"We often discover what will do, by finding out what will not do; and probably he who never made a mistake never made a discovery".

***Samuel Smiles** (1812–1904), Scottish writer.*
Self-Help.

CHAPTER 5

COMPOUNDING AND FORMING: PRELIMINARIES

5.1 INTRODUCTION.

This chapter provides details on the different mixing and compounding methods initially experimented with in order to find the most suitable technique to incorporate the electro-conductive complex with each of the polymer matrices. As will be seen, after compounding, the blends were subjected to a forming process to promote the in-situ formation of polyaniline fibres. An account of the details of the processing technique employed is also provided. Experimentation with different processing parameters was also carried out in order to determine the optimum processing conditions. This is also detailed here together with the criteria used in the evaluation. As has been seen, the results from the rheometry analysis suggested that PANIPOL^{TM} 2 was most likely to be successfully deformed into uniform fibres (refer to section 4.6 in chapter 4). Therefore, the experimentation was concentrated on systems containing this material. Experimentation was also performed with different weight compositions. Finally, with the purpose of assessing the effect of the different polymer matrices on the morphology of the polyaniline phase in the processed blends, these were subjected to a morphological analysis. This analysis also assisted in the selection of the most suitable polymer matrix to favour the in-situ production of polyaniline fibres. As in all the processing methods described in this chapter, a general account of the details of the technique employed will be presented followed by the results following from this. General conclusions are also presented at the end of the chapter.

5.2 MIXING AND COMPOUNDING TECHNIQUES.

5.2.1 MANUAL MIXING.

A mixture consisting of 5 wt.% of PANIPOL^{TM} 2 and 95 wt.% of LDPE was prepared at room temperature. For this, the correct amounts of the as-received materials in the form of pellets were placed in a plastic bag. The bag was tightly closed and the mixing was performed by manual agitation. As will be seen later, this method was not appropriate as the mixture had a high degree of segregation, thus resulting in irregular feed of the ingredients during processing. For this experiment, a batch of 100 g was prepared. Throughout the text, this mixture will be referred to as blend MA5PANIPOL/LDPE.

5.2.2 ROLL MILLING.

A BRIDGE two-roll milling machine (No. 70 M 1261), with rolls of 0.05 m in diameter, was used for thermally preparing blends consisting of 5 wt.% of PANIPOL™ 2 and 95 wt.% of LDPE, SBS and PP, respectively. These three blends will be referred to in the text as blends RM5PANIPOL/LDPE, RM5PANIPOL/SBS and RM5PANIPOL/PP, respectively. The blending temperatures were 200°C for the blend containing PP and 120°C for those with LDPE and SBS. The materials were used as received, and 5 and 95 g of PANIPOL™ and polymer matrix were respectively used in each blend. The compounding procedure was the same for all the blends, and the details are presented next.

The rolls, separated about 1-2 mm from each other, were heated to the corresponding compounding temperature. Once this temperature was reached, the polymer matrix was first fed (fig. 5.1) through the top into the gap between the counter-rotating rolls (at ca. 20-30 rpm) where it was drawn in. The material bypassed the slightly faster-driven roll and was returned to the gap entry.

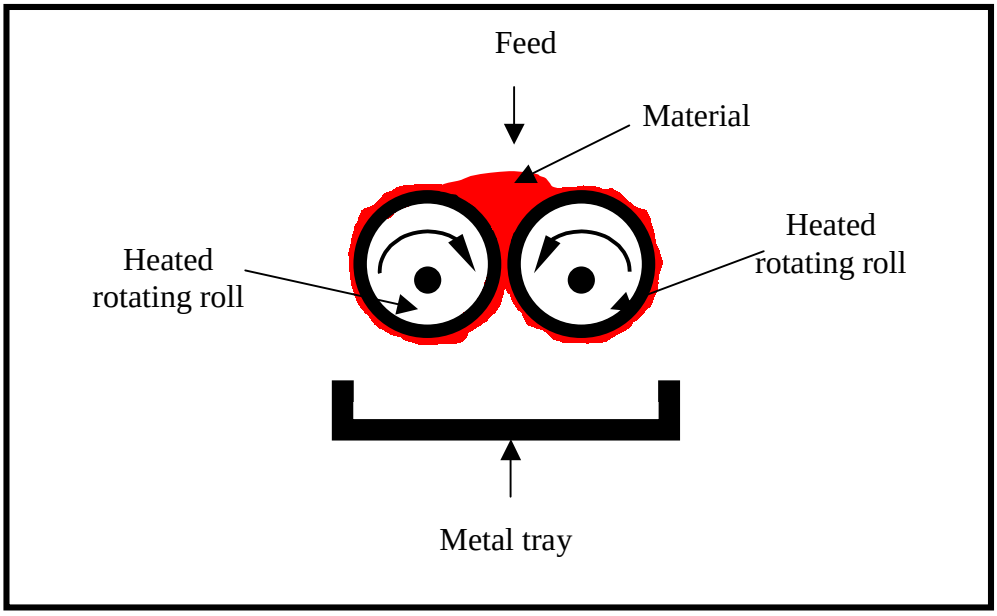


Figure 5.1. Diagram exemplifying the roll milling process.

The feed of the matrix was performed slowly, in increments, to allow the material to soften/melt. The PANIPOL™ complex was added to the polymer matrix as soon as this was looking like a soft paste. The pellets of PANIPOL™ softened and dispersion

was achieved as the paste was continuously passed through the gap between the rolls. The feed was performed in increments with varying rolls clearance to obtain uniform dispersion of PANIPOL^{TM} in the polymer matrix. Once all the PANIPOL^{TM} was added, the compounding continued (for ca. 5-10 more min) until a homogeneous paste was observed. Afterwards, the blend was peeled from the rolls by using a wooden spatula. The blend was collected in a metal tray already placed below the rolls at the beginning of the process. After cooling down to room temperature, all the blends were properly stored in sealed plastic containers to await further experimentation.

Some problems were found when following this compounding method. For example, the speed of the rolls was fixed. This sometimes presented a problem, especially during the feed of the materials, as this velocity was occasionally too high so as to make some of the pellets eject from the revolving rolls, thus causing the final composition of the blends to be different from that originally planned. There were also problems when trying to produce the blend RM5PANIPOL/PP. In this case the compounding temperature was probably too high. As a result, mostly of the molten material went to the sides of the rolls, which generated an inhomogeneous blending process. On the other hand, when the temperature was reduced to 180°C, it took much longer to melt the raw materials and it was not possible to obtain a homogeneous blend. No significant improvement was observed when the compounding temperature was increased to 190°C. As a result, the blend was discarded.

5.2.3 EXTRUSION.

In this compounding method, it was used a single screw extruder fitted in a film extrusion unit (Plasticisers Limited). Blends of the following compositions were prepared:

- 5 wt.% of PANIPOL^{TM} 2 and 95 wt.% of LDPE.
- 10 wt.% of PANIPOL^{TM} 2 and 90 wt.% of LDPE.

These blends will be referred to as blends EX5PANIPOL/LDPE and EX10PANIPOL/LDPE, respectively.

The extruder consists essentially of a feed hopper, a barrel with two heating zones and a revolving screw (fig. 5.2). The nominal dimensions of the barrel are 380 mm in length and 19 mm in internal diameter. The screw, with three sections (fig. 5.2), has a compression ratio of 4/1 (that is, the relation between the channel depths in the feed and metering sections, respectively). A flat die for producing films was attached to the end of the barrel. For the compounding, the two zones of the barrel and the die were heated at 200°C. The screw speed was set at 20 rpm.

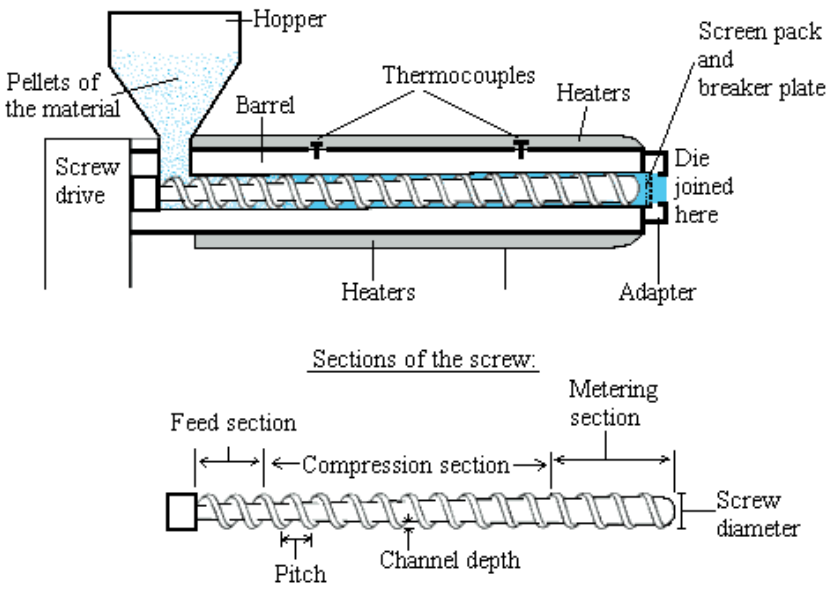


Figure 5.2. Essential components of the extruder.

Other components of the extruder include the screen pack, the breaker plate and the adapter. These are situated between the end of the barrel and the die head. The screen pack is a series of stainless steel screens having a very fine mesh. The screens are stacked together starting with a coarse screen followed by a finer screen and then a coarse screen again. These meshes serve primarily as a filter for foreign matter, which may have got into the extruder. It also increases back pressure in the barrel, which results in a better homogenisation of the melt. The screen pack is held in place by the breaker plate, which is a thick metal disc drilled with holes. The adapter joins the die head to the end of the extruder barrel.

Before compounding, the correct amounts of the as-received materials were mixed in a plastic bag following the method described in section 5.2.1. Afterwards, the mixture was fed to the hopper and, within the barrel; this was transported from the hopper to the

die by the revolving screw. The mixture was melted by the external heat applied to the barrel and the frictional heat generated by the shear action of the screw. In this way, the melt was forced at a constant rate through the slit in the die. The blends were obtained in the form of thin films cast on a metal chill roll (fig. 5.3). The films were cooled by contact with the rolls internally cooled by water. From the chill rolls the film was led to the rubber nip rolls. The chill and nip rolls were rotating at an appropriate speed ratio so that the nip rolls pull the film from the chill rolls just to maintain a certain tension in the film. After the nip rolls, the film was led to the winder that rolled it on a core. Films approximately 45 mm wide and 70 μm thick were produced. These were properly stored in sealed plastic containers to await further experimentation. Batches of 100 g were used in the preparation of both blends.

