

Droplet/fibre transitions in immiscible polymer blends generated during melt processing

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The modification of the morphology of immiscible binary blends in a co-rotating twin-screw extruder equipped with capillary dies of various lengths has been studied. Blends of polycarbonate and polypropylene were investigated using scanning electron microscopy. The size and shape of the dispersed phase were found to be significantly affected by the viscosity ratio. The morphology of the blends containing 5% minor phase varied with radial and axial positions in the die. Capillary instabilities were observed at the entrance of the die. The generation and disintegration of these capillary instabilities were found to occur rapidly. Fibre formation was favoured for all blends containing higher concentrations of minor phase (20%). To investigate the influence of the interface on deformation of the minor phase, blends of polyethylene and polyamide were compatibilized with a polyethylene copolymer ionomer. The compatibilizer was found to be effective in considerably reducing the size of the minor phase. The final state of deformation of the dispersed phase was reduced significantly with addition of the ionomer.

1. Introduction

In the last 15 years, research into polymer blends has increased significantly. The blending of thermoplastics can generate materials with unique properties. Depending on the size and shape of the minor phase, many properties can be improved such as impact strength, tensile strength and impermeability to solvents. Blending can also have many sound economic advantages.

Polymer blends differ from composite materials which contain a rigid phase. Polymer blends form a multiphase system with a deformable minor phase. When processed in the melt, an *in situ* morphology can be developed. Depending on the properties of the components and the processing parameters, polymer blends have the potential of generating various minor phase sizes and shapes such as spheres, ellipsoids, fibres, plates, etc. It is thus important to characterize thoroughly each component and to understand the influence of certain processing parameters.

Many aspects must be taken into account when trying to predict the morphology of the minor phase. The final size and shape of the dispersed phase will not only depend on parameters that control deformation but also on those that concern the stability of a deformed particle. Depending on the processing conditions and the physical properties of each component, a droplet will retain its original shape or be deformed into a cylindrical body. In the last case, the highly elongated droplet can be unstable and break up into satellite droplets. Most of the work concerning the deformation of particles in flow has been done on

newtonian droplets suspended in a newtonian matrix. The work of Taylor [1], generalized later by Cox [2], has shown that particle deformation is a function of the capillary number and viscosity ratio. Some theoretical work by Han takes into account the elastic character of a droplet subjected to an elongational field [3]. However, most of these pioneering studies have been carried out on single droplets subjected to simple shear or pure elongational flows.

Several basic parameters have been found to be important in controlling particle deformation during processing. Many of these parameters have been studied extensively [4–6]. They are: viscosity/elasticity ratios, composition, interfacial tension, shear stress/shear rate and processing conditions (time of mixing, screw or rotor speed, type of mixing, drawing).

The type of flow field present in melt processing greatly influences the mechanism of minor phase deformation. An elongational flow has proved to be more effective in deforming particles than shear flow. Grace [7] has confirmed this while studying the break-up of a droplet as a function of viscosity ratio. In the case of droplet/fibre transitions, numerous studies have confirmed this observation. Dreval *et al.* [8] observed that fibre formation was enhanced at the entrance of a capillary, where the contraction generates an elongational flow. They found that fibre formation occurred at specific values of viscosity ratios and shear stresses. These authors concluded that the role of elasticity of the components is negligible. However, other authors, such as Tsebrenko *et al.* [9], have found that viscoelastic droplets are

more difficult to deform. Elmendorp and Maalcke [10] have observed an important effect of the normal forces generated by a viscoelastic droplet on minor phase deformation and break-up. The mechanisms for break-up of a particle play an important role on its final size and shape. Under static conditions (no flow), Lord Rayleigh [11] observed that a liquid thread submerged into another liquid was unstable and subjected to capillary instabilities. The liquid cylinder eventually broke into droplets. Tomotika [12] has developed a theory considering a long cylinder submerged in another fluid and found that the time required for break-up by capillary instabilities depends on parameters such as interfacial tension, viscosity ratio and initial thread diameter. Stone *et al.* [13] have observed that another mode of break-up (called end-pinching) is in competition with capillary instabilities, which was shown to be dependent on the viscosity ratio and initial L/D ratio of the elongated droplet. Although these observations were made under static conditions, they can be useful when qualitatively evaluating the stability of a fibril generated during flow.

Another important factor influencing the dispersed phase morphology is coalescence. If particle-particle interactions are intense, due in particular to an elevated concentration or restricted geometries, numerous collisions and subsequent coalescence become critical parameters. Elmendorp and Van der Vegt have indicated that coalescence phenomena play a role at concentrations as low as 1% [14]. This coalescence of particles, in itself, may lead to the modification of the shape of a spherical drop. Tsebrenko has shown photographically that in the entrance region of a capillary rheometer, drops came together, collided and coalesced into a fibre-like morphology [9].

The size and shape of the minor phase can also be controlled by modification of the interface. The addition of a proper interfacial agent (compatibilizer) has been proved to increase adhesion between the components and favour the reduction of the minor phase size in numerous studies [15–17]. Few studies, however, have tried to quantify the influence of the addition of a compatibilizer on particle deformation. A recent study on ribbon extrusion by Gonzalez *et al.* [18] has shown that adding an interfacial agent diminished the final state of deformation of the minor phase compared with the uncompatibilized case. Coalescence can also be significantly reduced in interfacially modified systems, because the dispersed droplets become physically separated from each other during a given collision, by the interphase region [19, 20].

