

Morphology development in a polyethylene/polystyrene binary blend during twin-screw extrusion

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In this study, three PS/HDPE blend compositions (10, 30 and 70% PS) were processed in a twin-screw extruder via three procedures. In the first case, pellets of HDPE and PS were added in the hopper of the twin-screw extruder and were blended exclusively on the twin-screw in the classical manner. In the second case HDPE pellets were fed at the hopper of the twin-screw extruder and the PS was added as a melt using a single screw extruder connected midway to the twin-screw. In the third case the PS melt was added even farther downstream with a residence time in the extruder of approximately 25 s. The results show that at all three compositions, the dispersed phase diameter and size distribution are independent of the mixing procedures. These results clearly illustrate that the final blend morphology does not depend on the melting or softening step, but is determined predominantly in the melt state and this even at high compositions. The morphology is developed very rapidly under these dynamic conditions and it is essentially the last flow environment experienced by the blend melt that determines its final morphology.

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INTRODUCTION

One of the key factors to achieve desired final properties in polymer blends is the control of morphology. Understanding the mechanisms controlling the morphology during processing is thus of fundamental importance. Earlier work in this laboratory¹ studied the influence of the time of mixing in a Brabender mixer on the size of the dispersed phase. It was shown for highly immiscible PP/PC blends, that the most significant particle size deformation and disintegration process took place within the first 2 min of mixing. After 2 min very little reduction in the size of the dispersed phase was observed up to 20 min mixing time. Based on these results it was suggested in that paper that the melting process may be important in generating the final morphology of an immiscible blend.

In a previous investigation on the processing of a PS/LDPE blend in several industrial mixers, Plochocki *et al.*² proposed that the initial dispersion mechanism might be the abrasion of solid or partially softened pellets on the wall of the processing equipment.

In 1991, Scott and Macosko³ have reported the evolution of morphology development from pellets to sub-micron particles in a batch mixer. Sundararaj *et al.*⁴, performed a similar study in a twin-screw extruder for both polyamide/polystyrene and polypropylene/polystyrene blend systems. Both studies^{3,4} showed that the major reduction in phase domain size occurs during the melt softening step. The initial mechanism involves the formation of sheets or ribbons of the softened dispersed phase. Due to the effect of interfacial tension and flow characteristics, those sheets become unstable and holes are formed and coalesce.

Rapidly, the holes grow in size and in concentration until the sheet forms a lace like structure. This lace structure is then disintegrated into particles of the size of the final dispersed phase. Continued mixing essentially reduces the size of the largest particles and rounds off the particles. The authors conclude that the melt softening step must be an important step in the control of the morphology.

More recent work in our laboratory indicates that the morphology of the dispersed phase is modified very rapidly under dynamic conditions in the melt. Chapleau and Favis⁵ have reported, for blends of 5% PC dispersed in PP, that passing from an *L/D* ratio of 0.73–2.2 is sufficient to promote the disintegration of capillary instabilities after twin-screw extrusion. Also, neither fibres nor capillary instabilities were observed at the centre of the extrudate, due possibly to the cooling time required to fix the morphology. In another twin-screw extrusion study, Favis and Therrien⁶ have shown that the die has a significant effect on the blend morphology. Proximity to the die wall was shown to result in preferential fibre formation for the dispersed phase. These points suggest that the final morphology can be modified rapidly when both phases are in the liquid state.

Gonzalez *et al.*⁷ have studied the effect of reprocessing on blends of 20% PA-6 dispersed in HDPE. Samples initially prepared on a twin-screw extruder showed a significant increase in the dispersed phase size when they were reprocessed in a single screw extruder. This size increase can be related to the fact that a single-screw extruder is a less efficient mixer compared to a twin-screw extruder. These results indicated that for a particular type of screw configuration and processing equipment, there exists a quasi-equilibrium morphology. This again points out that the morphology responds rapidly to the particular flow environment it is exposed to.