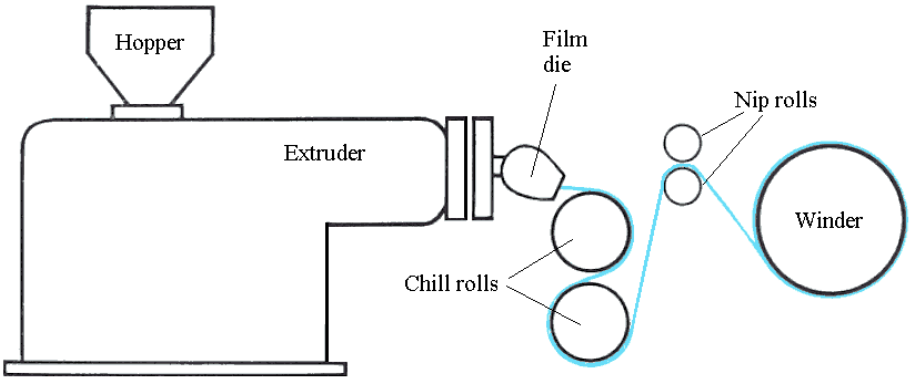


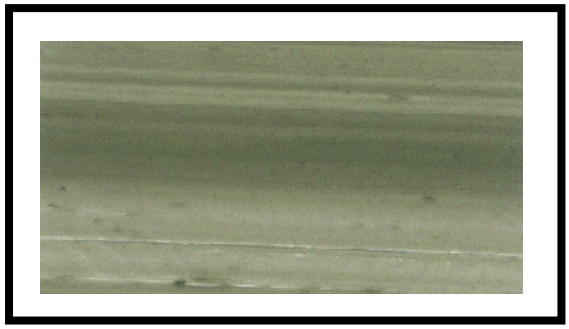
Figure 5.3. Essential components of the film extrusion unit.

It was observed that the films presented a certain degree of anisotropy. That is, the PANIPOL^{TM} phase was preferentially orientated in the extrusion direction. This can be observed in the samples presented at the end of this section. In the samples, the dark green regions correspond to the PANIPOL^{TM} phase, whereas the whitish regions correspond to the LDPE phase.

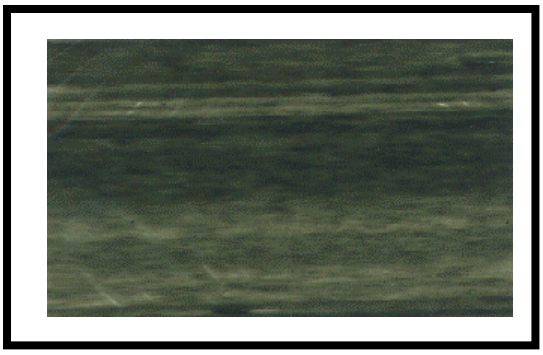
As can be seen from the samples provided, these display a texture that may indicate that this compounding technique has potential for in-situ deforming the polyaniline phase into fibres. However, this would need to be verified by further microscopic analysis of the films' morphology. The use of this technique, however, even only as a mere compounding method, would be restricted in that the processing temperatures would be so high as to cause the PANIPOL^{TM} to lose its intrinsically

electro-conductive properties. For instance, processing a blend of PANIPOL™ and PP would imply that the extrusion temperatures would have to be set at around 250°C to allow the PP phase to have the required melt viscosity to flow through the slit in the die. As has been seen, for the PANIPOL™ samples, this is the maximum allowable processing temperature without risk of loss of their intrinsic conducting properties (refer to section 4.5.1). Moreover, as has been also found, some additives present in the conductive complexes are affected at temperatures even lower than 250°C (refer to section 4.5.2).

On the other hand, this technique would be also limited to the type of polymer matrix. For example, this processing method is not recommended for the particular grade of SBS used in this work because, as has been observed (refer to section 4.6), this polymer would display a higher level of viscosity than that of the LDPE at a comparable temperature. This would imply that, in order to have the required melt viscosity, the polymer would have to be processed at temperatures well above 200°C. Again, the properties of PANIPOL™ would be at risk if blends with SBS were intended to be produced following this compounding method. What is more, processing of this particular grade of SBS in high shear equipment can cause the temperature to rise, and it is therefore advisable to avoid temperatures in excess of 225-230°C because of fire risk [152].



Sample 5.1 Film of blend EX5PANIPOL/LDPE.



Sample 5.2 Film of blend EX10PANIPOL/LDPE.

5.2.4 MELT MIXING.

The compounding was performed in a two-piece batch mixer mounted on a torque rheometer instrument (BRABENDER® PLASTI-CORDER® PLE 330). A similar mixer is presented in fig. 5.4a. PP and SBS were respectively blended with PANIPOL™ 2 at 190 and 130°C, respectively.

The content of PANIPOL™ 2 in the blends were as follows:

- 5 wt.% (blends MM5PANIPOL/PP and MM5PANIPOL/SBS).
- 10 wt.% (blends MM10PANIPOL/PP and MM10PANIPOL/SBS).
- 15 wt.% (blends MM15PANIPOL/PP and MM15PANIPOL/SBS).
- 50 wt.% (blends MM50PANIPOL/PP and MM50PANIPOL/SBS).

The mixer, with a capacity of 60 cm^3, consists essentially of two counter-rotating rotors (roller-blade-type, fig. 5.4b) inside of a double C-shaped mixing chamber (fig. 5.5). The chamber can be closed or opened when required by means of a metal lid pivoted on one of the mixer pieces. In this way, the lid serves as a ram that forces the feed into the chamber and that can be removed or raised depending on the specific compounding stage. Once the mixer is securely mounted on the torque rheometer instrument, the rotors can be driven at any selected speed. One rotor is driven by the motor (primary rotor), which turns the second one via connecting gears.

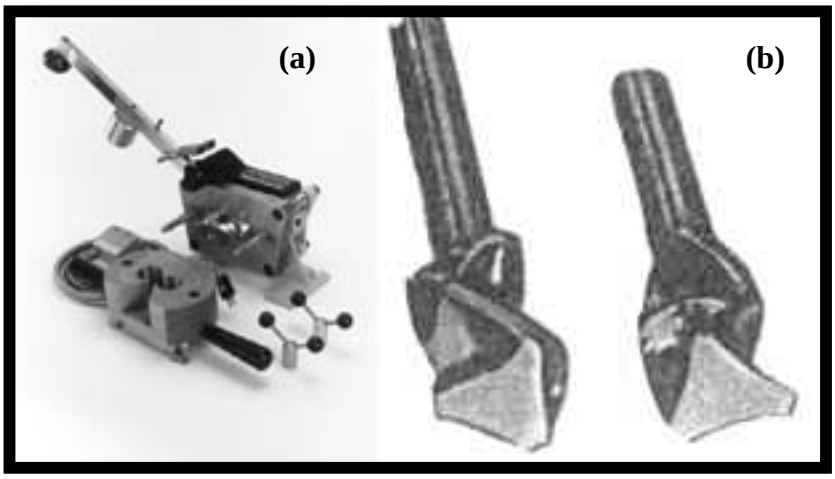


Figure 5.4. The BRABENDER® batch mixer (a) and rotors (b).

The mixer is heated at the selected compounding temperature by the heat transferred from the oil flowing through the channels within the metal chamber walls. The temperature control occurs in the oil bath connected to the mixer and, to monitor the temperature of the melt, a thermocouple is inserted in the bottom of the chamber. During compounding, the mixer masticates the materials by the milling action occurring in the shear gap between the rotor tips and the inner surface of the mixing chamber. In practice, the mix passes through transitional stages, especially at the beginning of the mixing operation, and finally becomes a homogeneous material. The torque in the mixer shows a peak at the start of mixing, then decreases gradually, and finally stabilises. The torque is generated by shearing and compressing the materials in the space between the front face of the primary rotor and the inner wall of the mixing chamber. When the compounding is finished, the mixer is discharged by opening one of its sides.

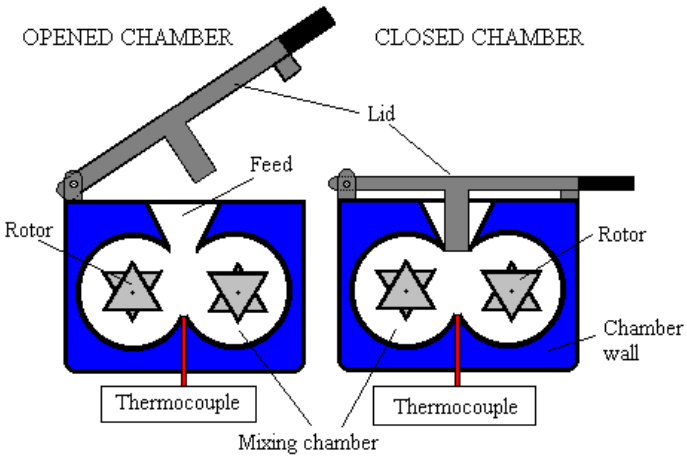


Figure 5.5. Essential components of the mixer.

The blending parameters initially studied were a mixing speed of 10 rpm and a mixing time of 2 min. The general sequence for preparing the blends is described next.

1. Depending on the materials for blending, the mixing chamber was heated to the appropriate temperature.
2. As soon as the compounding temperature was reached, the speed of the rotors was set at one rpm.
3. The mixing chamber was slowly charged in small increments with the polymer matrix.
4. The chamber was closed as soon as the feed with the polymer matrix was completed.
5. The torque was monitored and, occasionally, the chamber was opened to observe the physical state of the material.
6. When the material was in its molten state and the torque was steady, the speed of the rotors was increased to 10 rpm.
7. The chamber was opened and the PANIPOL^{TM} complex was added to the melt.
8. The chamber was closed and the compounding was performed for 2 min.
9. After the compounding time elapsed, the mixing chamber was opened and the mixer was discharged by opening one of its sides.

The materials were used as received and the blends, in the form of a soft paste, were peeled off the rotors and chamber with the aid of a brass spatula. These were collected in a metal tray and after cooling down to room temperature they were properly stored in sealed plastic containers to await further experimentation.

Initially, three batches of 30 g each were used in the preparation of each of the blends containing PP. However, it was observed that some of the prepared blends, especially those with a high content of PANIPOL^{TM} 2, were not homogeneous. That is, the conductive complex was not well dispersed within the PP phase. The reason for this is that the shear stresses occurring in the melt required to induce good dispersion were not high enough because the batch size was not adequate. The batch was too small, thus resulting in a melt that was flowing slowly between the rotors and the inner walls of the chamber. As a result, it was decided to use batches of different size for the production of the blends containing SBS. The adequate batch size was estimated using the fill factor principle. The fill factor (*FF*) is the fraction of the total volume of the mixing chamber

that the final fluxed batch should occupy in order to produce a homogeneous blend. This factor typically ranges from 0.7 to 0.8 [186]. Accordingly, the batch size (*BS*) was estimated using the following equation:

$$BS = (MC)(\rho_{BATCH})(FF) \text{.....} Eq.\ 5.1,$$

where:

MC = mixer capacity = 60 cm^3 and

ρ_{BATCH} = density of the final fluxed batch.

