Influence of composition on the morphology of polypropylene/polycarbonate blends*

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The size and size distribution of the minor phase in melt blended polypropylene/polycarbonate blends is studied as a function of composition. Composition has a marked effect on the dispersed phase size, particularly at intermediate concentrations where the region of dual-phase continuity was observed for these blends. The volume average diameter was found to increase more than four-fold on increasing the concentration of polycarbonate from 5 to 40 wt%. The particle size distribution of the minor phase demonstrates wide polydispersity, but narrows as dimensions decrease. Lowering the viscosity ratio of the blends from 7 to 2 has a significant impact on the phase size/composition relationship and the region of dual-phase continuity is found to shift to a higher composition. The position and shift of the region of dual phase continuity are not consistent with predictions based exclusively on composition and viscosity ratio.

INTRODUCTION

Polymer blends, by definition, are physical mixtures of structurally different homo or copolymers. In the past 10 years, research into polymer blends has increased significantly. Blending has several sound economic advantages. It can: generate a material with unique properties and/or processability; extend the performance of expensive resins; allow for the quick modification of performance; increase plant capacity since most polymer blends are processed on standard processing equipment; be achieved through low capital investment; and be accomplished much more rapidly than developing a totally new polymer.

Blends with engineering resins have been the focus of significant activity. Commercial utilization of engineering blends has been predicted to grow at $\approx 17\%$ per annum and represents the most active growth area for polymer blends as a whole[1,2].

Most polymers are immiscible from the thermodynamic standpoint and most 'blends of commerce' are immiscible. Immiscible blends have distinct potential advantages because of their physical properties. They form a multi-phase system with a deformable minor phase, and under the appropriate conditions morphological structures such as spheres, ellipsoids, fibres and plates or ribbons can be produced. Co-continuous phases may also be formed. The morphological structures mentioned are generated *in situ* during processing which offers the potential to modify the dispersed phase through a wide range of size and shape. Control of these parameters, however, can be a very complex task. As the commercial importance of these materials increases, a more rigorous understanding

will be needed of how to control the morphology during processing.

It is well known that both the size and the shape of the minor phase can significantly affect the mechanical properties of an immiscible polymer blend. Impact strength, for example, is very dependent on the dispersed particle size as well as the interparticle distance. Recently Wu[3] studied the notched impact toughness of nylon-rubber blends and found that a sharp tough-brittle transition occurred at a critical particle size when the rubber volume fraction and rubber-matrix adhesion are held constant. Hobbs[4] has developed a model which predicts a non-linear rise in fracture energy with the addition of large rubber particles to a resin containing predominantly small rubber particles, followed by a more gradual drop in fracture energy as the overall number of particles falls with increasing average radius. His predictions are supported by notched impact data on HIPS blends. Stell *et al.*[5] have shown that significant improvements in blend ductility may be achieved by organizing the phases through flow processing so that they are oriented in the direction of the test. Despite the critical importance of controlling size and shape during processing, most studies on the topic have been qualitative and few studies have attempted to quantify carefully the parameters controlling the morphology of immiscible blends.

During the processing of polymer blends, several factors are especially important in determining the final size and shape of the minor phase: composition, interfacial tension, time of mixing, shear rate or shear stress, elasticity of the components and viscosity ratio (ratio of viscosity of the dispersed phase to that of the matrix). The objective of this paper is to study the morphology of the minor phase in polycarbonate/polypropylene blends quantitatively as a function of composition. The effect of

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the viscosity ratio on the phase size/composition dependence will also be considered.

EXPERIMENTAL

Materials

A commercial polycarbonate and two polypropylene samples were examined in this study. The polycarbonate was Merlon M-39 obtained from the Mobay Corporation and is derived from bisphenol-A. The polypropylene samples were Pro-Fax 6301 and 6701 obtained from Himont. Their properties, including the number average and weight average molecular weights, M_n and M_w, are summarized in *Table 1*. Throughout this paper the polycarbonate sample will be referred to as PC. Polypropylene 6301 and 6701 will be referred to as PP-1 and PP-2, respectively.

Mixing

Before a typical mixing experiment the sample mixture in solid form was dried for 17 h under vacuum at 90°C to avoid hydrolytic degradation of the polycarbonate. The polypropylene was stabilized with 0.2% antioxidant. The materials were then melt blended in a Brabender mixing chamber using the roller blade attachment normally used for viscous materials. The volume of the material in the chamber was kept constant at 60 ml. The densities of the polycarbonate and polypropylene at 250°C were 1.08 and 0.75 g cm^{-3}, respectively (data obtained from Mobay and Himont). Blending conditions were maintained at 250°C and 50 rev min^{-1} for 5 min. A temperature of 250°C was chosen deliberately to minimize the thermal degradation of polypropylene. After blending the melt was rapidly shaped into a block and cooled in ice water. The samples were stored at −25°C to eliminate any long term morphological change.