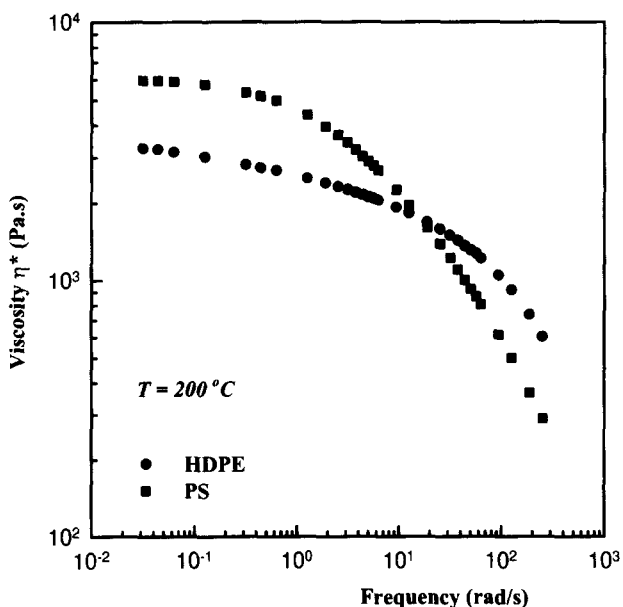
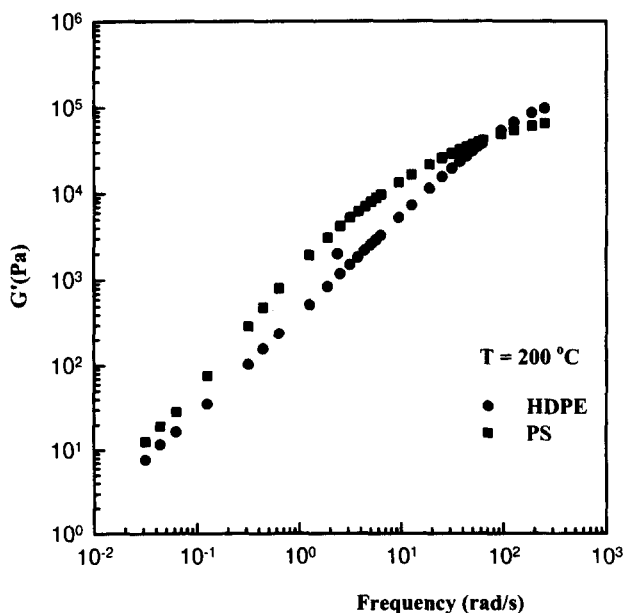
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Table 1 Properties of materials

	PS	HDPE	SEBS
Producer	Dow	Dow	Shell
Molecular weight	$M_w = 215\,000$, $M_n = 100\,000$, $P = 2.15$	$M_w \approx 190\,000$	EB bloc: $M_w = 35\,000$, PS bloc: $M_w = 7500$, composition: 29% _w styrene
Density: 20°C (g/cm ³)	1.04	0.962	1.00
Density: 200°C (g/cm ³)	0.974	0.754	—
Melt index	8.0 (200°C/5.0 Kg)	4.0 (190°C/2.16Kg)	—

The objective of this study is to critically consider the rapidity of morphology development under dynamic conditions and its influence on morphology development in the twin-screw extruder. Also, the influence of the melting zone on the final morphology for an immiscible blend of PS and HDPE will be examined. A twin-screw extruder has been

modified by connecting a single-screw extruder midway down its length. This allows the polymers to be mixed in the liquid state. In this way, the influence of the melting of mixed pellets on the final blend dispersed phase morphology could be isolated. By positioning the single-screw extruder progressively downstream on the twin-screw it should also be possible to analyse the rapidity of morphology formation in the melt state.

**Figure 1** Viscosity as a function of the frequency at 200°C**Figure 2** Elasticity as a function of the frequency at 200°C

EXPERIMENTAL

Materials

The polymers used in this study were general purpose polystyrene and polyethylene, both obtained from Dow Chemical Canada. Some properties of these materials are shown in *Table 1*.