To estimate the density of the final fluxed batch, the following rule of mixtures (*Eq. 5.2*) was used,

$$\rho_{BATCH} = (\phi_{PANIPOL})(\rho_{PANIPOL}) + (\phi_{MATRIX})(\rho_{MATRIX}) \text{.....} Eq.\ 5.2,$$

and the following equations:

$$\phi_{PANIPOL} = \frac{V_{PANIPOL}}{V_{PANIPOL} + V_{MATRIX}} \text{.....} Eq.\ 5.3a,$$

$$\phi_{MATRIX} = \frac{V_{MATRIX}}{V_{PANIPOL} + V_{MATRIX}} \text{.....} Eq.\ 5.3b,$$

$$V_{PANIPOL} = \frac{Wt.\%_{PANIPOL}}{\rho_{PANIPOL}} \text{.....} Eq.\ 5.4a,$$

$$V_{MATRIX} = \frac{Wt.\%_{MATRIX}}{\rho_{MATRIX}} \text{.....} Eq.\ 5.4b,$$

where:

$\phi_{PANIPOL}$ = volume fraction of PANIPOL™,

ϕ_{MATRIX} = volume fraction of the polymer matrix,

$\rho_{PANIPOL}$ = density of PANIPOL™,

ρ_{MATRIX} = density of the polymer matrix,

$V_{PANIPOL}$ = volume of PANIPOL™,

V_{MATRIX} = volume of the polymer matrix,

$Wt.\%_{PANIPOL}$ = weight percent of PANIPOL™ in the blend, and

Wt.% $_{MATRIX}$ = weight percent of the polymer matrix in the blend.

For the calculations of the batch size, the maximum and minimum values recommended for the fill factor were used, that is, 0.7 and 0.8. To estimate the density of the final fluxed batch the density values for PANIPOL^{TM}, PP and SBS presented in chapter 3 were used. The results are presented in Table 5.1. From the results, it can be seen that the optimum batch size for the blends containing PP should have been at least 38.6 g, which explains why the conductive complex was not well dispersed in the blends prepared with batches of 30 g. On the other hand, it can be seen that for the blends containing SBS, the optimum batch size ranges from 39.8 to 48.7 g depending on the blends' composition. However, for practical reasons batches of 40 g. were used in the preparation of the blends. In addition, it was considered that working with batches of 40 g would ensure the operation of the instrument within its safety limits, that is, at torque levels not higher than 50 Nm.

Table 5.1. Optimum batch sizes calculated for blends containing PANIPOL^{TM}, PP and SBS.

BLENDS	**BATCH SIZES (g)**	
	Fill factor = 0.7	**Fill factor = 0.8**
MM5PANIPOL/PP	38.6	44.1
MM50PANIPOL/PP	41.8	47.8
MM5PANIPOL/SBS	39.8	45.5
MM50PANIPOL/SBS	42.6	48.7

Overall, it was noticed that the dispersion of PANIPOL^{TM} in the blends improved considerably. However, it was noticed that the blend MM15PANIPOL/SBS was still showing a poor degree of homogeneity. It was thought that the main reason for this was that the conductive complex was not being given enough time to mix properly with the polymer matrix. At this point, it was decided to increase the mixing time to 5 min for the preparation of blend MM50PANIPOL/SBS. Some improvement was observed. However, the blend was still lacking the required level of homogeneity. It is believed that better results would have been obtained if the proper batch sizes had been used in

the preparation of the blends, that is, average sizes estimated using *FF* values of 0.7 and 0.8.

During the course of the blending process, it was observed that the torque levels varied depending on the blend composition and compounding stage. In general, it was observed that during the addition of PANIPOL™ to the polymer matrix (stage 7 of the compounding sequence), the torque increased and then gradually decreased until it reached a stable level (stage 8). To illustrate this variation, Table 5.2 presents the torque levels before and after the addition of PANIPOL™ to the polymer matrix. In the Table, stage 6 refers to the compounding stage in which the polymer matrix was already in its molten sate. As can be seen in Table 5.2, the torque levels for the blends containing PP are lower than those for the blends with SBS. This is mainly because the batches used in the preparation of the blends were smaller (i.e., 30 g for the blends containing PP in contrast to 40 g for those with SBS). The level of torque observed for the blend MM50PANIPOL/SBS during the stage 8 is higher than that of the blend MM15PANIPOL/SBS because the conductive complex was given more time to mix with the polymer matrix. In general, the torque decreased after adding PANIPOL™ to the polymer matrices mainly because, as pointed out before (refer to chapter 3), this complex acts as a processing aid in lowering the melt viscosity of the blends.

Table 5.2. Torque levels during the compounding of the blends.

BLENDS	**TORQUE (Nm)**	
	STAGE 6	**STAGE 8**
MM5PANIPOL/PP	3	2-3
MM10PANIPOL/PP	3	2-3
MM15PANIPOL/PP	3	2-3
MM50PANIPOL/PP	2	0
MM5PANIPOL/SBS	34-35	14-25
MM10PANIPOL/SBS	29-32	6-15
MM15PANIPOL/SBS	29-30	0-1
MM50PANIPOL/SBS	15-16	5-6

With respect to the temperature monitored in the melt during the final compounding stage (stage 8), an increment of only 1-4°C, with respect to the prefixed temperature in the mixing chamber, was observed. This was observed in the majority of the blends.

Some additional modifications were performed to the compounding sequence, namely mixing time and speed, respectively. These will be detailed in the relevant section (chapter 6).

Overall, it was found that this blending technique, compared with the previous ones, would favour best the compounding due the following reasons:

- The temperature that is required to process a specific polymer matrix is lower than that required when using the single screw extruder. This broadens the number of possible systems with which experimentation could be performed without exposing the PANIPOL^{TM} complex to temperatures that may put at risk its electro-conductive performance. Moreover, when working with a specific system, this also offers the possibility of experimenting with different compounding temperatures even though these are within the allowable processing temperature range for the PANIPOL^{TM} complex.
- Contrasting with the two-roll mill machine, the instrument offers the possibility of varying the speed of the rotors, which assists in the optimisation of the process. Also, the special geometry of the rotors provides better dispersion and mixing action. Moreover, the final composition of the blends is controlled better because the possibilities of losing some material during the feed and mixing stages are minimised because the compounding takes place in an enclosed space, which also promotes a cleaner process.

5.3 SIZE REDUCTION.

Before subjecting the blends to the forming process, they were granulated (excepting blend MA5PANIPOL/LDPE) using a USI-Cumberland granulating machine (Model 5X7) with a metal screen plate drilled with holes of ca. 3 mm in diameter. The

machine (fig. 5.6) consists essentially of three rotary knives inside a special chamber where stationary knives are mounted.

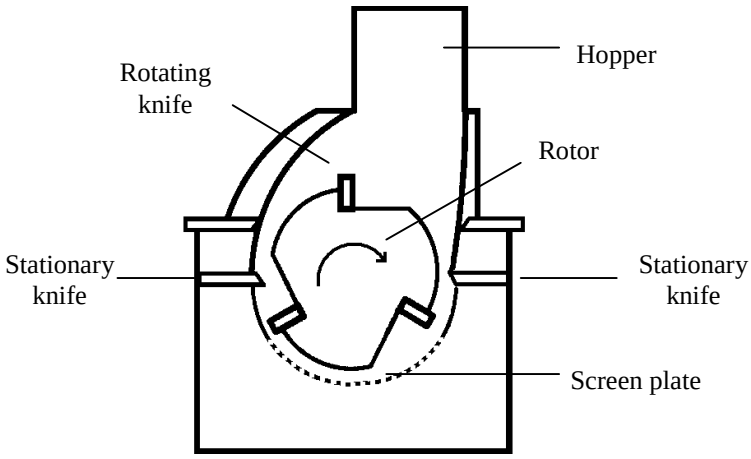


Figure 5.6. Diagram of the granulating machine.

Before granulation, the films of blends EX5PANIPOL/LDPE and EX10PANIPOL/LDPE were cut into shorter sections. During the process, the blends were collected in a bucket placed beneath the screen plate and afterwards they were properly stored in sealed plastic containers to await further experimentation.

5.4 FORMING PROCESS.

To promote the in-situ formation of polyaniline fibres in the blends, these were formed into filaments following a ram extrusion process. The instrument and accessories used are the ones used in the rheological analysis performed on the raw materials (refer to section 4.6), that is, a Davenport extrusion rheometer and a capillary die 35 mm in length and 0.8 mm in radius.

In order to determine the optimum processing conditions, different piston drive speeds and temperatures were studied.

The instrument was operated in the same way as in the rheological analysis, that is, with the capillary die securely attached to its end, the barrel (refer to fig. 4.19 in section 4.6) was heated to the required temperature. The material was charged into the barrel once the temperature of the barrel was stable. This operation was performed in increments and, to minimise air inclusions, each increment was lightly tamped down

with a metal rod before adding the next portion. Adequate amounts of the material (ca. 40 g) to fill the barrel up to about its maximum capacity were used. The piston was inserted into the barrel by manually winding it down until a slight positive pressure was shown on the recorder. To ensure that the material reached the extrusion temperature, this was extruded after being 10 min in the barrel. Lower piston drive speeds were used at the beginning of the extrusion with increments to the next levels up to the maximum selected piston drive speed. Each increment was performed after the resultant pressure at each piston drive speed reached a constant level. To allow the pressure to stabilise, the material was extruded at each selected piston drive speed for a maximum period of 10 min.

During the extrusion, the piston forced the melt at a constant rate through the capillary die. After passing through the capillary die, the melt cooled down and solidified by contact with the surrounding air. The extrudates flowed downwards aided by gravity and were collected on a metal tray where they coiled themselves and cooled down to room temperature. Extrudates approximately 1.6 mm in diameter were produced. These were properly stored in sealed plastic containers to await further examination.

As mentioned before, different piston drive speeds and temperatures were studied to determine the optimum processing conditions. The main criterion used was the final appearance of the extrudates, that is, the quality of the surface finish. During the process, it was found that there was a correlation between the quality of the extrudates and the pressure behaviour. In general, it was observed that the poorer the quality the more erratic behaviour of pressure. In some cases, despite behaving erratically, the pressure displayed a constant trend with respect to time. This behaviour, also observed during the extrusion of the samples of PANIPOL^{TM} (refer to fig. 4.20 in section 4.6), is attributed to the inhomogeneous character of the samples. In some cases, however, even this constant trend was not displayed. Some additional remarks on the processing of specific blends are presented next.