The objective of this work is to study the morphological behaviour of polycarbonate/polypropylene and polyethylene/polyamide blends prepared by twin-screw extrusion with a particular emphasis on factors resulting in droplet/fibre transitions. These phenomena are related to the processing parameters and the material characteristics of the components. Also, the polyethylene/polyamide blend has been compatibilized in order to determine the influence of a modified interface on minor phase deformation.

TABLE I Properties of polymers used. Values of dynamic viscosity and storage modulus estimated at 700 s^{-1}

Component	Density at 250 °C (kg m^{-3})	Zero shear viscosity (Pa s)	Dynamic viscosity (Pa s)	Storage modulus (10^3 Pa)
PP	750	1800	80	36
PC	1080	3000	850	81
PE	740	800	170	15
PA	960	1000	290	26

2. Experimental procedure

2.1. Materials

The polycarbonate (PC) used in this study was Merlon M-39 obtained from the Mobay Corporation. The polypropylene (PP) was Pro-Fax 6501 from Himont. The high-density polyethylene (PE) used was HDPE 56056 obtained from Dow Chemical. The polyamide (PA) used was Zytell 211 from Du Pont. The ionomer used to compatibilize PE and PA was Surlyn 9020, also from Du Pont. This ionomeric resin is a random terpolymer consisting of roughly 80% PE and 20% of a mixture of methacrylic acid, partially neutralized with zinc, and isobutyl acrylate. A previous study has shown that an amidation reaction takes place between the amine groups of the polyamide and the carbonyl groups of this ionomer [21]. The properties of all the polymers used are listed in Table I. Unless specified otherwise, all blend concentrations are calculated by volume.

2.2. Compounding

Prior to a typical mixing experiment, the sample mixture was dried in order to minimize hydrolytic degradation. The PP was stabilized with 0.2% antioxidant. The PP/PC blends were dried under vacuum for 17 h at 90 °C. The PA was dried under vacuum at 110 °C for 24 h. The ionomer was dispersed in polyethylene prior to mixing in a 9 to 1 ratio. In a previous study [15], premixing the Surlyn with polyethylene was proved to be more effective in decreasing the dispersed particle size.

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. The standard screw configuration used for all experiments is shown in Fig. 1. Feeding was performed under dry nitrogen, and vacuum was applied in the decompression zone. Three capillary dies of different lengths were used, all having the same diameter of 3 mm and a 40° angular entry. The L/D ratios were 0.73, 2.2 and 4.4. The dimensions and configuration of this die are shown in Fig. 2. Cooling of the extrudates after die exit was performed in cold water in order to freeze-in the morphology.

The following conditions were used for blending. Experiments were performed at a constant volumetric flow rate of $250\text{ cm}^3\text{ min}^{-1}$ which corresponds to an apparent shear rate of 775 s^{-1} in the die. The screw speed was maintained at 300 r.p.m. The temperature profile of the barrel was set at 230/236/240/244/244 °C

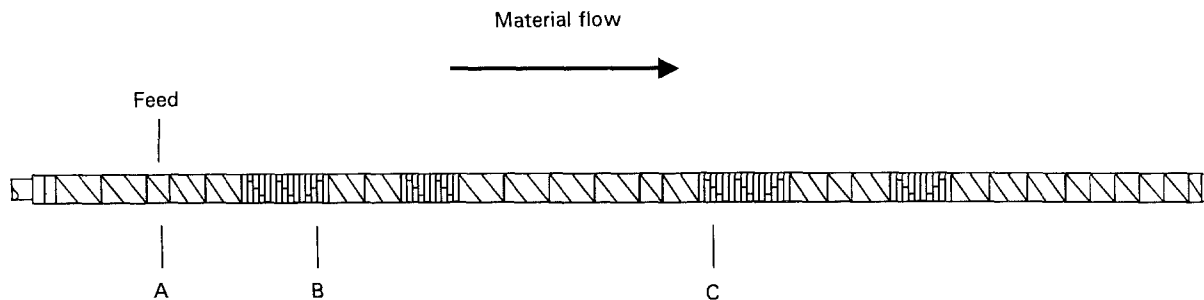


Figure 1 Configuration of the screw used in this study. A, Transport element; B, left-handed kneading block; C, right-handed kneading block.