Rheology

The dynamic viscosity and the storage modulus were measured as a function of the frequency on a Rheometrics Mechanical Spectrometer (RMS, Model 605). Experiments were performed under dry nitrogen at 200°C (*Figures 1 and 2*). At low frequency, the PS phase is more viscous than the HDPE. Both curves cross each other at around 10 rad/s, and at this point the viscosity ratio is about one. At higher frequency the HDPE phase is more viscous. The elasticity of HDPE and PS are similar over a wide frequency range. Above 100 rad/s the HDPE is more elastic than the PS, while at lower frequency the opposite is true.

Blends

Three compositions were examined in this study: 10% PS/90% HDPE; 30% PS/30% HDPE and 70% PS/30% HDPE. All volume fractions are calculated based on the densities at 200°C. Prior to blending, 0.2% of Irganox 1010 was added as antioxidant.

Extruder

Figure 3 illustrates three ways in which PS and HDPE were blended. The traditional procedure, referred to as dry blend in the text, consists of pre-mixing the two polymer pellets and feeding at the hopper of the twin-screw extruder. The second procedure, referred to as melt position 1, consists of feeding HDPE pellets at the hopper of the twin-screw extruder and adding PS melt at the fourth zone of the twin-screw extruder using a single-screw extruder. In the third procedure, referred to as melt position 2, PS melt is added at zone 6 of the twin-screw extruder.

The twin-screw extruder used is a Leistritz co-rotating twin screw extruder 960 mm long and 34 mm in diameter. The following conditions were used for all compositions. Blending was performed at a total volumetric feed rate of 375 cm³/min. The screw speed was maintained at 200 rpm. The temperature profile was controlled at