5.4.1 RAM EXTRUSION OF THE BLEND MA5PANIPOL/LDPE.

This blend was extruded at 120°C and at piston drive speeds *(V)* ranging from 0.25 to 40 mm/min. The extrudates showed a very poor surface finish with isolated inclusions of the conductive complex in the bulk. This was observed at all the extrusion speeds used. However, the quality worsened as the speed was gradually increased. The resultant pressure displayed very erratic behaviour arising from the high degree of segregation initially present in the blend, which caused irregular distribution of the components into the extruder barrel. As a result, portions of the blend, richer in SBS and passing through the capillary die generated higher levels of pressure than those generated by portions richer in PANIPOL^{TM}. It was observed, however, that the erratic behaviour of pressure was most evident at higher *V*.

5.4.2 RAM EXTRUSION OF THE BLENDS EX5PANIPOL/LDPE AND EX10PANIPOL/LDPE.

The extrusion was carried out at 120°C and at *V* ranging from 0.50 to 20 mm/min. In general, the quality of the extrudates slightly improved with respect to that of the extrudates of blend MA5PANIPOL/LDPE, indicating that these blends had a higher degree of homogeneity. However, as observed before, the quality of the extrudates decreased with the increase of *V*. Regarding the pressure, it displayed a less erratic behaviour than that observed during the extrusion of the previous blend. However, this behaved in a similar manner with respect to *V*. With respect to the content of PANIPOL^{TM} in the blends, the extrudates produced from EX5PANIPOL/LDPE were slightly better in quality than those produced from EX10PANIPOL/LDPE. To some extent, the erratic behaviour of pressure was most evident during the extrusion of blend EX10PANIPOL/LDPE.

5.4.3 RAM EXTRUSION OF THE BLENDS RM5PANIPOL/LDPE AND RM5PANIPOL/SBS.

The processing conditions were as follows:

- Blend RM5PANIPOL/LDPE. Temperatures: 120, and 150°C. Piston drive speeds: from 0.5 to 20 mm/min.

- Blend RM5PANIPOL/SBS. Temperatures: 120 and 150°C. Piston drive speeds: from 0.25 to 30.00 mm/min.

In general, the quality of the extrudates was better than that of the previous ones. Overall, the resultant pressure behaved less erratically, remaining constant at lower piston drive speeds (i.e., 0.25, 0.50 and 1.00 mm/min) and temperatures. The reason for this is that the homogeneity of the present blends, produced by using the two-roll mill machine, is considerable higher than that of the previous ones. However, the level of quality and the behaviour of pressure displayed the same tendency with respect to *V* as that displayed during the extrusion of the previous blends. With respect to the processing temperatures, it was observed that for blend RM5PANIPOL/LDPE slightly better results were obtained at 150°C. The worse results were obtained for blend RM5PANIPOL/SBS extruded at 150°C. The quality of the extrudates of blend RM5PANIPOL/LDPE processed at 150°C is comparable with that of the extrudates of blend RM5PANIPOL/SBS processed at 120°C.

5.4.4 RAM EXTRUSION OF THE BLENDS PRODUCED BY MELT MIXING.

All the blends were extruded at piston drive speeds ranging from 0.25 to 20 mm/min. The extrusion temperatures were as follows:

- Blends containing PP: 180°C.
- Blend MM5PANIPOL/SBS: 120, 130 and 140°C.
- Blend MM10PANIPOL/SBS: 120 and 150°C.
- Blend MM15PANIPOL/SBS: 100 and 110°C.
- Blend MM50PANIPOL/SBS: 100 and 120°C.

The quality of the extrudates was generally better than that of the previous ones. The resultant pressure behaved less erratically and remained constant for the majority of the piston drive speeds. This was observed particularly in the extrudates from the blends with the lowest content of the conductive complex (i.e., 5 and 10 wt % of PANIPOL^{TM}). This suggested that, compared with the previous compounding methods, the melt mixing process was best for the production of blends with a higher degree of homogeneity. As observed during the extrusion of the previous blends, the level of quality and the behaviour of pressure displayed the same tendency with respect to *V*. It

was observed that the quality of the extrudates seemed to decrease with increase of the content of PANIPOL^{TM}. Moreover, some sections of the extrudates, especially those with the highest content of the conductive complex were very brittle. This is because the blends with the highest content of the conductive complex (i.e., 15 and 50 wt. % of PANIPOL^{TM}) were not homogeneous (the reasons have been already discussed in section 5.2.4). In consequence, the erratic behaviour of pressure also increased with increase of the content of PANIPOL^{TM}. In general, concerning the blends containing SBS, better results were obtained at 120°C. The worse results were obtained for the blends MM15PANIPOL/SBS and MM50PANIPOL/SBS extruded at 100°C. The quality of the extrudates of the blends MM5PANIPOL/SBS and MM10PANIPOL/SBS processed at 120°C is comparable with that of the extrudates of the blends MM5PANIPOL/PP and MM10PANIPOL/PP.

The reader may have noticed a common phenomenon occurring during the processing of all the blends: The decline in the quality of the extrudates with the increase of the extrusion speed *(V)* and corresponding shear rate. This is attributed to elastic turbulences (i.e., the so-called “melt fracture” phenomenon) occurring in the flow of the molten blends during processing. This has also been observed by other workers (for example Brydson [175] and other researchers cited by him) during the processing of several types of commercial polymer. Similarly, these researchers also noticed that whilst smooth extrudates may be obtained at lower shear rates, above a critical shear rate the extrudate became uneven.

The mechanisms of melt fracture are not completely understood. However, there have been many theories proposed (see for example reference 175 and those ones cited therein). For example, it has been proposed that relaxation of oriented material leaving the capillary die caused buckling. In a similar way, the helical nature of many extrudates was explained as a result of a fracture propagating circumferentially round the die inlet. The origin of the fracture was believed to be the result of the stress exceeding the strength of the melt, which in turn would result from slow relaxation times relative to the deformation rates. On the other hand, a number of published experimental results suggest a fracture mechanism in which long molecular chains, adhered to the wall of the die, are stressed in an axial direction by entanglement with other molecules flowing down the capillary. Upon reaching a critical shear stress (and corresponding critical

shear rate), the drag force on the molecules would exceed the adhesive force between the molecules and the capillary wall, thus resulting in slippage. Many of these results could be explained in terms of fracture in the melt very close to the wall where the rate of shear is high. Other studies suggest that both "inlet fracture" (originating in the die entry region) and "land fracture" (originating on the die walls or lands) can occur.

Summarizing, the following factors appear to have a clear influence on the quality of the extrudates:

- The degree of homogeneity in the blends. This was in close relation with the compounding method used. As already mentioned, extrudates of better quality were obtained from the blends produced by melt mixing suggesting that, compared with the other compounding methods studied, the melt mixing process was best for the production of blends with a higher degree of homogeneity.
- Extrusion speed. Whilst smooth extrudates were obtained at lower shear rates, above a certain critical shear rate (i.e., ca. 29.53 s^{-1}, V = 2.5 mm/min) the extrudates started to become uneven. The phenomenon is attributed to melt fracture occurring in the flow of the molten blends during processing.
- Extrusion temperature. This seemed to relate to the polymer matrix in the blends. For the blends containing LDPE, better results were obtained at 150°C whereas for the blends containing SBS the optimum temperature appeared to be 120°C. Good quality extrudates were also obtained at 180°C from the blends containing PP.

5.5 MORPHOLOGICAL ANALYSIS.

This section is concerned with the morphological analysis performed on the extrudates produced from the blends (except those produced from blend MA5PANIPOL/LDPE). Throughout the text, the extrudates will be referred to in accordance with the nomenclature used for the blends from which they were produced. For the purpose of experimental convenience, the analysis was carried out using an optical microscope (Reichert Microstar 110) and concentrated on the extrudates that had a better surface appearance. For this, thin sections (ca. 100 μm thick) were cut parallel and transverse to the extrusion direction using a scalpel and a pair of tweezers with

smooth inside jaws. Short segments of the extrudates (ca. 3.0 mm long) were placed on a glass slide and between the tweezers' jaws. The sectioning was slowly performed, simultaneously applying pressure on the samples by the tweezers' jaws (fig. 5.7). The sections parallel to the extrusion direction were obtained from regions as close as possible to the centre of the specimens (fig. 5.7). A magnifying glass was used to assist in the operations above described.

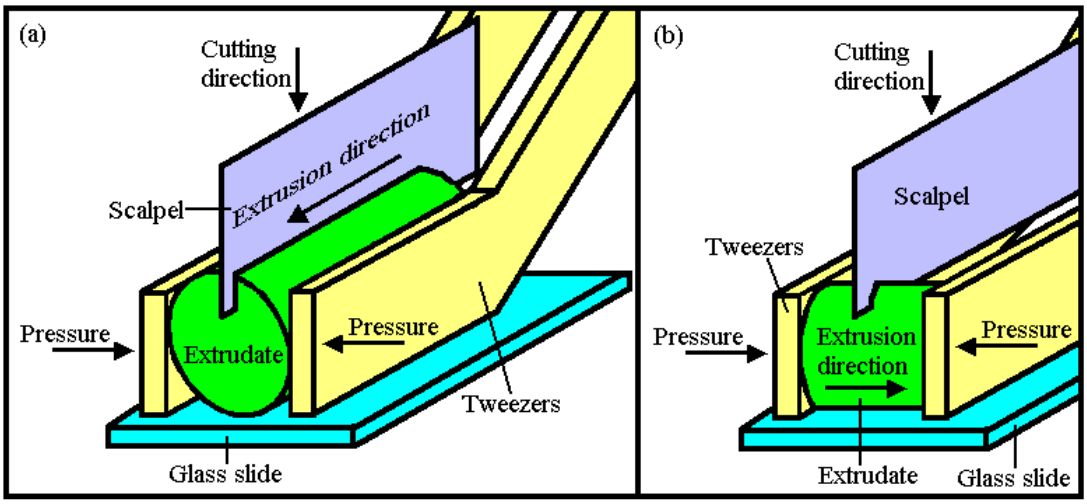


Figure 5.7. Diagram showing the sectioning of the extrudates parallel (a) and transverse (b) to the extrusion direction.

For the analysis, the sections were mounted on a glass slide and, depending on their opacity, they were examined using transmitted or incident light, or both. The results from the analysis as well as some additional comments on specific extrudates are presented in the next sections.