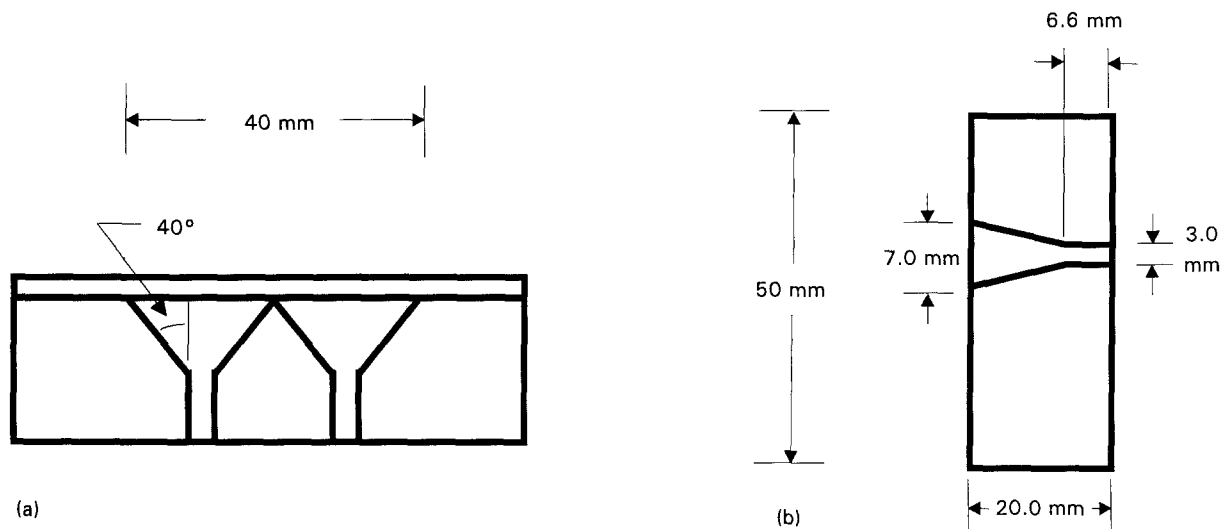


Figure 2 Dimensions and configuration of the die used in this study. (a) Top view, (b) side view.

TABLE II Properties of blends

Blend	Interfacial tension (10^{-3} N m^{-1})	Shear stress (wall) (10^3 Pa)	Viscosity ratio (centre)	Viscosity ratio (wall)
PP in PC	7.9	150	0.6	0.1
PC in PP	7.9	55	1.7	10.6
PE in PA	12.6	110	0.8	0.6

from feed hopper to exit. Under these conditions, the melt temperature in the die remained constant at 250°C . Some properties of the blends are reported in Table II. The values of the interfacial tension were calculated using the harmonic-mean equation. Values of the shear stress at the wall are given for the blends containing 20% minor phase.

2.3. Electron microscopy

A scanning electron microscope (Jeol JSM-T-220) was used to examine the shape and size of the dispersed phase. Longitudinal fracture surfaces were obtained from samples vitrified in liquid nitrogen. Samples were then coated with a gold/palladium alloy. Micrographs were taken in the centre and at the periphery of the cross-section of fractured samples. In the case of the compatibilized PE/PA blends, dissolution of the minor phase was performed. Samples were treated in decalin at 120°C for 1 h and rinsed in methanol. They were subsequently dried at 90°C for 24 h.

2.4. Image analysis

A semi-automatic method of image analysis was used to quantify the size of the minor phase, when applicable. Two hundred measurements of diameter were considered for a given sample. The number-average diameter, d_n , and the volume-average diameter, d_v , were obtained. Details about this method have already been reported elsewhere [6].

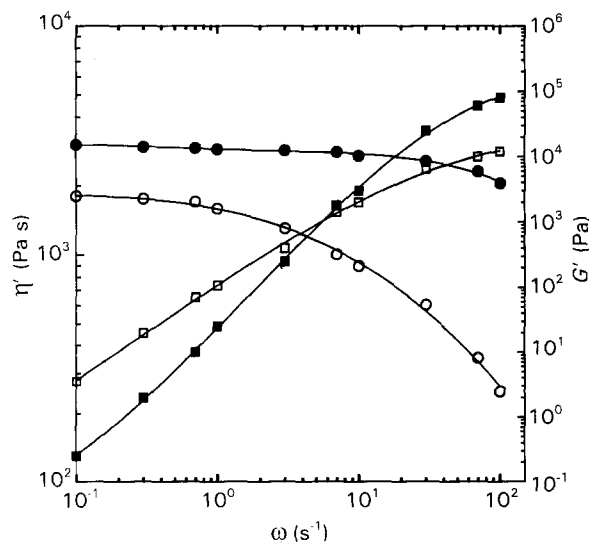


Figure 3 (●, ○) Dynamic viscosity, η' , and (■, □) storage modulus, G' , as a function of frequency for (●, ■) polycarbonate and (○, □) polypropylene.

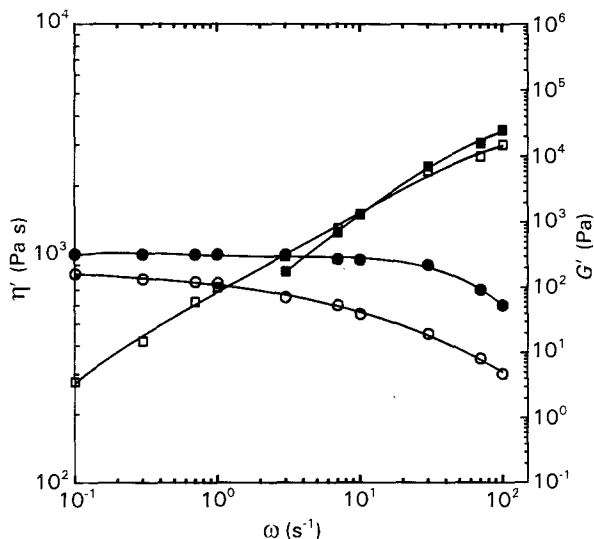


Figure 4 (●, ○) Dynamic viscosity, η' , and (■, □) storage modulus, G' , as a function of frequency for (○, □) polyethylene and (●, ■) polyamide.

2.5. Rheological analysis

The dynamic viscosity and the storage modulus as a function of frequency were measured using a Rheometrics Mechanical Spectrometer (RMS, Model 605). The experiments were performed in parallel-plate geometry under a nitrogen atmosphere at a temperature of 250 °C. The curves representing these rheological properties versus frequency are shown in Figs 3 and 4 for the PP/PC and PE/PA systems, respectively.