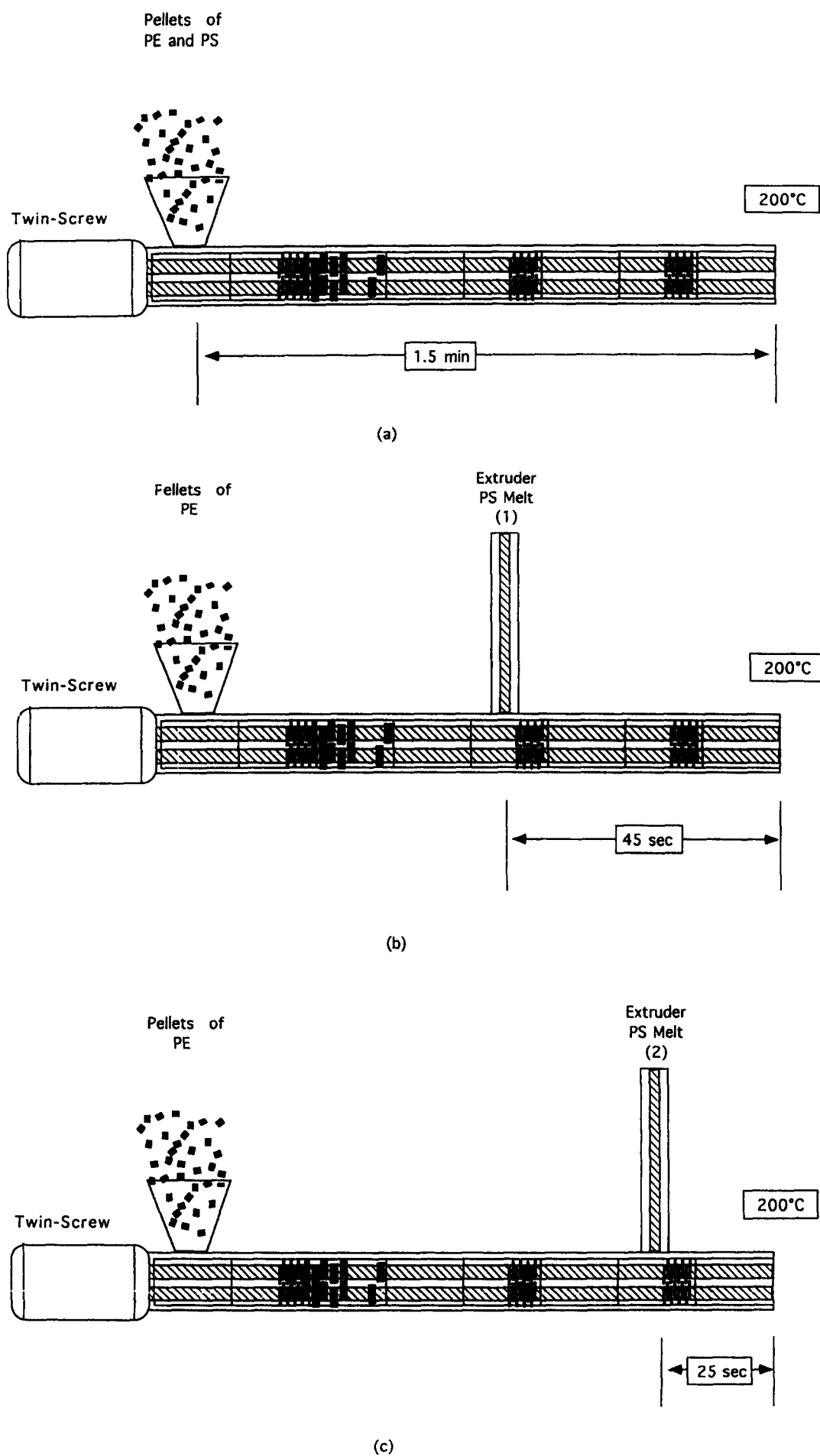


Figure 3 Illustration of the three procedures used to mix and melt the polymers. An estimate of the residence time in the twin-screw extruder is also shown for each procedure

MORPHOLOGY

Dispersed Phase

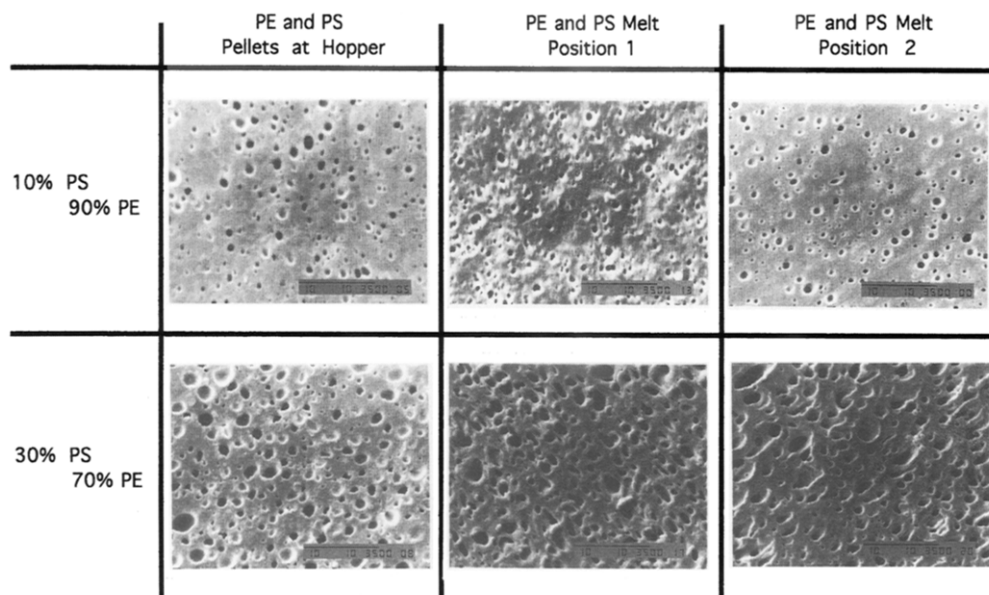


Figure 4 Scanning electron micrographs of microtomed surfaces of PS/HDPE blends (10% PS/90% HDPE and 30% PS/70% HDPE) for the three different mixing procedures. All micrographs are at a magnification of $3500\times$. The $10\ \mu\text{m}$ bar is indicated in the photos

190, 200, 200, ..., 207°C from feed to exit. The last zone was over heated due to viscous heat generation. To avoid any influence of the converging region of a die, samples were taken at the end of the extruder without a die. Pieces of melted polymer blend were taken from the end of the extruder and rapidly quenched in water to freeze in the morphology.