5.5.1 EXTRUDATES RM5PANIPOL/LDPE AND RM5PANIPOL/SBS.

From the extrudates RM5PANIPOL/LDPE, those produced at 0.5 (120°C) and 1.0 (150°C) mm/min were selected for the analysis. The analysis was performed using transmitted light and the results are presented in figure 5.8 that shows, from left to right, the longitudinal and transverse sections of each extrudate. For the longitudinal sections, the arrow in the figures represents the extrusion direction (this symbol will be used in the subsequent figures of this section unless otherwise stated). In the figures some dark regions can be seen near to the edge of the specimens (or those like the encircled areas), which are due to high opacity resulting from irregular thickness. However, mostly of the

dark regions in the illustrations correspond to the PANIPOL phase. On the other hand, the whitish regions correspond to the LDPE phase.

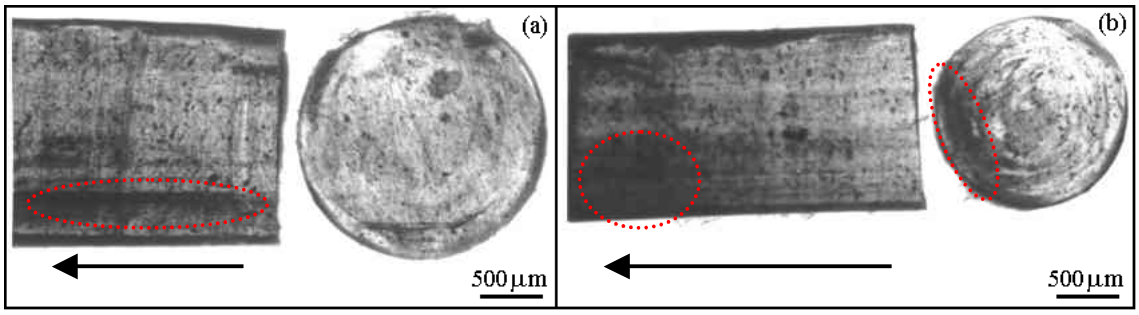


Figure 5.8. Transmitted light optical micrographs of longitudinal and transverse sections of extrudates RM5PANIPOL/LDPE produced at 120°C, 0.5 mm/min (a) and 150°C, 1.0 mm/min (b).

Comparing the longitudinal and transverse sections presented in figure 5.8, some anisotropy can be observed in the morphology. That is, the PANIPOL phase seems to be preferentially oriented in the extrusion direction. However, the presence of uniform elongated structures of PANIPOL is not clearly observed. Instead, segregated features showing some degree of orientation are abundant. The presence of irregular-shaped features is also observed. All this is better exemplified in figure 5.9 that shows the same longitudinal sections presented in fig. 5.8 but examined at a higher magnification. In figure 5.9, the areas encircled in red show sections of the specimens with features showing a certain degree of orientation. On the other hand, the regions encircled in yellow exemplify areas with irregular-shaped features. Again, the dark sections near to the edges of the specimens are the result of irregular thickness. In the figures, the lines perpendicular to the extrusion direction are due to cutting artifacts.

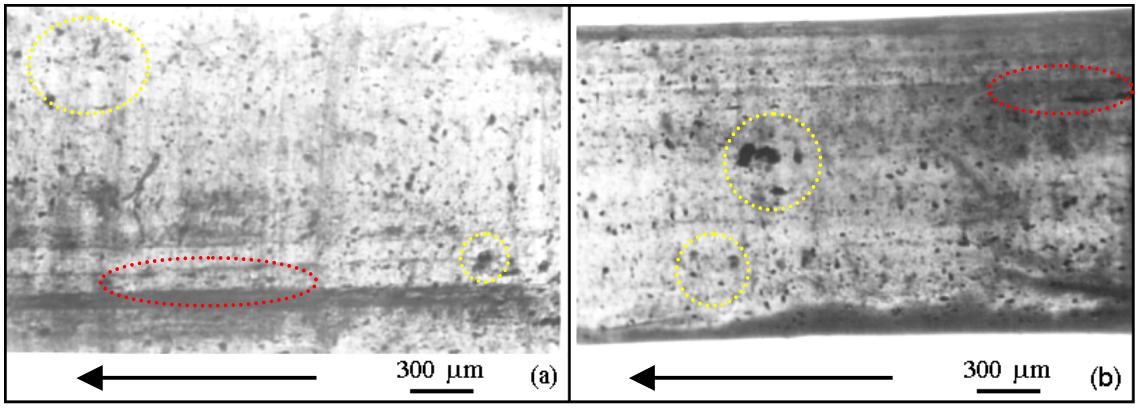


Figure 5.9. As in fig. 5.8 but at a higher magnification. Longitudinal sections.

As can be noticed from the previous figures, no significant differences are observed in the morphology of the specimens with respect to the extrusion temperature.

With respect to the extrudates RM5PANIPOL/SBS, the analysis was carried out on the extrudates produced at 0.5 mm/min. The analysis was performed using transmitted light and the results are presented in figures 5.10 and 5.11. As in the previous figures, irregularities in the thickness of the sections (especially near to the edge of the longitudinal sections, fig. 5.10a) resulted in some areas showing a high degree of opacity, causing them to appear as dark regions in the photographs. Some of these areas are encircled in fig. 5.10. Most of the dark regions, however, correspond to the PANIPOL phase. On the other hand, the whitish regions represent the SBS phase.

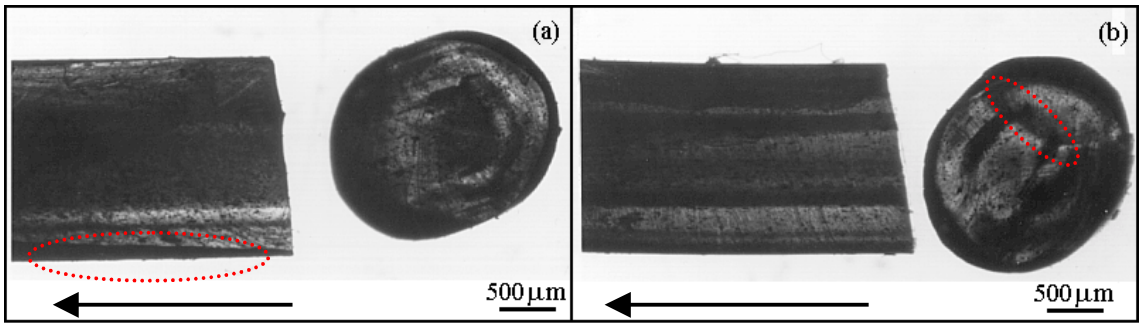


Figure 5.10. Transmitted light optical micrographs of longitudinal and transverse sections of extrudates RM5PANIPOL/SBS produced at 0.5 mm/min and 120 (a) and 150°C (b).

As in the previous extrudates, by comparing the longitudinal and transverse sections presented in fig. 5.10, it is possible to notice anisotropy in the observed morphology. This is observed better in figure 5.11 that corresponds to the longitudinal sections of the extrudates presented in fig. 5.10, but examined at a higher magnification.

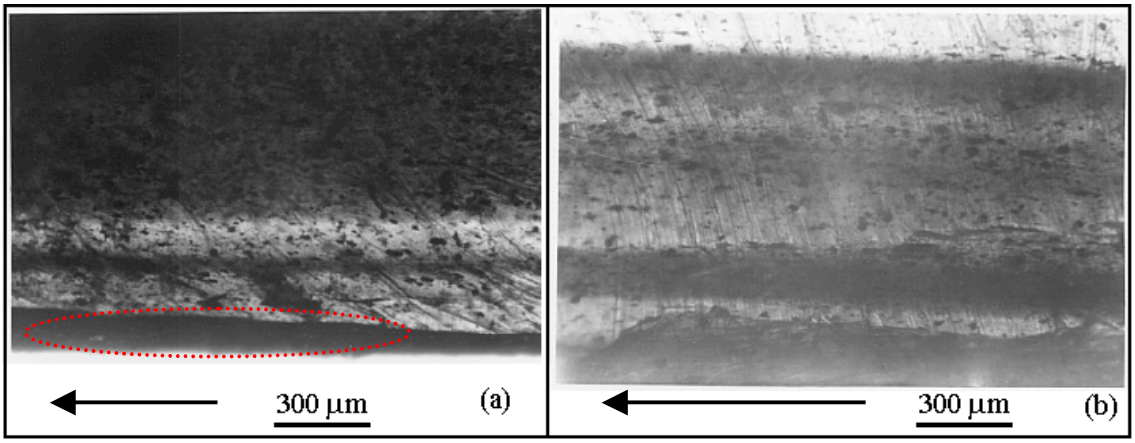


Figure 5.11. As in fig. 5.10 but at a higher magnification. Longitudinal sections.

In figure 5.11, it can be noticed that the PANIPOL phase is preferentially oriented in the extrusion direction. However, as in the extrudates RM5PANIPOL/LDPE, the presence of uniform elongated structures of PANIPOL is not clearly observed. The presence of features orientated in the extrusion direction are, however, more abundant in the extrudates RM5PANIPOL/SBS than in the previous ones. Considering that these extrudates have the same content of PANIPOL and comparable processing history, these observations suggest that the SBS, apparently, would best favour the in-situ formation of polyaniline fibres in the extrudates, providing that the processing conditions and composition are successfully optimised. Again, the dark sections near to the edges of the specimens (as the one encircled in fig. 5.11a) are the result of irregular thickness. On the other hand, the lines perpendicular or oblique to the extrusion direction are cutting artifacts. As in the previous extrudates, no significant differences are observed in the morphology of the specimens with respect to the extrusion temperature.

5.5.2 EXTRUDATES EX5PANIPOL/LDPE AND EX10PANIPOL/LDPE.

Extrudates produced at 0.5 mm/min were selected for the analysis. These were examined using transmitted light and the results are presented in figures 5.12 and 5.13. As in the previous specimens, irregularities in the thickness resulted in some opaque areas (as the ones encircled in red in the figures). However, most of the observed dark features correspond to the PANIPOL phase. On the other hand, the whitish regions correspond to the LDPE phase. As in the previous extrudates, even when the PANIPOL phase in EX5PANIPOL/LDPE (figs. 5.12a and 5.13) is preferentially oriented in the extrusion direction, the presence of uniform elongated structures is not clearly observed. Instead, segregated features with some degree of orientation are most evident. For example, notice the features indicated by the white arrows in fig. 5.13. Regarding the extrudate EX10PANIPOL/LDPE (fig. 5.12b), two types of morphologies are clearly observed, one in which the PANIPOL phase seems to be arranged as radially expanding concentric rings (transverse section), and another one with the already observed conductive phase oriented in the extrusion direction (longitudinal section). This morphology, also observed in some of the previous extrudates (e.g.,

RM5PANIPOL/LDPE, fig. 5.8b), suggests that during the forming process, the PANIPOL phase is arranged in radially expanding concentric tubular-like configurations oriented in the extrusion direction. The observed morphology thus suggests that the elongated features in the longitudinal section are the edges of longitudinally sectioned tubular structures, whereas the rings in the transverse section are the rims of these structures transversely sectioned (fig. 5.14).