3. Results and discussion

Fig. 5 will be referred to in this section in order to identify qualitatively the different types of flow encountered in the die used. This die can be divided into three regions. The converging region principally generates an elongational flow. The contraction will therefore favour the deformation of a droplet. Also particle-particle interactions are most likely to occur in that region. An elongated droplet will be subjected to two mechanisms in competition in the second region of the die. At the wall, the shear rate is important and deformation is favoured. In the centre, the blend is not subjected to any shear and more recovery/recoil can take place. Finally, the cooling region is also important because the time required to cool the centre of the extrudate is much longer than that needed for the periphery. It has been estimated that for a 3 mm extrudate this time can be of the order

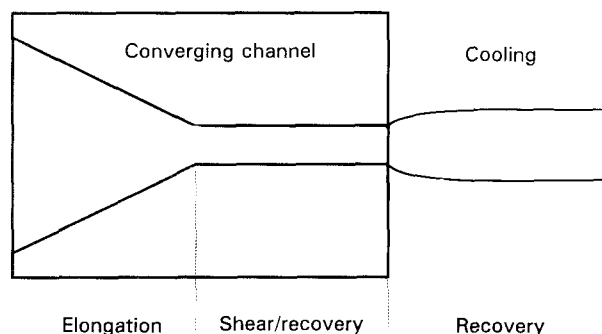


Figure 5 Dominant types of flow fields encountered in the die.

of 3 s. This cooling time is much higher than the characteristic times of the polymers at this temperature and it is possible that the morphology observed in the centre does not represent exactly the reality experienced during processing. For this reason, attention will be focused primarily on the periphery region.

3.1. PP/PC blends (uncompatibilized)

The size of the minor phase versus L/D (or axial) and radial positions in the capillary die is shown in Table III for the PC dispersed in PP blend containing 5% dispersed phase. The results for the complementary blend are shown in Table IV.

3.1.1. Influence of radial position

For both 5% polypropylene dispersed in polycarbonate and the complementary mixture, it can be seen that the minor phase is in the form of spherical droplets having diameters less than a micrometre. A reduction in size is observed at the periphery as compared to the centre of the thread for all blends. This illustrates the influence of the capillary wall, where shear rate is the highest. Depending on the radial position in the capillary, the blends are subjected to two mechanisms in competition, shearing and recovery. Because the shear rate is not constant over the radius of the capillary, the viscosity ratio varies significantly from centre to periphery. For instance, as can be seen in Table II, calculations based on zero shear viscosity at the centre show values of the viscosity ratio of 0.6 compared to 0.094 at the periphery, for PP dispersed in PC.

3.1.2. Influence of capillary length

The type of flow present in the die used in this work also varies along axial position or L/D . At the entrance of the capillary (see Fig. 5), the converging

TABLE III Number and volume average diameters measured at different radial and L/D (axial) positions in the capillary for PC dispersed in PP

L/D	Centre		Periphery	
	d_n (μm)	d_v (μm)	d_n (μm)	d_v (μm)
0.73	0.66	0.98	0.58	0.74
2.2	0.53	0.84	0.50	0.72
4.4	0.59	0.87	0.56	0.80

TABLE IV Number and volume average diameters measured at different radial and L/D (axial) position in the capillary for PP dispersed in PC

L/D	Centre		Periphery	
	d_n (μm)	d_v (μm)	d_n (μm)	d_v (μm)
0.73	0.92	1.25	0.81	1.03
2.2	0.93	1.30	0.75	0.99
4.4	0.95	1.48	Fibres	Fibres

region generates principally an elongational flow. It is a well known fact that an elongational field is much more effective in deforming the minor phase [7]. Fig. 6 shows this feature for the 5% PC/PP blend in the shortest capillary, which has an L/D ratio of 0.73 and is considered to represent essentially the entrance of the capillary. The importance of the deformation in elongational flow can be observed. For this 5% PC/PP sample a high level of fibre formation was observed throughout the periphery region. Further-