Morphological analysis

Optical microscopy. Polypropylene-rich samples for light microscopy were microtomed, extracted with methylene chloride to etch the polycarbonate, immersed in oil, and then photographed with high contrast film under bright field conditions. The microscope used was a Leitz/Wetzlar, Dialux 20. A similar procedure was used for the polycarbonate-rich samples, except that etching was carried out in decalin at 130°C.

Electron microscopy. A scanning electron microscope (type JEOL 35 CF) was used to examine samples where the dispersed phase had a volume average diameter of less than 2 μm. Scanning electron microscopy was also used

to verify the morphology in some cases where the light micrographs were not of acceptable quality. The samples were microtomed to create a plane face using an ultramicrotome (Reichert–Jung Ultracut) equipped with a glass knife. The samples were then also subjected to the appropriate chemical treatment to dissolve the minor phase. Since the microtome does not necessarily cut the dispersed sphere at the widest point, a correction was applied to obtain the true diameter[3].

Image analysis. A semi-automatic method of image analysis was used to quantify the size of the minor phase. It consists of a unidirectional digitizing device that operates as follows: as the crosshairs of a magnifier connected to the mobile part of a linear variable differential transformer (LVDT) are moved over the photomicrograph, the Ferrets diameter of a domain is recorded and stored in a microcomputer for the calculation of statistical parameters. Four fields of view and 200 diameters are considered for a given sample. The number average diameter, d_n, the volume average diameter (also known as the moment mean diameter), d_v, and the full distribution curve were obtained in this way. Increasing the number of measurements to 400 or 600 did not significantly alter the results.

Rheological analysis

A 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 1.2mm. The tests were performed under dry nitrogen.

The torque values reported in this paper were measured in the mixing chamber at 250°C and for 5 min mixing. Values for pure materials are reported in *Table 1*.

RESULTS AND DISCUSSION

Phase size/composition dependence

In *Figure 1* dynamic viscosity is plotted *versus* shear rate for the two commercial polypropylene samples and the polycarbonate at 250°C. The polycarbonate sample exhibits high viscosity and long plateau-like behaviour over a wide range of frequency, indicating little shear sensitivity. The polypropylene samples cover a 2.4-fold range of viscosity at 100 rad s^{-1}.

Figure 2 shows the dependence of the storage modulus on frequency. At 100 rad s^{-1}, which is close to the shear rate of 185 s^{-1} calculated for the mixing chamber,

Table 1 Characterization of polycarbonate and polypropylene materials

	Melt index (ASTM)[a] (g/10min)	Density at 250°C[a] (g cm^{-3})	Torque for 5 min mixing at 250°C[b] (N m)	η' at 100 rad s^{-1} [b] (Pa s)	G' at 100 rad s^{-1} [b] (Pa)	$\bar{M}_n$[a]	$\bar{M}_w$[a]
Polycarbonate (M-39) PC	18	1.08	26.9	1.79×10^3	8.1×10^4	12 300	26 500
Polypropylene (6301) PP-1	12	0.75	3.9	1.60×10^2	1.3×10^4	31 300	200 000
(6701) PP-2	0.8	0.75	12.7	3.93×10^2	5.2×10^4	72 000	470 000