A special screw configuration was designed to make sure that HDPE was melted before position 1 and to allow the pre-melted PS to be properly blended to the HDPE at that position. To do so, mixing elements were added to the screw configuration immediately after melt/melt mixing. A diagram of the screw configuration is given in *Figure 3*. Diagonal lines indicate right handed transport elements and solid rectangles indicate kneading blocks. Both 7.5 mm, 30 and 15 mm, 60 kneading blocks were used. In order to ensure melting a gear mixer was used at the end of zone 3.

Addition of melted polymer to the twin-screw extruder in procedures two and three was done using a single-screw extruder 45 cm long and 19 mm in diameter. The screw speed was adjusted to obtain the desired flow rate. The temperature profile was controlled at 190, 200, 200, ..., 200°C from feed to the end. A special adapter was added to connect the single-screw and the barrel of the twin-screw extruder.

Microscopy and image analysis

A thin section of each sample was cut as near as possible from the surface in order to assure rapid cooling of the studied morphology. Plane surfaces were obtained by using a Leica model Jung RM 2065 microtome equipped with a glass knife. During cutting, samples were held below -150°C to reduce the degree of surface deformation. The samples prepared at 10 and 30% PS were microtomed as above. In order to improve contrast in the subsequent microscopic analysis, the minor phase was dissolved by immersion of the samples in tetrahydrofuran for 10 h at

room temperature. The samples at 70% PS represent the region of dual-phase continuity and in that case, freeze fracture surfaces were observed on the SEM (no microtoming, no solvent dissolution).

Prior to microscopy, the samples were coated with a gold/palladium alloy. A scanning electron microscope (Jeol T300) was used to study the sample surface. A semi-automatic method of image analysis (reported elsewhere⁸) was used to quantify the average size and the size distribution of the minor phase. The number average diameter (d_n) and the volume average diameter (d_v) were obtained from the measurement of at least 200 particles. A correction procedure⁸ was applied to the diameters determined from the micrographs. This was done to take into account the polydispersity in particle size, and the fact that the knife rarely cuts through the particles at their equator.

RESULTS AND DISCUSSION

Morphology

The morphology of 10% PS/90% HDPE and 30% PS/70% HDPE are shown at the same magnification in *Figure 4*

Table 2 Dependence of phase size (d_v and d_n) on composition and mixing procedure for blends of 10% PS/90% HDPE and 30% PS/70% HDPE

	Pellets	Melt zone 1	Melt zone 2
Blends of 10% PS/90% HDPE			
d_v (μm)	1.15	0.95	0.86
d_n (μm)	0.46	0.36	0.29
d_v/d_n	2.5	2.6	2.9
Blends of 30% PS/70% HDPE			
d_v (μm)	1.68	1.84	1.56
d_n (μm)	0.77	0.92	0.88
d_v/d_n	2.1	2.0	1.8

for the three mixing procedures. Dispersed droplets of the minor phase in the matrix are observed for the two compositions. For a given mixing procedure, the droplets of minor phase increase in diameter with the concentration as would be expected. The size of the dispersed phase, as a function of the composition and the mixing procedure, is given in Table 2. For 10% PS/90% HDPE, it is evident that the mixing procedure does not affect the size or shape of the dispersed phase. The particle size varies within a range of 0.15 μm for all three procedures. The particle size distribution is also very similar even on the highly expanded scale of Figure 5.