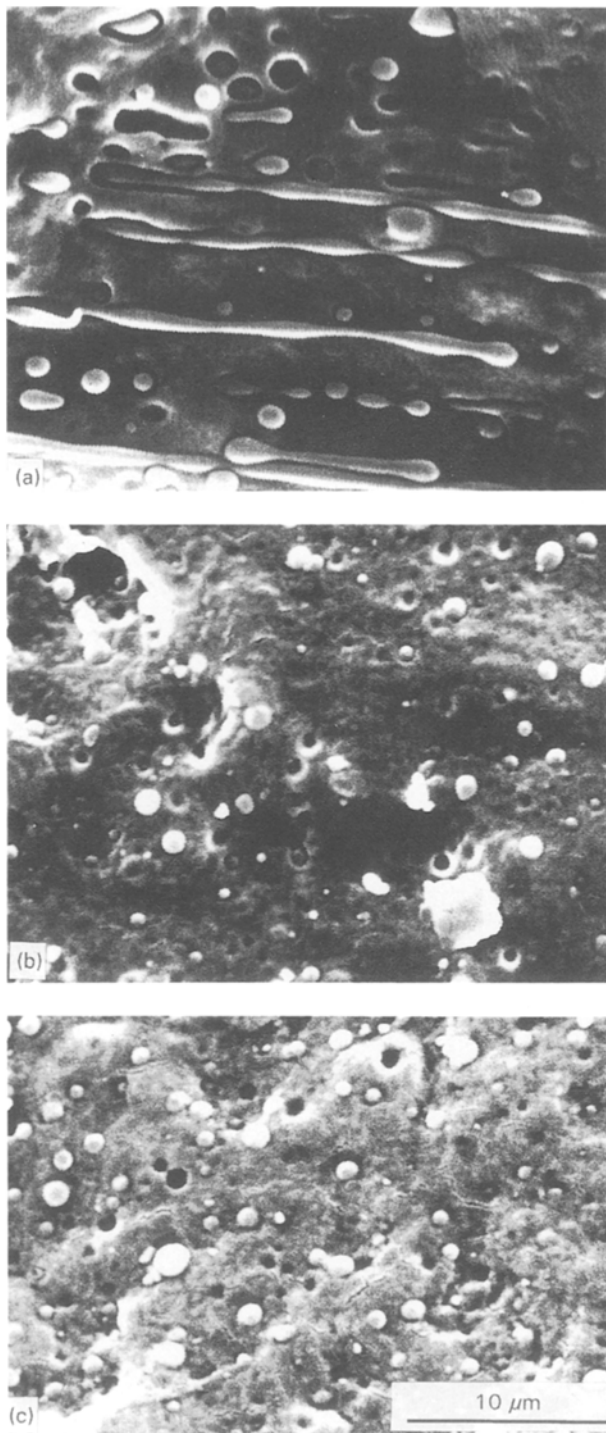


Figure 6 Scanning electron micrographs showing the influence of capillary length for the 5% PC dispersed in PP blend (periphery of extrudate). Note capillary instabilities at $L/D = 0.73$. (a) $L/D = 0.73$, (b) $L/D = 2.2$, (c) $L/D = 4.4$.

more, it can be seen that the disintegration of highly elongated fibres is already taking place. In fact, all stages of sinusoidal distortion of a typical capillary instability are present. This suggests several important points. Firstly, it indicates that important deformation takes place at the entrance region. It also indicates that capillary instabilities play an important role in dispersed phase recovery/recoil mechanisms. Fig. 6 also emphasizes the short time-scale for generating capillary instabilities in flow because fibres are no longer observed at higher L/D . Furthermore, the break-up of fibrils by this mechanism is also accelerated by the low-viscosity PP matrix. Tomotika [12] has shown that the time required for break-up is inversely proportional to the viscosity of the matrix. Neither fibres nor capillary instabilities were observed at the centre of the thread for this sample where the effects of an elongational flow field could be expected to be most dominant. This is likely due to the finite time required to cool the centre of the thread, as mentioned previously.

Capillary instabilities were not observed for the 5% PP dispersed in PC blend (Fig. 7). Certain studies showed that a matrix generating high normal forces will destabilize droplets or fibrils [10]. In this work, the PC matrix, which has a higher storage modulus than PP at this processing temperature could favour the disintegration of elongated structures. In the 5% PP/PC case, spheres are always observed with the exception of the longest capillary where droplets/fibrils are observed. These fibres may be an indication that the total strain experienced in the capillary is an important factor. It is interesting to note in the case of low viscosity ratio 5% PP dispersed in PC blend that capillary length plays an important role in minor phase deformation. In the capillary, shear flow would be the dominant flow field and it is well known that deformation in shear flow is enhanced at low viscosity ratio.

An unexpected result is the fact that the size of the minor phase is greater when PC is the matrix, an effect that is apparent at low L/D and hence is due to phenomena before the capillary. According to Taylor's work [1], a highly viscous matrix like PC should enhance deformation. In this study, the size of the PC minor phase is much smaller than that of the complementary blend. This occurs even though PC is more viscous and has a higher storage modulus than PP (see Table I). Furthermore, the shear stress generated by the low-viscosity PP matrix is 5.5×10^4 Pa compared to 1.5×10^5 Pa when PC is the matrix. These results illustrate that deformation in an elongational field is not sensitive to the viscosity ratio as calculated with values of viscosity obtained in shear flow. Measurements of elongational viscosities are difficult to perform but general considerations of the behaviour of different types of polymers can be made. For instance, an amorphous polymer such as polycarbonate would be expected to retain its newtonian-like behaviour when subjected to an extensional flow. On the other hand, crystalline polymers such as PP are known to exhibit strain hardening, inducing an increase in viscosity, at high elongational rates. These