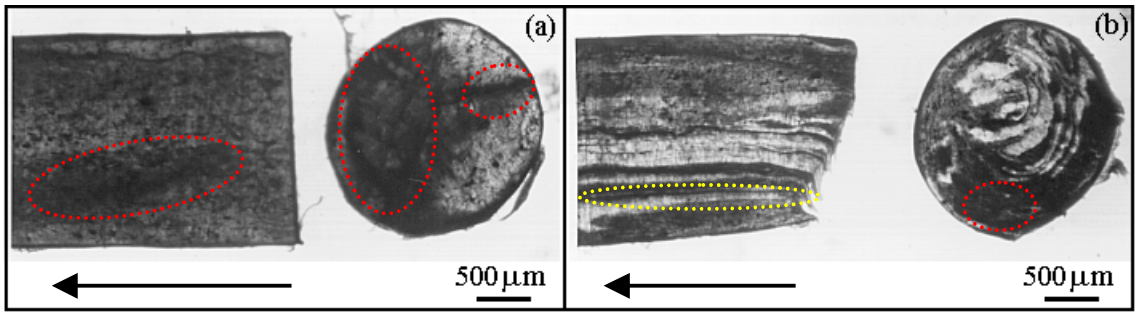


Figure 5.12. Transmitted light optical micrographs of longitudinal and transverse sections of extrudates EX5PANIPOL/LDPE (a) and EX10PANIPOL/LDPE (b) produced at 120°C and 0.5 mm/min.

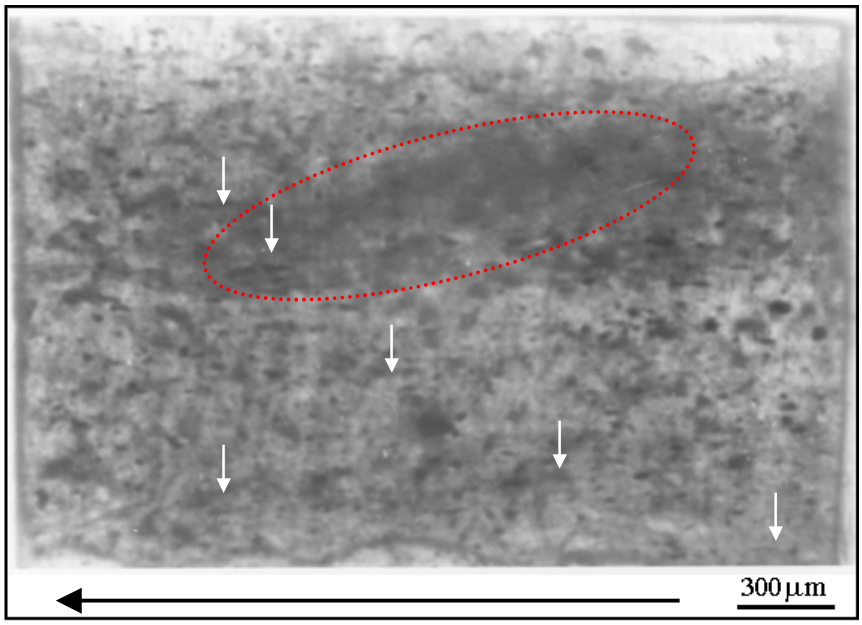


Figure 5.13. As in fig. 5.12a but at a higher magnification. Longitudinal section.

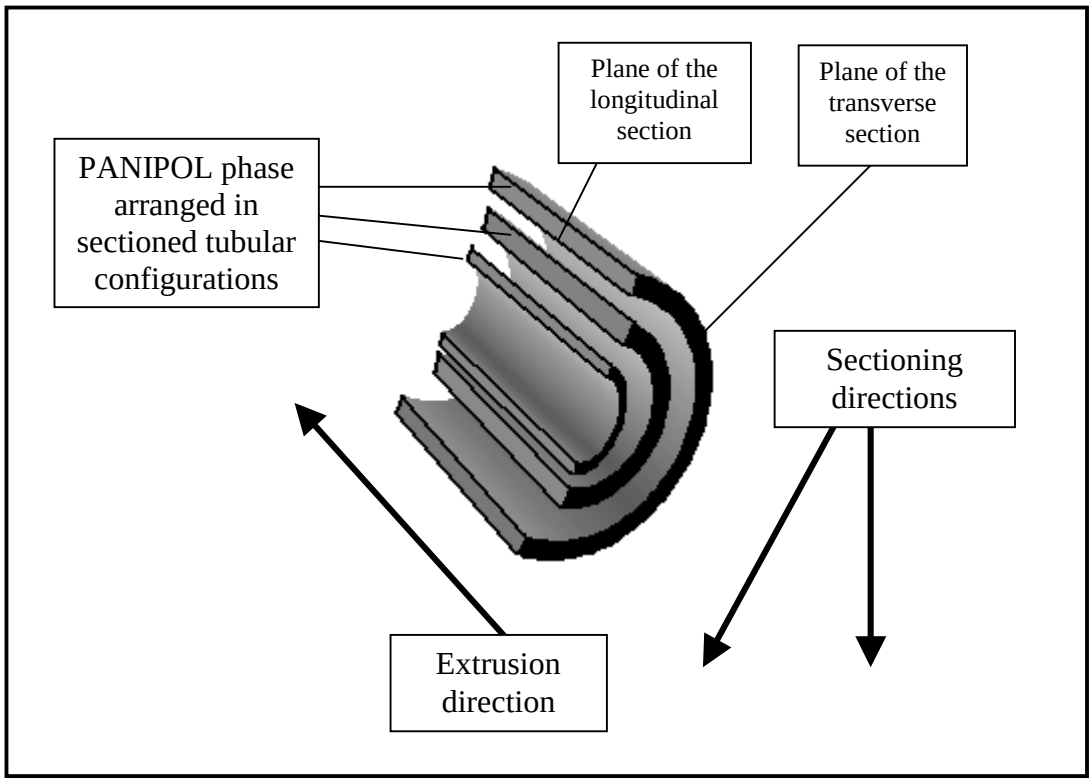


Figure 5.14. Schematic representation of the PANIPOL phase in the extrudates, arranged in concentric tubular-like configurations as a result of the forming process.

As can be seen, the oriented structures in the extrusion direction are more abundant in EX10PANIPOL/LDPE than in EX5PANIPOL/LDPE. Moreover, oriented features with a high degree of uniformity can be observed in EX10PANIPOL/LDPE (notice the areas encircled in yellow in fig. 5.12b). All this is the result of a higher content of PANIPOL in the extrudate. In the micrographs, some lines perpendicular or oblique to the extrusion direction may be noticed. Again, these are cutting artifacts.

5.5.3 EXTRUDATES MMPANIPOL/SBS.

Extrudates, respectively produced at 1.25 mm/min and 120°C (MM10PANIPOL/SBS and MM50PANIPOL/SBS) and 110°C (MM15PANIPOL/SBS), were selected for the analysis. MM10PANIPOL/SBS and MM15PANIPOL/SBS were examined using transmitted light, whereas for MM50PANIPOL/SBS the analysis was performed using incident light. The results are presented in figures 5.15 to 5.18. As can be noticed, some areas in some of the photographs are blurred (or extremely bright, fig. 5.18) indicating that those areas in the sections (some of them encircled in red) were out

of focus during the analysis. Again, this is the result of irregular thickness. As in the previous micrographs, cutting artefacts are also observed.

Observing the longitudinal and transverse sections of MM10PANIPOL/SBS (fig. 5.15), a similar morphology to that observed in EX10PANIPOL/LDPE (fig. 5.12b) can be noticed. The PANIPOL phase is preferentially oriented in the extrusion direction (longitudinal section) and arranged as concentric rings in the transverse section. This suggests again that, during the forming process, the PANIPOL phase is arranged in radially expanding concentric tubular-like configurations oriented in the extrusion direction. However, it is interesting to notice that the longitudinal section in figure 5.15 also shows elongated features, with a considerable degree of uniformity, oriented in the extrusion direction and embedded in less dark cloud-like regions (e.g., notice the areas encircled in yellow). In addition, some isolated elongated features (indicated by the arrows in yellow) can also be observed.

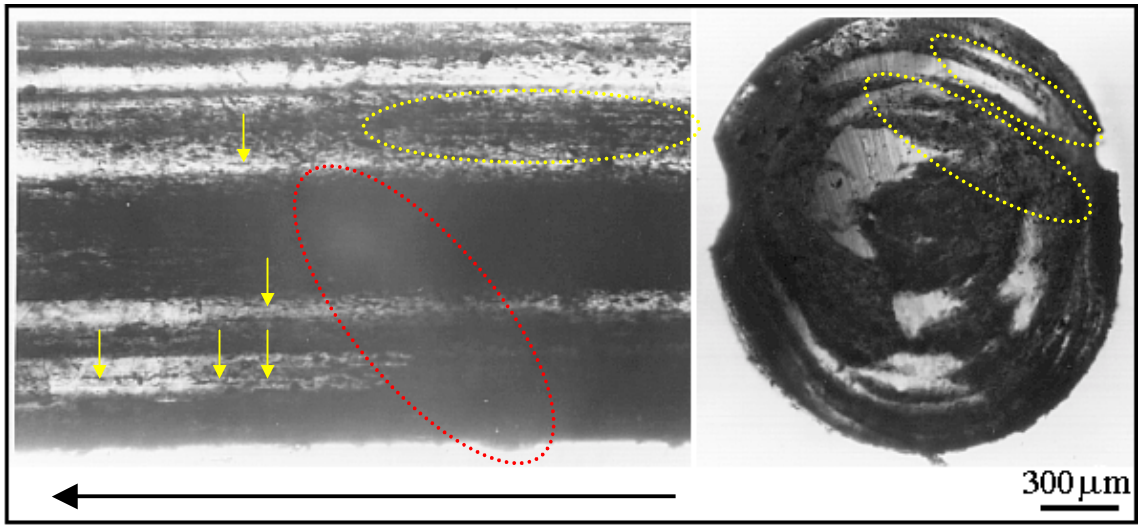


Figure 5.15. Transmitted light optical micrographs of longitudinal and transverse sections of extrudate MM10PANIPOL/SBS produced at 120°C and 1.25 mm/min.