[a] Obtained from suppliers
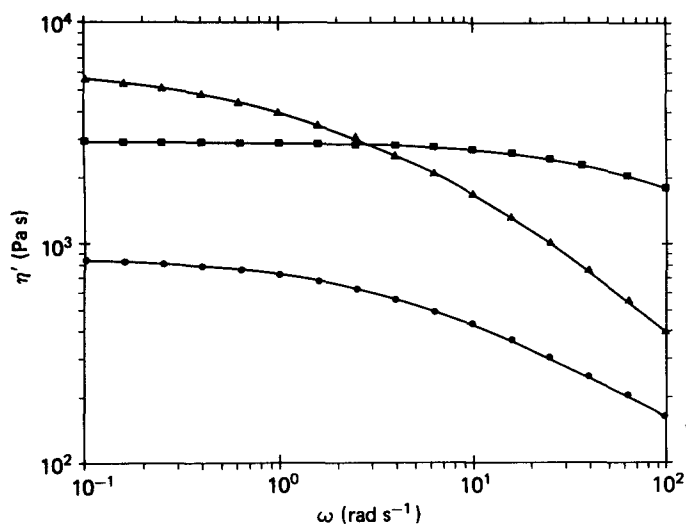[b] Measured

Figure 1 η' *versus* ω for the polycarbonate (■) and two polypropylene samples, PP-1 (●) and PP-2 (▲), at 250°C
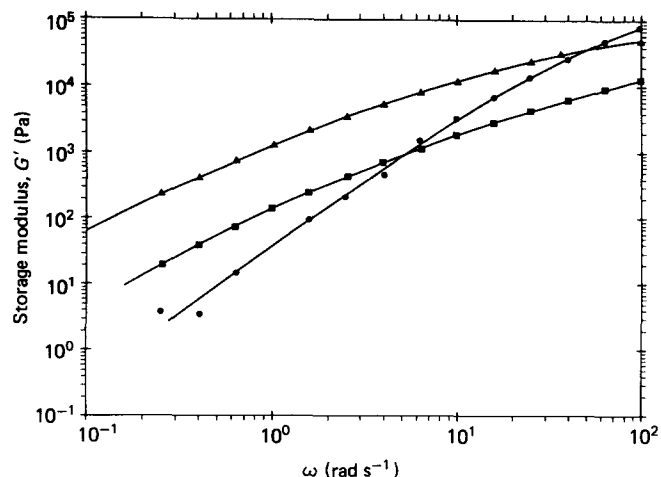

Figure 2 G' *versus* ω for the polycarbonate (●) and two polypropylene samples, PP-1 (■) and PP-2 (▲), at 250°C

polycarbonate has similar elasticity to PP-2, but is much more elastic than PP-1.

Figure 3 shows the dependence of phase size on composition for the PC/PP-1 blend. The torque ratio, TR, of the virgin materials (torque of the dispersed phase/ torque of the matrix) for this blend at 250°C is 6.9. The composition dependence for the blend is characterized by two separate curves which display asymptotic behaviour at intermediate concentrations. At a low concentration of polycarbonate, there is a very gradual increase of phase dimensions with increasing composition: d_v increases from 3.7 to 5.9 μm when the PC concentration is increased from 10 to 30%. At about 40% PC (volume fraction, $\phi_{PC} = 0.32$) the dimension of the minor phase becomes very sensitive to concentration, the result of significantly increased particle–particle interactions. The region of dual-phase continuity for this blend occurs at about 50% PC ($\phi_{PC} \approx 0.4$). A sequence of photographs of PC dispersed in PP-1 is shown in *Figure 4* for 5–40% PC.

Figure 3 also shows the dependence of the number average diameter with composition. It can be seen that the d_v and d_n curves approach one another as the

concentration of the minor phase is decreased. This indicates decreasing polydispersity in the size of the minor phase with decreasing concentration of the minor component and is more clearly demonstrated in *Figures 5* and *6* where complete particle size distribution curves are shown for PC dispersed in PP-1 for 5–40% PC, and for PP-1 dispersed in PC. *Figures 5* and *6* indicate two main points: first, these systems exhibit wide polydispersity (d_v/d_n), especially at high concentration of the minor phase; and second, the polydispersity decreases with decreasing concentration of the minor phase. These effects are observed for both PC in PP-1 and PP-1 in PC although they are somewhat less pronounced in the latter case. These data are consistent with observations made for the droplet breakup of Newtonian fluids. Droplet deformation involves the stretching of the drop, in a particular flow field, which later breaks up into smaller droplets. An example of droplet deformation in shear flow in *Figure 7* illustrates that particles of significantly different size can be formed during the deformation process[7]. It is not unexpected, therefore, that the size of the minor phase exhibits wide polydispersity. As the droplets become progressively smaller it becomes more difficult to deform and disrupt the droplet (see equation (2) below). A point exists where the interfacial tension balances the viscous forces tending to disrupt the drop and a critical minimum diameter is obtained. Polydispersity would therefore be expected to decrease with decreasing droplet size, as is shown in these experiments. *Figures 8* and *9* illustrate, at three concentrations, that the particle size follows the log normal distribution.