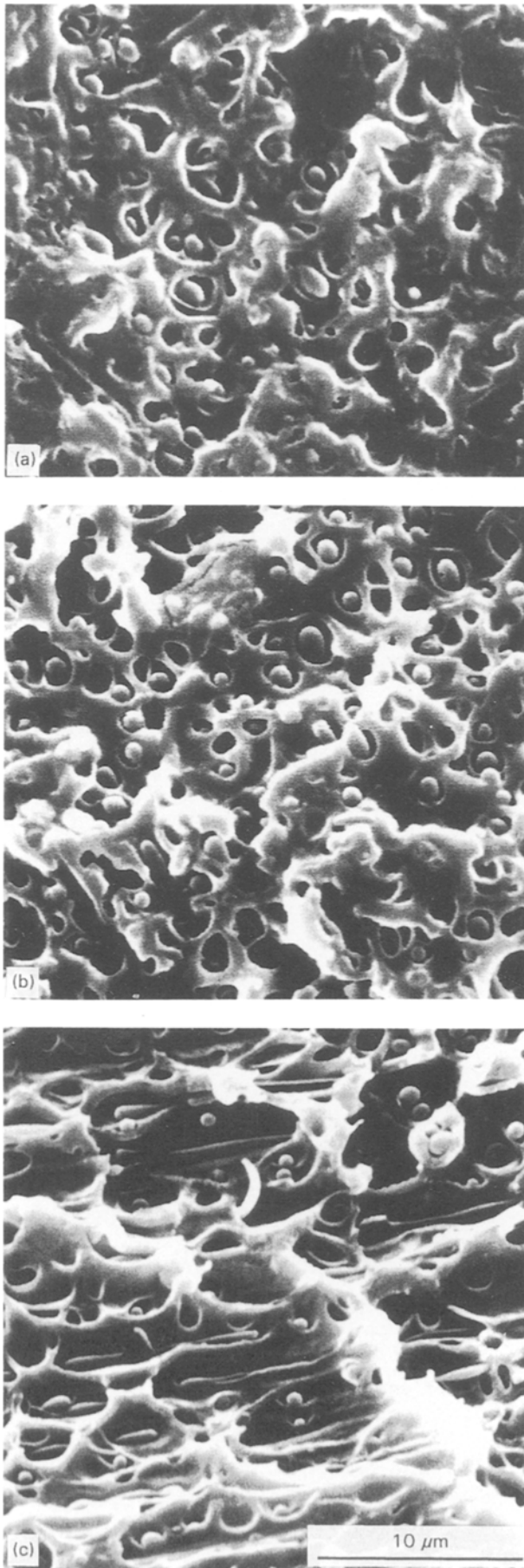


Figure 7 Scanning electron micrographs showing the influence of capillary length and droplet/fibre transition for the 5% PP dispersed in PC blend (periphery of extrudate). (a) $L/D = 0.73$, (b) $L/D = 2.2$, (c) $L/D = 4.4$.

considerations could justify our observations but cannot be supported by experimental data at this time. Other laboratories have also observed a smaller minor phase size for high viscosity ratio blends [22].

3.1.3. Influence of composition

The effect of composition on minor phase size is shown in Fig. 8. Transitions from droplets (5% minor phase) to fibres (20% minor phase) are observed for all blends. These fibre-like structures can arise from the collision of small droplets or from the deformation of

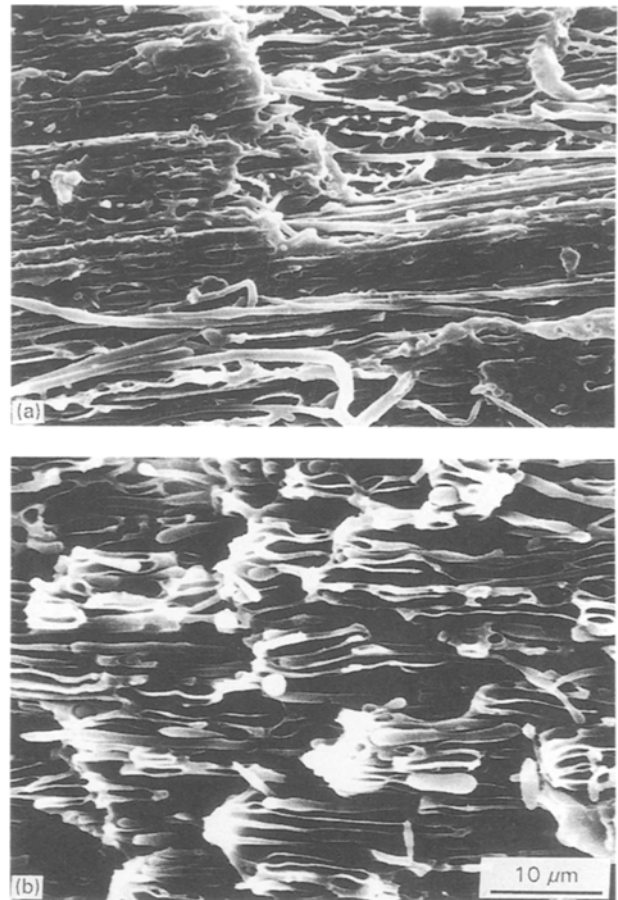


Figure 8 Scanning electron micrographs showing fibre formation for PC/PP blends when concentration is increased to 20% ($L/D = 2.2$). (a) 20% PC dispersed in PP (b) 20% PP dispersed in PC.

TABLE V PE dispersed in PA: comparison of number and volume average diameters between the uncompatibilized blends and the blends containing 10 wt% ionomer (based on the dispersed phase). Results shown for the capillary of $L/D = 2.2$

Blend		Centre		Periphery	
		d_n (μm)	d_v (μm)	d_n (μm)	d_v (μm)
5%	Uncomp.	1.63	2.37	Ellipsoids	
	Comp.	0.64	1.70	0.63	1.18
20%	Uncomp.	6.47	7.83	Fibres	
		+	+		
		Fibres	Fibres		
	Comp.	0.99	2.50	Ellipsoids	