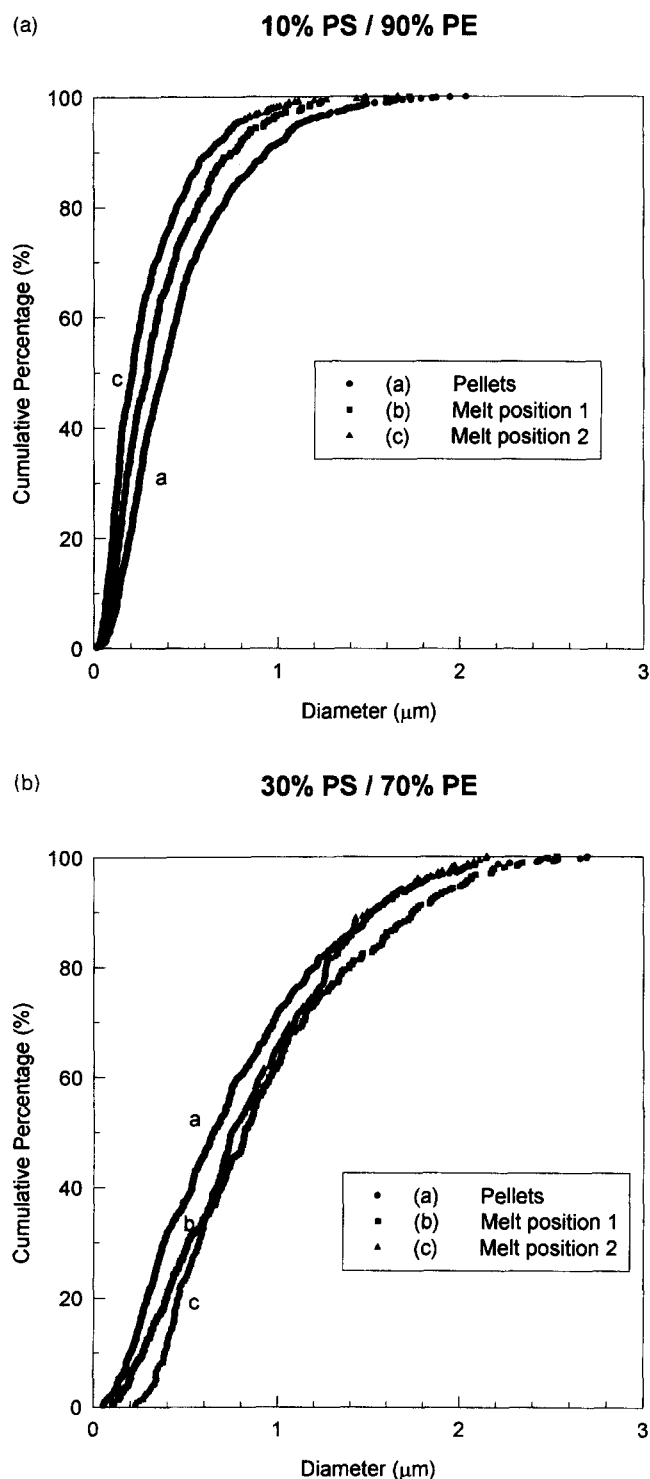


Figure 5 Particle size distribution for blend of (a) 10% PS/90% HDPE and blend of (b) 30% PS/90% HDPE

For 30% PS/70% HDPE, the type of mixing procedure again does not significantly influence the morphology of the final dispersed phase (see Table 2). This is an important result since it would be expected that this higher composition 30% PS blend is experiencing significant coalescence and particle-particle interactions. During microscopic observations the contour of the dispersed phase appears slightly less spherical when PS was added in the melt state compared to the first case when pellets of PS and HDPE were added to the hopper of the twin-screw.

In order to maximise coalescence phenomena, blending using the dry blend and the melt position 1 procedures were carried out at the region of dual-phase continuity. This had been previously determined in another study by Bourry⁹ to be at 30% HDPE/70% PS for this system. The morphologies obtained are shown in Figure 6. Although it is difficult to quantify this morphology due to its complex structure, detailed observations on the microscope revealed a very similar dual phase continuous structure for both procedures.