Effect of torque ratio on phase size/composition dependence

Taylor[8,9] defined a dimensionless parameter, E, which represents the ratio of viscous to surface tension forces. E may be expressed as:

$$E = We[(19p + 16)/(16p + 16)] \qquad (1)$$

where p is the ratio of viscosity of the droplet phase to the suspending medium. We may be expressed as follows:

$$We = \eta_m a\dot{\gamma}/\sigma \qquad (2)$$

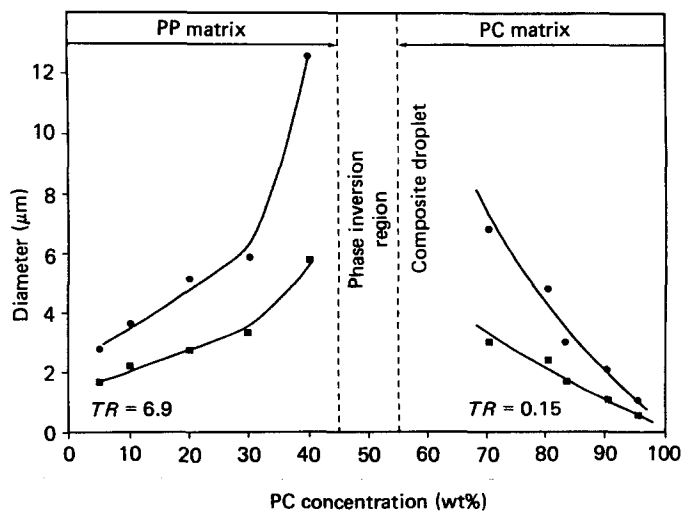where η_m represents the viscosity of the matrix, a

Figure 3 Dependence of phase size – d_n (■) and d_v (●) – on composition for a blend of PC and PP-1
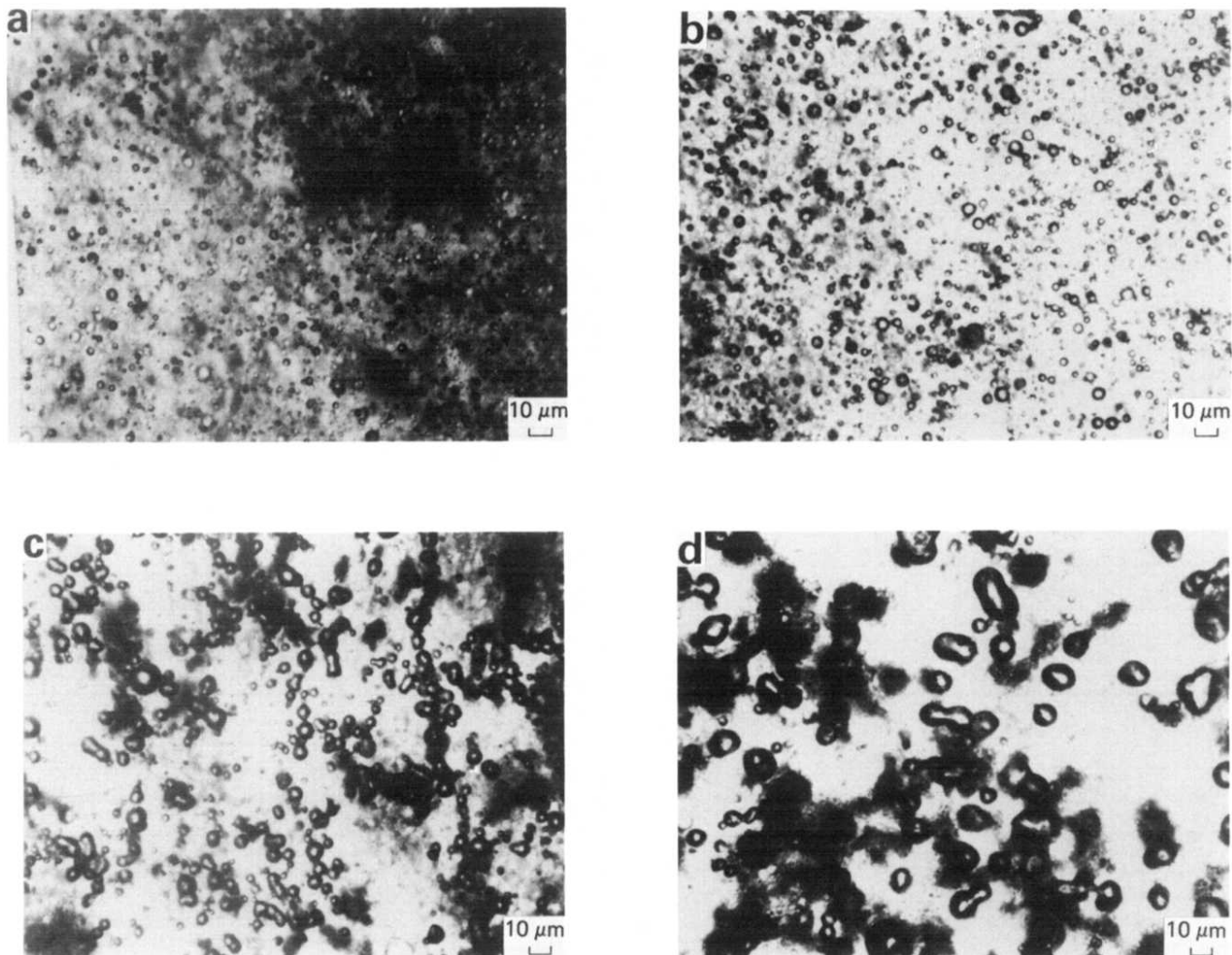
Figure 4 Light micrographs showing PC dispersed in PP-1 for (a) 5, (b) 20, (c) 30, and (d) 40% PC
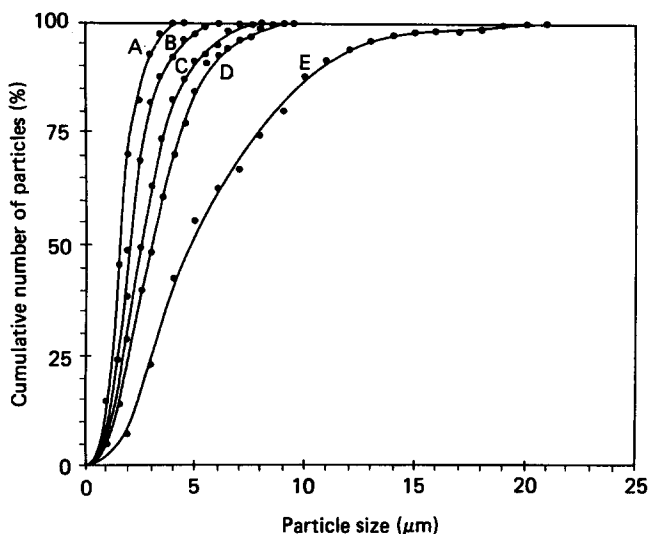