Regarding the transverse section of MM10PANIPOL/SBS, this shows a similar morphology of cloud-like regions. However, contrasting with the elongated features observed in the longitudinal section, these regions are abundant in small round features (e.g., notice the small dark dots in the areas encircled in yellow). This morphology, also observed in the extrudates RM5PANIPOL/SBS (fig. 5.10), resembles that observed in the granules of PANIPOL (refer to fig. 4.33d in section 4.8.1) in which the polyaniline particles (the dark features) are surrounded by a continuous phase (the Zn salt of DBS,

possibly together with other kind of additives). It is therefore believed that the elongated features oriented in the extrusion direction may correspond to clusters of polyaniline particles deformed into elongated domains (perhaps fibres) by the action of the SBS. On the other hand, the small round features observed in the transverse section may correspond to the ends of the elongated domains of polyaniline. The less dark cloud-like regions surrounding the features in both the longitudinal and transverse sections, may correspond to the Zn salt of DBS (possibly together with other kind of additives).

The presence of elongated domains of polyaniline in the extrusion direction is also evident in the extrudate MM15PANIPOL/SBS (fig. 5.16). In figure 5.16, the elongated features are more abundant than in MM10PANIPOL/SBS due to the higher content of PANIPOL.

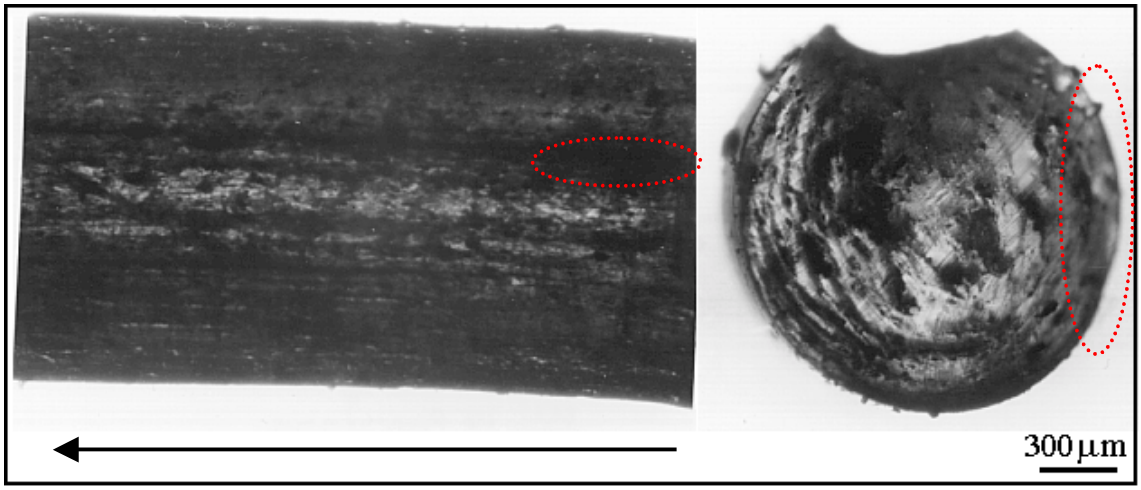


Figure 5.16. Transmitted light optical micrographs of longitudinal and transverse sections of extrudate MM15PANIPOL/SBS produced at 110°C and 1.25 mm/min.

As observed in the previous extrudates, the PANIPOL phase tended to arrange in radially expanding concentric tubular-like configurations oriented in the extrusion direction. Figure 5.17, which corresponds to the same longitudinal section showed in fig. 5.16 but examined at a higher magnification, shows better the presence of elongated domains of polyaniline displaying a reasonable degree of uniformity. A high degree of continuity can also be observed in the features (e.g., notice that indicated by the yellow arrows). However, whether this is genuine is arguable as the sections were considerable thick for the analysis, and the observed continuity may be a visual effect due to the overlapping of various elongated features. As in the previous extrudates, some irregular-

shaped domains of polyaniline were also observed in the longitudinal section (some of them indicated by the arrows in red).

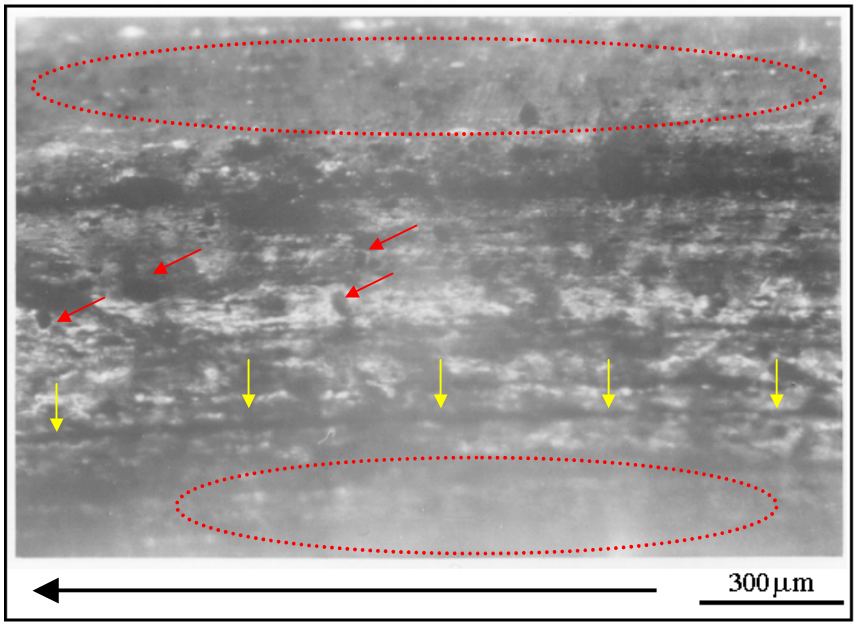


Figure 5.17. Transmitted light optical micrograph of the longitudinal section of extrudate MM15PANIPOL/SBS produced at 110°C and 1.25 mm/min.

With respect to the extrudate MM50PANIPOL/SBS, the analysis was performed using incident light because the sections were extremely opaque. This, mostly due to the higher content of PANIPOL in the extrudate (50 wt.%), also impeded, to some extent, the production of proper sections as the specimens were very brittle. Nevertheless, some morphological information (topographical) was obtained and the results are presented in figure 5.18. By comparing the longitudinal and transverse sections presented in the figure, anisotropy can be observed in the morphology of the extrudate. For example, notice the elongated features (some of them indicated by yellow arrows in the longitudinal section) aligned parallel to the extrusion direction and absent in the transverse section. Through this analysis, it is difficult to be certain about the nature of the observed features, which look like micro-cracks on the surface of the longitudinal section. However, considering the morphologies previously observed in this section, it is very likely that they resulted from the orientation of the polyaniline phase in the extrusion direction.

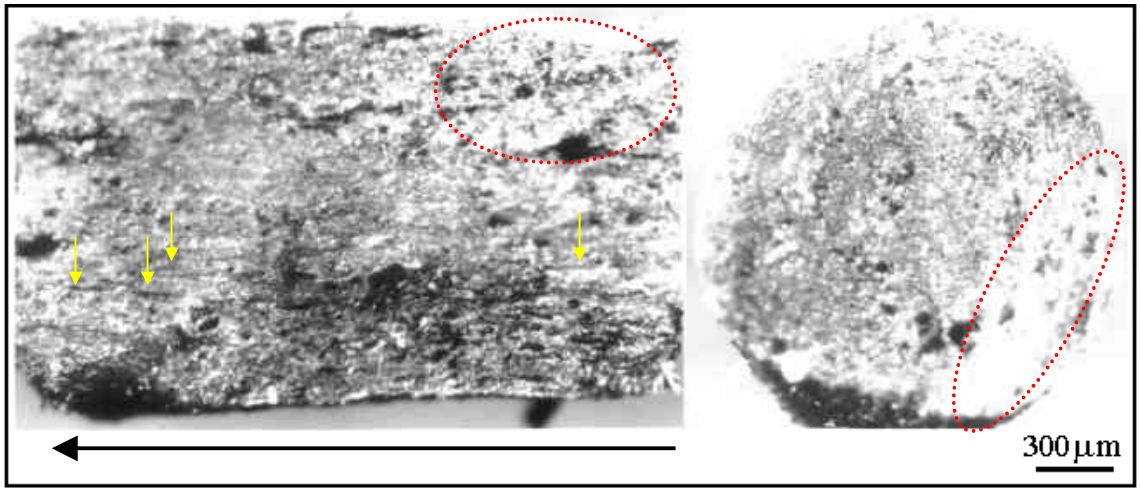


Figure 5.18. Incident light optical micrographs of longitudinal and transverse sections of extrudate MM50PANIPOL/SBS produced at 120°C and 1.25 mm/min.

5.5.4 EXTRUDATES MMPANIPOL/PP.

Extrudates, respectively produced at 0.50 (MM5PANIPOL/PP) and 0.25 (MM15PANIPOL/PP and MM50PANIPOL/PP) mm/min, were selected for the analysis. MM5PANIPOL/PP was examined using both transmitted and incident light, whereas MM15PANIPOL/PP and MM50PANIPOL/PP were examined using transmitted and incident light, respectively. The results are presented in figures 5.19 to 5.21. In the transmitted light micrograph (fig. 5.20), the PANIPOL phase corresponds to the dark regions, whereas the whitish regions correspond to the PP phase. Cutting artifacts can also be observed corresponding to the lines perpendicular to the extrusion direction (or oblique) and the straight ones in the transverse sections.

With respect to the extrudate MM5PANIPOL/PP (fig. 5.19), the longitudinal section shows two regions of interest. A very thick one (encircled in red), which did not allow the light to pass through and from which topographical information was only obtained; and another one (encircled in yellow), which was thinner and allowed an examination through the bulk of the specimen. As observed, the morphology displayed in the first of these regions is, to some extent, similar to that observed in a previous extrudate (i.e., fig. 5.18). For example, notice some very fine lines (looking like micro-cracks) parallel to the extrusion direction (indicated by the red arrows). On the other hand, in those areas in which the light could pass through, some dark features (the polyaniline phase), elongated and aligned parallel to the extrusion direction, can also be

observed. Although these features do not seem to show continuity, these suggest that the polyaniline phase is preferentially oriented in the extrusion direction as a result of the action of the PP phase. This concept is reinforced by the morphology observed in the area encircled in red. Regarding the transverse section, the specimen was too thick and only irregular-shaped domains of polyaniline were observed on the surface of the specimen. Some of them, also present in the longitudinal section, are indicated by the white arrows in fig. 5.19.