Rapidity of dispersed phase morphology formation

The above results indicate clearly for this PE/PS system, that the final blend morphology is critically determined in the melt and not during melting. Furthermore this morphology is obtained quite rapidly. The final morphology for all three mixing procedures used in this study lead to the same average diameter and distribution at a given composition. In Figure 3, the estimate of the time of mixing is given for each mixing procedure. Even when the time of mixing was only 25 s, the dynamic equilibrium morphology was obtained. This is a clear indication that the morphology responds extremely rapidly to its particular flow environment when both polymers are in their melt state.

As was mentioned before, previous work^{1,3,4} reported that significant particle size reduction was observed during the melting process. This study however, indicates, for a similar system, that since morphology development in the melt state is so rapid, it is essentially the last flow environment in the extruder that influences the final morphology. This has the effect of essentially wiping out the previous mixing history. The results from this work therefore indicate that although a major reduction in size does occur during the melting process as shown in previous studies, it does not mean that it is that step that controls the final dispersed phase morphology.

These findings confirm the observations made by Gonzalez *et al.*⁷. Based on a study of the influence of coalescence, they reported that blends of high concentration of minor phase produced in a twin-screw extruder display a significant increase in diameter of dispersed phase after they have been reprocessed in a single-screw extruder. They concluded that at high concentration, unmodified blends respond rapidly to the forces associated with disintegration and coalescence. In this case it was also observed that it is the last flow environment experienced by the blend melt that controls the morphology.

This work suggests that it is the absolute value of applied stress and shear that influence the morphology of this PE/PS blend as opposed to total stress and total shear. These results emphasise the critical role of the screw configuration at the end of the extruder and also the need to give special attention to morphology variations in the die. The data also indicate for PE/PS that a large part of the twin-screw extrusion device is essentially redundant in the melt compounding operation.

MORPHOLOGY Phase Inversion

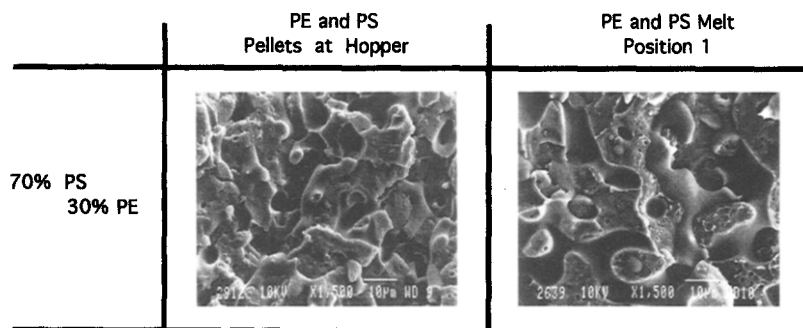


Figure 6 Scanning electron micrographs of fracture surfaces of the co-continuous blend (70% PS/30% HDPE) for two different mixing procedures. All micrographs are at a magnification of 1500 \times . The 10 μ m bar is indicated in the photos

In future studies other polymer blends will also be tested to validate this study including systems containing interfacial modifiers. Work is currently underway to establish viscosity ratio, elasticity ratio and interfacial tension limits to the above findings for a variety of blend systems.

CONCLUSION

In these PS/HDPE blends, it has been shown that the final morphology from twin-screw mixing is not determined during melting or gradually over the entire length of the extruder, but is achieved rapidly in the melt state even at high compositions. Even when the residence time of mixing was reduced to approximately 25 s, the blending of PS and HDPE melts yields the same morphology as mixing pellets over the entire length of the twin-screw extruder. The morphology of the dispersed phase is modified so rapidly in the melt during mixing that it is essentially the last flow environment experienced by the blend that determines its

final morphology. This has the effect of wiping out the previous mixing history. For this PE/PS system it is shown that a large part of the twin-screw extrusion device is essentially redundant in the melt compounding operation.

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