Figure 5 Minor phase size distribution curves for PC dispersed in PP-1 for PC concentration from 5 to 40wt%; A, 5; B, 10; C, 20; D, 30; E, 40wt% PC. Size distribution, d_v/d_n, for A is 1.6 and for E is 2.2
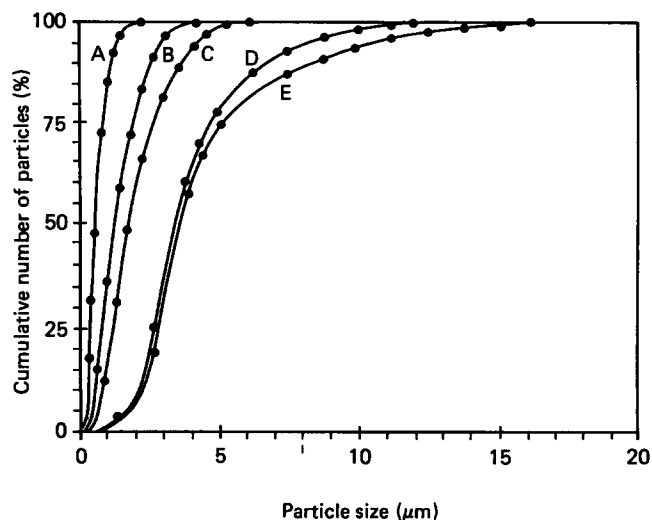
Figure 6 Minor phase size distribution curves for PP-1 dispersed in PC for PP concentration from 5 to 30wt%: A, 5; B, 10; C, 17; D, 20; E, 30wt% PP. Size distribution, d_v/d_n, for A is 1.9 and for E is 2.2

represents the radius of the droplet, $\dot{\gamma}$, the rate of shear and σ the interfacial tension. Droplet breakup occurs at E_{crit}. Hence if $We > We_{crit}$ the droplet will deform and break. From equations (1) and (2) it can be seen that droplet deformation is enhanced with high viscosity of the matrix, high rate of shear and low interfacial tension. For

viscoelastic systems the elasticity of the phases being mixed is also an important criterion. In general it is more difficult to deform an elastic material than a non-elastic one[10].