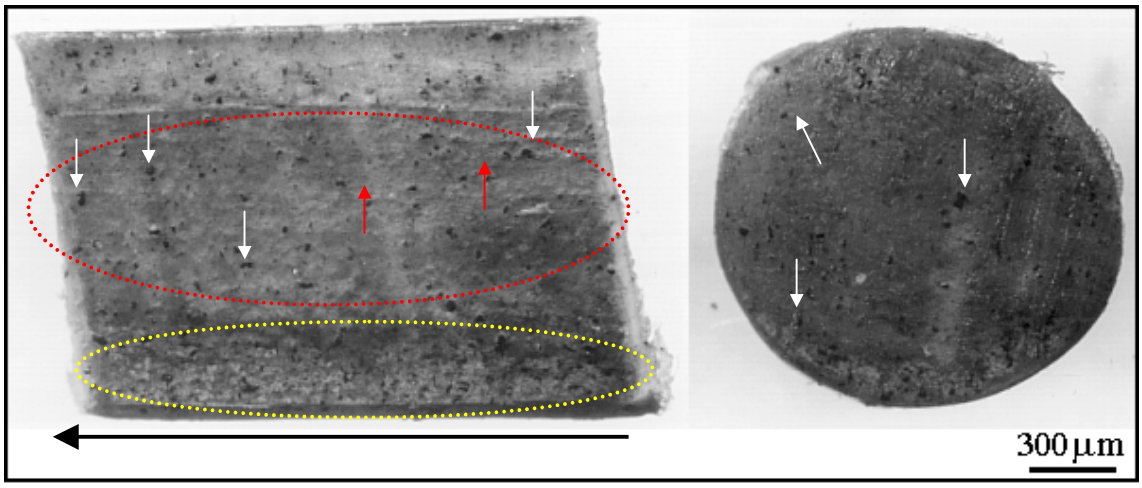


Figure 5.19. Optical micrographs of longitudinal and transverse sections of extrudate MM5PANIPOL/PP produced at 0.50 mm/min and 180°C, and examined using incident and transmitted light.

The presence of elongated domains of polyaniline in the extrusion direction is also evident in the extrudate MM15PANIPOL/PP (fig. 5.20). In figure 5.20, the elongated features (some of them indicated by red arrows) seem to be more abundant than in MM5PANIPOL/PP. This is expected, as the content of PANIPOL in MM15PANIPOL/PP is higher. However, compared with MM15PANIPOL/SBS (fig. 5.16), the elongated domains of polyaniline in MM15PANIPOL/PP seem to be less uniform and barely show any sign of continuity. Once again, considering that these extrudates have the same content of PANIPOL and comparable processing history (i.e., same compounding method and low extrusion speeds), these observations suggest that the SBS, apparently, would best favour the in-situ formation of polyaniline fibres in the extrudates. As in previous extrudates, some irregular-shaped domains of polyaniline (indicated by yellow arrows) were also observed.

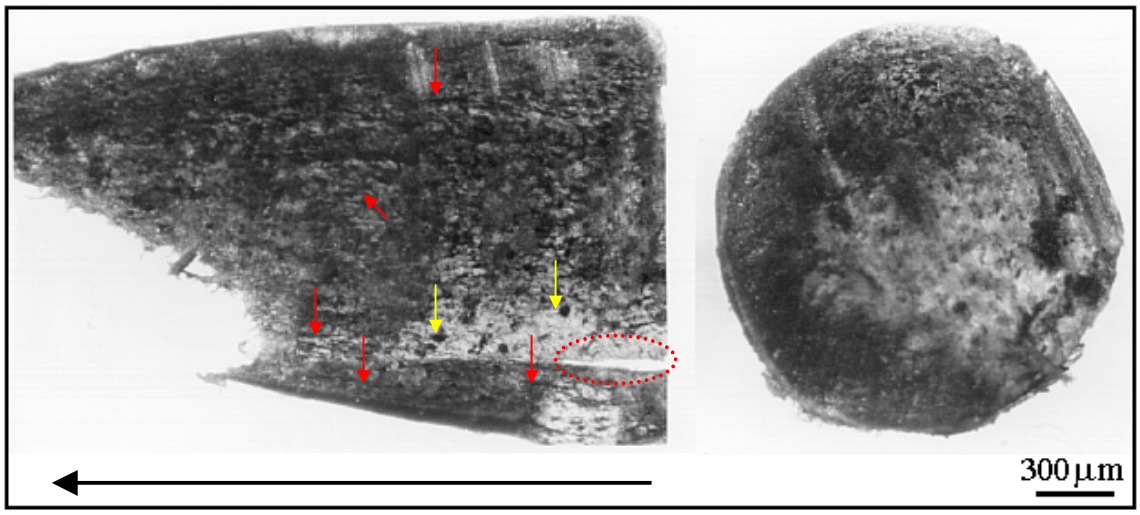


Figure 5.20. Optical micrographs of longitudinal and transverse sections of extrudate MM15PANIPOL/PP produced at 0.25 mm/min and 180°C, and examined using transmitted light.

Concerning the transverse section of MM15PANIPOL/PP, the specimen was extremely thick and mostly dark irregular-shaped features (not necessarily corresponding to the PANIPOL phase) were observed. As in previous extrudates (e.g., figs. 5.15 and 5.16), the less dark cloud-like regions surrounding the features in the longitudinal section, may correspond to the Zn salt of DBS, possibly together with other kind of additives. In figure 5.20, the white wedge-shaped area encircled in red is an incision accidentally made on the specimen that caused the observed small section to detach partially and misalign with respect to the rest of the specimen.

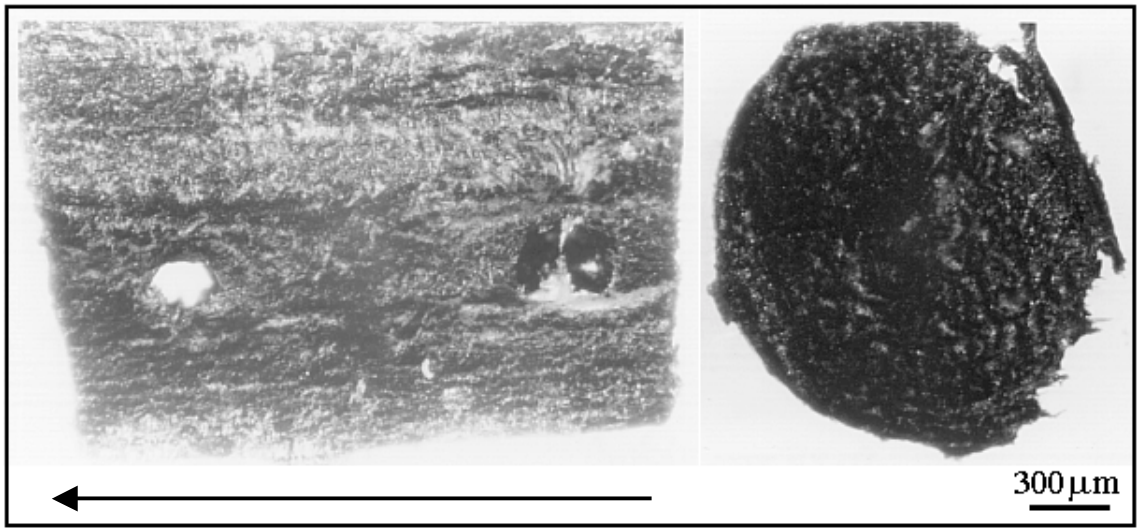


Figure 5.21. Optical micrographs of longitudinal and transverse sections of extrudate MM50PANIPOL/PP produced at 0.25 mm/min and 180°C, and examined using incident light.

Regarding the extrudate MM50PANIPOL/PP (fig. 5.21), the sections were extremely opaque mainly because of the high content of PANIPOL (50 wt.%) in the specimens. However, as in the longitudinal section of MM50PANIPOL/SBS (fig. 5.18), some elongated features aligned parallel to the extrusion direction could be observed. Again, it is very likely that these features resulted from the orientation of the polyaniline phase in the extrusion direction. The transverse section did not provide any relevant morphological information because it was extremely dark and opaque.

In summary, the micrographs presented in this section may have not been entirely clear, perhaps because the technique used to produce the sections for the analysis was not accurate. However, they provided a valuable first insight of the morphology of the extrudates, and at the same time, assisted in the process of searching for the most suitable polymer matrix to use in this work. Accordingly, the following main points can be established as a result of the present analysis:

- The PANIPOL phase preferentially oriented in the extrusion direction during the forming process.
- The polyaniline phase, deformed into elongated domains by the carrying action of the polymer matrix, preferentially oriented in the extrusion direction. These structures displayed a reasonable degree of uniformity, and in some cases, signs of continuity were also observed.
- The presence of uniform and continuous elongated domains of polyaniline was most evident in extrudates containing 15 wt.% of PANIPOL and in those in which the polymer matrix was SBS.
- The extrusion temperature did not affect (apparently) the morphology of the examined extrudates.

5.6 CONCLUSIONS.

Compared with the other compounding methods studied, melt mixing in a batch mixer was the most favourable technique because the temperatures required to process a specific polymer matrix are lower, which broadens the number of possible systems with which experimentation could be performed without exposing PANIPOL to temperatures

that may put at risk its electro-conductive performance. Moreover, the batch mixer offers the possibility of varying the speed of the rotors, which assists in the optimisation of the process. The special geometry of the rotors also provides better dispersion and mixing action, which favour the production of blends with a higher degree of homogeneity. In addition, the final composition of the blends is better controlled because the possibilities of losing material during the feed and mixing stages are minimised because the compounding takes place in an enclosed space, which also promotes a cleaner process.

The degree of homogeneity in the blends together with the extrusion speed and temperature had a clear influence on the quality of the extrudates. In general, extrudates of better quality were obtained from blends with a higher degree of homogeneity and at extrusion speeds below 2.5 mm/min. Above this speed, the extrudates started to become uneven due to melt fracture occurring in the flow of the molten blends during processing. The optimum extrusion temperature seemed to be related to the polymer matrix in the blends. For the blends containing LDPE, better results were obtained at 150°C whereas for the blends containing SBS the optimum temperature appeared to be 120°C. Good quality extrudates were also obtained at 180°C from the blends containing PP.

The results from the morphological analysis performed on the extrudates revealed that the polyaniline phase, deformed into elongated domains by the carrying action of the polymer matrix, was preferentially oriented in the extrusion direction. These structures displayed a reasonable degree of uniformity, and in some cases, signs of continuity were also observed. The presence of uniform and continuous elongated domains of polyaniline was most evident in extrudates containing 15 wt.% of PANIPOL and in those in which the polymer matrix was SBS. On the other hand, the extrusion temperature did not appear to affect the morphology of the examined extrudates.