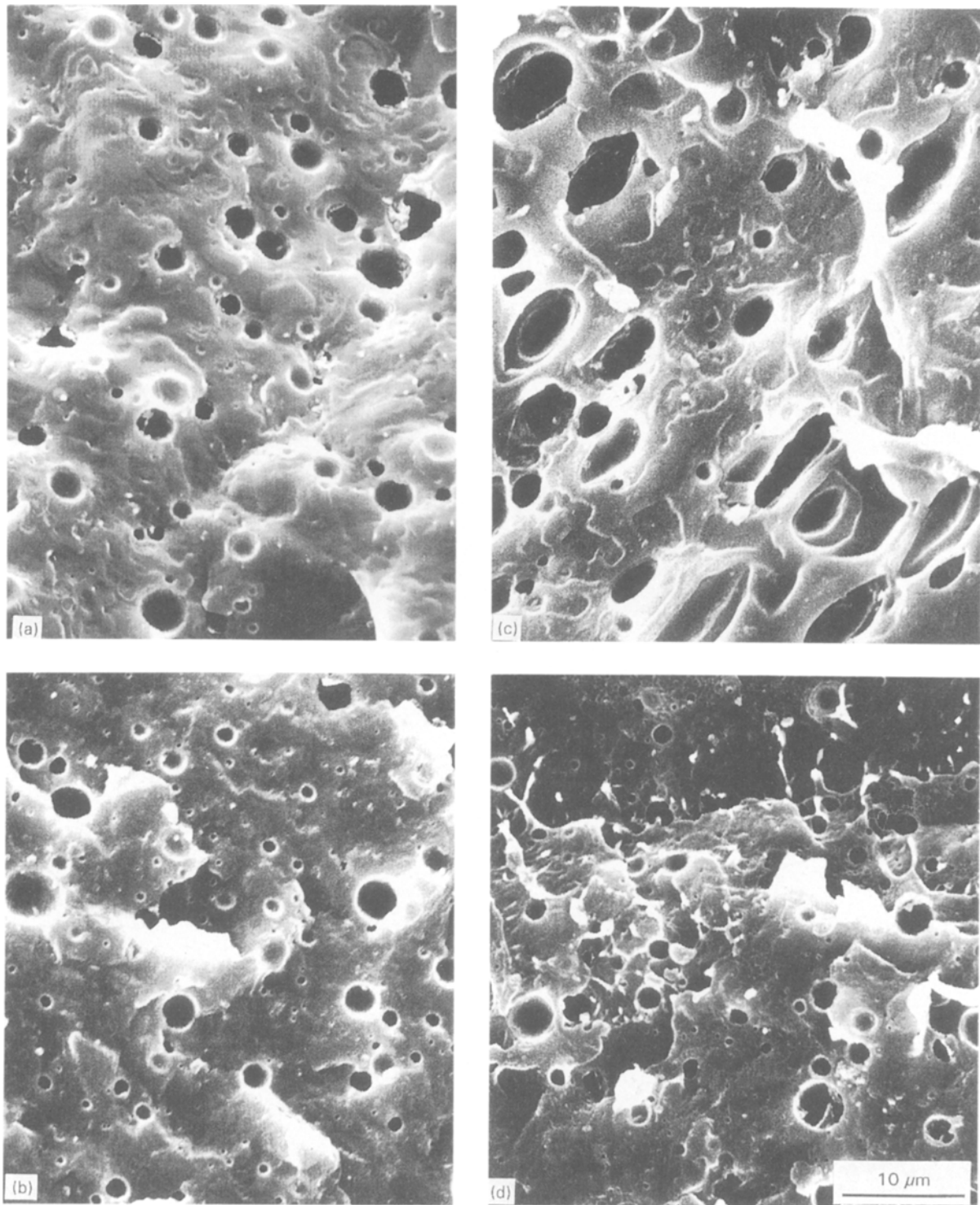


Figure 9 Scanning electron micrographs showing the reduction in minor phase size achieved through compatibilization of 5% PE/PA blends with Surlyn ($L/D = 2.2$), at (a, b) the centre, and (c, d) the periphery. (a, c) Without ionomer, (b, d) with ionomer.

larger droplets exiting the extruder. Differences, such as effect of periphery and L/D , typically observed at 5% are no longer apparent at 20%. This would suggest a coalescence-dominated mechanism for fibre formation at this higher dispersed phase concentration. A previous study [19] has shown that coalescence plays an important role in the increase of the minor phase size.

3.2. PE/PA blends (influence of compatibilization)

Table V shows the size and shape of the dispersed PE phase for the blends containing 5% and 20% PE, in

the centre and at the periphery of the extrudate. Values for both uncompatibilized and compatibilized blends are given. The data presented are for the capillary with L/D of 2.2. The micrographs corresponding to the blend containing 5% minor phase (uncompatibilized and compatibilized cases) are shown in Fig. 9.

3.2.1. Influence of radial position

The 5% PE uncompatibilized blend exhibits similar behaviour to the low-viscosity ratio PP in PC blends discussed previously. A transition from spheres in the centre to ellipsoids at the periphery is observed. Also,

fibre formation is again enhanced at 20% PE both in the centre and at the periphery of the extrudate (micrographs not shown).

The blends consisting of PE and PA have been compatibilized with a polyethylene copolymer ionomer. The interactions between the ionomer, polyethylene and polyamide have been reported previously [21]. The ionomer acts as an interfacial agent and reduces considerably the dimension of the minor phase, as shown in Fig. 9. In the case of the 5% compatibilized blend, it can be seen that the droplet size has decreased by a factor of three compared to the uncompatibilized case. Furthermore, no effect of radial position is observed and a spherical morphology is observed throughout. In the case of the 20% compatibilized blend, the decrease in size is even more dramatic in the centre and only ellipsoids are observed at the periphery. It can be seen that the final state of elongation in these compatibilized blends has been dramatically reduced compared to the uncompatibilized case. This seems to be in contradiction with the fact that good adhesion is believed to decrease interfacial slip and therefore favour deformation of the minor phase. However, these results are expected based on two phenomena. Firstly, the significant reduction in particle size would hinder deformation because it follows directly from Taylor's theory that it is more difficult to deform a small drop. Secondly, modification of the interface would be expected to reduce coalescence effects. Both of these phenomena would be expected to result in a reduction of the final state of elongation.