Despite the significant importance of the viscosity of the phases on phase size, seen from both theory and
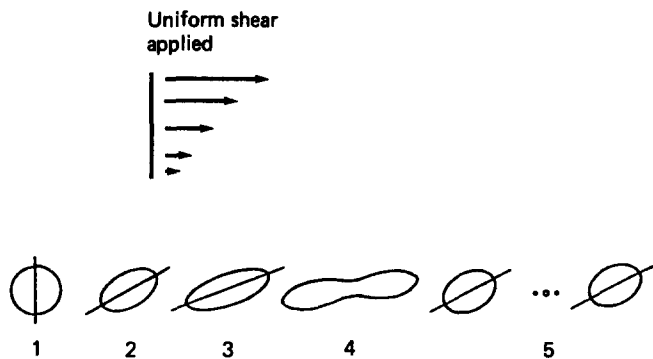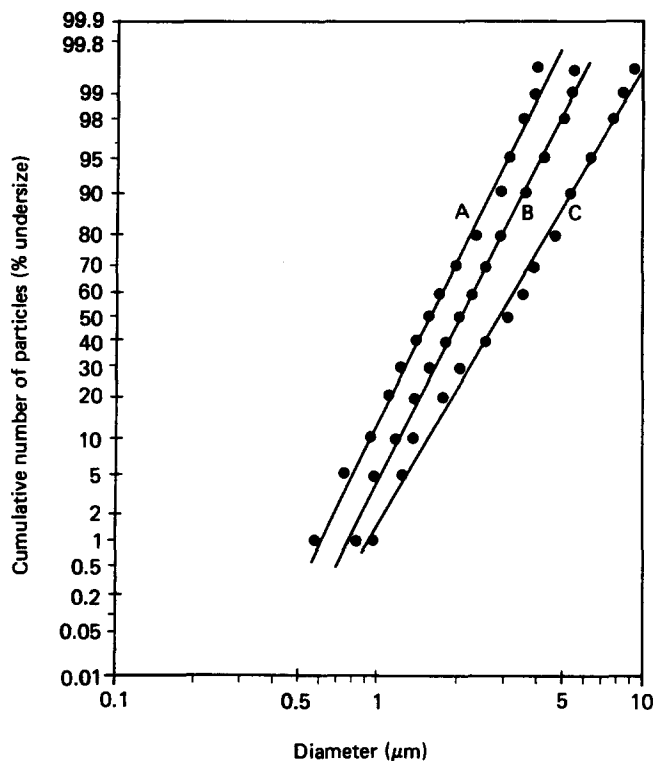
Uniform shear
applied

Figure 7   Schematic diagram of droplet break-up in shear flow[7]

and 0.48. At low concentration of polypropylene (90–95% PC) the $TR = 0.15$ blend has smaller dimensions for the minor phase than that at $TR = 0.48$. The size of the minor phase grows more rapidly with composition for the $TR = 0.15$ blend. This is related to phase growth, which occurs at low torque ratio. The dependence of phase size on torque ratio becomes complex below $TR \approx 0.3$; this is studied in more detail in another publication[6].

Heikens[11] has studied the size of the dispersed phase as a function of composition for polyethylene dispersed in polystyrene. The viscosity ratio was about 0.5. Heikens observed an increase in dimensions from 1 to 9 μm when the composition was varied from 1 to 20 wt% PE. Above 20% a significant increase in dimensions was observed and at 30% PE a number average diameter of 28 μm was reported. White *et al.*[12,13] reported that the ordering of coarseness of polyethylene in various matrices is nylon 6 > polycarbonate > polystyrene.

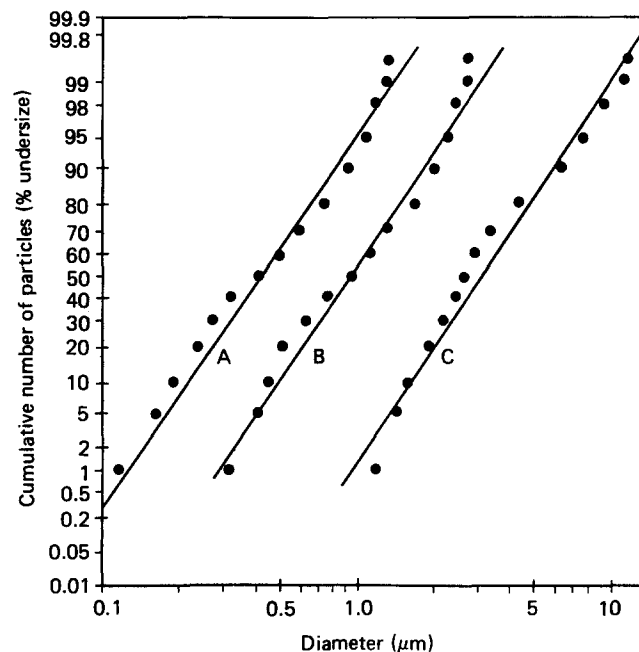Figure 8   Log normal distribution curves for: A, 5; B, 10; C, 30 wt% PC blended with PP-1

