extruder. At lower viscosity ratio, the morphologies obtained by the two different compounding techniques were identical.

The influence of screw speed (at constant volumetric flow rate) and the influence of volumetric flow rate (at constant screw speed) are shown to have no significant effect on phase size in the centre of the extruded strand at both low and high viscosity ratio. This indicates that the system is not highly sensitive to the influence of energy and shear stress imposed on the material before the die.

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