3.2.2. Influence of capillary length

The compatibilized 5% PE/PA blends do not show a morphology dependence on L/D . It is interesting to note in Fig. 10, however, that the compatibilized 20% blend becomes more elongated at higher L/D . This again is probably due to a combination of larger dispersed phase size and increased particle-particle interactions. With respect to the influence of the elongational flow in the converging zone (before the capillary), it should be emphasized that a nearly spherical morphology was observed at the L/D of 0.73. Two possibilities may explain this morphology. Firstly, it may be that deformation took place in the converging zone followed by very rapid recoil and/or break-up of elongated structures as in the PP/PC blends. A second possibility may be that, due to very small dispersed phase size, nearly no deformation occurred in the converging zone at all. Of the two possibilities, the second is most likely because strong interfacial interactions would also be expected to increase significantly the time of break-up of a fluid thread.

3.2.3. Influence of composition

The influence of composition for a compatibilized blend has already been discussed to a certain degree in the previous section. It is obvious that even though higher composition leads to a dependence of the morphology on L/D , the overall influence of composi-

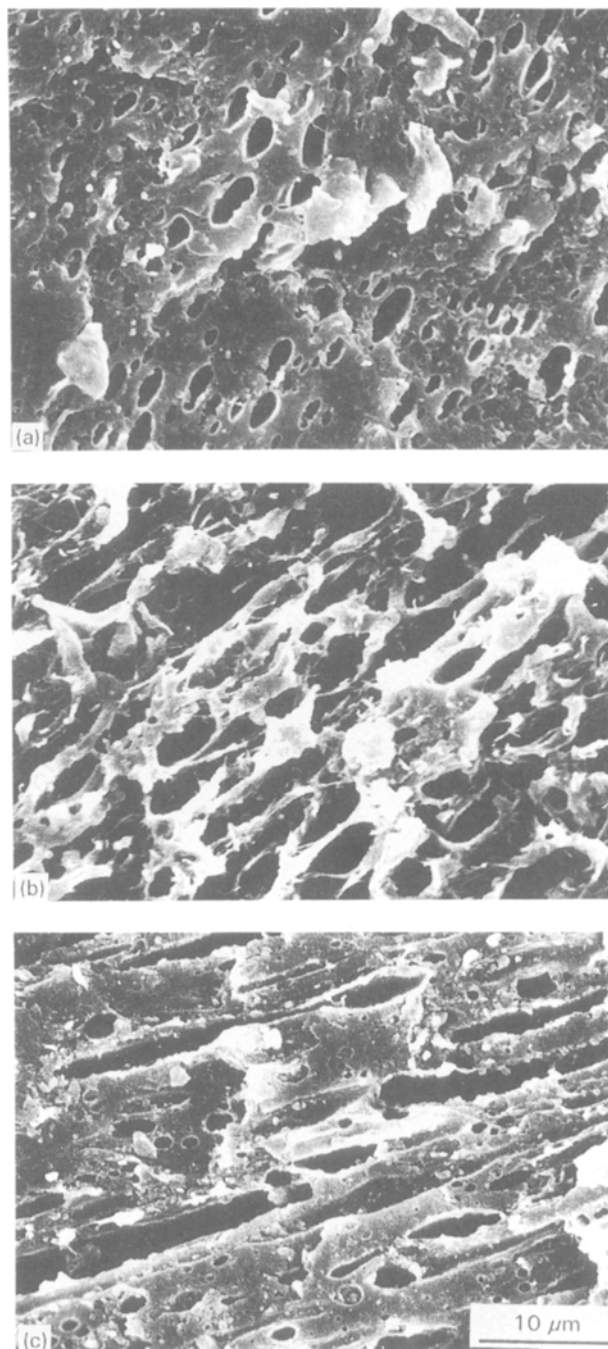


Figure 10 Scanning electron micrographs showing the influence of capillary length for the 20% PE dispersed in PA compatibilized blend (periphery of extrudate). (a) $L/D = 0.73$, (b) $L/D = 2.2$, (c) $L/D = 4.4$.

tion on the morphology of these compatibilized blends is significantly reduced compared to the uncompatibilized case. These results would tend to support the previous statement that coalescence plays an important role in the formation of elongated morphologies. Previous work in this laboratory has shown that interfacial modification significantly reduces dispersed phase coalescence effects [20].

4. Conclusion

The size and the shape of the minor phase in PP/PC and PE/PA blends prepared by twin-screw extrusion through a capillary die have been studied. From scanning electron micrographs of fracture surfaces, it

has been seen that intensive deformation takes place in the elongational flow generated in the converging region of the capillary. Typical capillary instabilities were observed near the entrance of the capillary ($L/D = 0.73$) for the 5% PC dispersed in PP blend. A spherical morphology was observed at higher L/D ratios, indicating that the time required to generate these instabilities is very short. This feature was not observed for the complementary blend.

Evidence of coalescence was shown for all blends containing 20% minor phase, for which fibre formation was enhanced at any radial or axial position whatsoever. Coalescence phenomena appear to be dominant under these conditions.

The addition of an ionomer to the PE dispersed in PA blends resulted in a dramatic decrease of the minor phase size. It has been observed that the final state of deformation of the dispersed phase is significantly diminished in the compatibilized blends.

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