Figure 9   Log normal distribution curves for: A, 5; B, 10; C, 30 wt% PP-1 blended with PC

practice, this parameter has been little studied for polymer systems. In *Figure 10*, we show the effect of the viscosity ratio (torque ratio, *TR*) on the phase size/composition relationship. The flow fields existing in the mixing chamber are a complex combination of shear and elongational effects and the torque is directly related to this complex viscosity in the mixing chamber itself. The torque ratio therefore reflects the viscosity ratio of this particular processing environment. Varying the torque ratio of the components from 6.9 to 2.1 has significantly diminished the phase size at all concentrations for the polypropylene rich samples. The region of dual-phase continuity for the $TR = 2.1$ blend has been shifted to about 60% PC ($\phi_{PC} \approx 0.5$). Both curves, however, have a similar form and may be superimposed by a horizontal shift on the composition axis of approximately 12–15 units.

The polycarbonate rich blends show the influence of composition at low torque ratio. The two blend systems presented in *Figure 10* correspond to torque ratios of 0.15
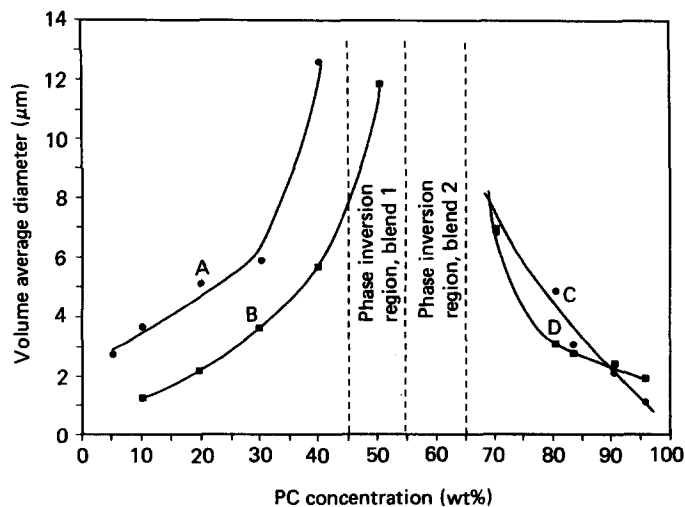
Figure 10   Effect of torque ratio on phase size/composition dependence. ●, Blend 1 (PC/PP-1); ■, blend 2 (PC/PP-2). $TR = $: A, 6.9; B, 2.1; C, 0.15; D, 0.48
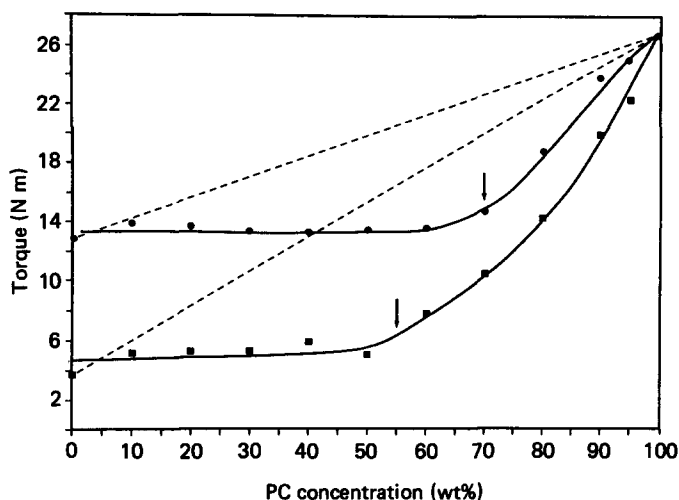
Figure 11 Dependence of the torque in the mixing chamber at 250°C on composition. ■, Blend 1; ●, Blend 2

Figure 12 Scanning electron micrograph of co-continuous phases at 50% PC for blend 1

Figure 11 illustrates the torque in the mixing chamber at 250°C over the entire composition range for the same systems as presented in *Figure 10*. Increasing the concentration of polycarbonate has little effect on the torque up to $\approx 50\%$ composition. It can be seen, however, that a small amount of polypropylene added to polycarbonate significantly reduces the torque compared to virgin polycarbonate. A low viscosity polypropylene has an even more dramatic effect on this phenomenon. The use of polyolefins as processing aids to polycarbonates has been discussed by other authors[14,15]. These blends show a strong negative deviation from additivity typical for immiscible systems[16]. As the concentration of polycarbonate is increased the torque in the mixing chamber undergoes a sudden increase in magnitude. The point at which this occurs, indicated by an arrow in *Figure 11*, corresponds closely to the region in *Figure 10* just after phase inversion where polycarbonate has become the matrix. The displacement of this point for blend 1 and blend 2 is similar to the displacement in the morphological data observed in *Figure 10*.

Dual-phase continuity

In *Figure 5* the region of dual-phase continuity occurs at $\approx 50\%$ PC ($\phi_{PC} \approx 0.4$) for blend 1 and at $\approx 60\%$ ($\phi_{PC} \approx 0.5$) for blend 2. *Figure 12* illustrates co-continuous phases for blend 1. For blend 2 both a dispersed phase and co-continuous phase morphologies were observed at 60% PC concentration.

A very unusual composite droplet type morphology was observed for both blend 1 and blend 2 at 60% PC (see *Figure 13*). This type of structure consists of a matrix phase, a dispersed phase and dispersed droplets within the dispersed phase. The overall structure is highly reminiscent of some rubber based blends where low molecular weight polystyrene remains dissolved in the dispersed rubber particle[17]. The controlling mechanism in this case is clearly different since both constituents of the blend in this study are immiscible high polymers. Work is under way to elucidate the mechanism.

Recently, a semi-empirical expression has been proposed to predict the point of co-continuous phases based on viscosity ratio[18]:

$$\frac{\eta_1}{\eta_2}\frac{\phi_2}{\phi_1} \approx 1 \tag{3}$$

where η_1, η_2 are the viscosities of phase 1 and 2 respectively and ϕ_1, ϕ_2 are the volume fractions of phases

Figure 13 Composite droplet structure for blend 1 at 60% PC

Table 2 Concentration for dual-phase continuity

	ϕ_{PC}(pred.)	ϕ_{PC}(obs.)
Blend 1 PP-1/PC	0.87	≈ 0.4
Blend 2 PP-2/PC	0.68	≈ 0.5

1 and 2. Substituting the torque ratio for the viscosity ratio, the region of dual-phase continuity would be theoretically predicted to occur at $\phi_{PC} = 0.87$ for blend 1 and at $\phi_{PC} = 0.68$ for blend 2 (see *Table 2*). Experimentally, however, as is mentioned above, co-continuous phases were observed at approximately $\phi_{PC} = 0.4$ for blend 1 and $\phi_{PC} = 0.5$ for blend 2. These experimental results may be supported by those of Kunori and Geil[19], who observed co-continuous structures at 50 wt% for a blend of HDPE with a more viscous polycarbonate, prepared in a CSI-MAX mixing extruder at about 245°C and processed through a $\frac{1}{8}$ in (3 mm) diameter die. It seems clear from these data that the viscosity ratio is not the only parameter controlling the region for dual-phase continuity in these systems.

In *Figure 2* the storage modulus, which is a measure of the elasticity of the system, is plotted *versus* shear rate for PP-1, PP-2 and PC. At $100\,\mathrm{s}^{-1}$, which is close to the empirically calculated shear rate of $185\,\mathrm{s}^{-1}$ in the Brabender mixing chamber at $50\,\mathrm{rev\,min}^{-1}$ (references 18 and 20), it can be seen that PP-2 and PC are of similar elasticity. G' is 5.2×10^4 Pa for PP-2 and 8.1×10^4 Pa for PC. PP-1 is significantly less elastic, with a G' of 1.3×10^4 Pa. Van Oene[21] has demonstrated that an elastic material can tend to encapsulate one of low elasticity in order to lower the overall surface free energy. The position of the region of dual-phase continuity in *Figure 10* indicates that in blend 1, PC has a tendency to preferentially encapsulate PP-1, while in blend 2 no apparent preference for encapsulation is observed for PP-2 and PC. The morphological data concerning the region of co-continuous phases appears therefore to correlate with the relative elasticity of the components in the particular blend for these systems.

CONCLUSIONS

The size of the minor phase for PC–PP blends is strongly affected by composition, especially as the region of dual-phase continuity is approached. The blends exhibit wide polydispersity in the size of the minor phase, a phenomenon which is particularly pronounced at high concentration of minor phase. This polydispersity narrows with decreasing phase size. Changing the torque ratio has a significant impact on phase dimensions, especially for blends with $TR > 1$. A shift in the region of dual-phase continuity was observed for blends of different torque ratios.

A correlation was observed for the point of phase inversion from morphology and viscosity data. The concentration at which dual-phase continuity occurs does not correlate with predictions based exclusively on viscosity ratio and composition. A composite droplet morphology was observed at 60 wt%.

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