"Every great advance in science has issued from a new audacity of imagination".

***John Dewey** (1859–1952), U.S. philosopher and educator. The Quest for Certainty.*

CHAPTER 7

FORMING: RAM EXTRUSION OF PANIPOL™-SBS BLENDS

7.1 INTRODUCTION.

Following the production and characterisation of the PANIPOL^{TM}-SBS blends, which has been the topic of chapter 6, this chapter is about the forming process to which the blends were subjected in order to promote the in-situ formation of polyaniline fibres. As has already been seen in chapter 5, earlier experimentation with an extrusion rheometer established the feasibility of producing in-situ continuous elongated domains of polyaniline highly oriented in the extrusion direction (section 5.5). Additionally, it was observed that, in general, extrudates of superior quality were produced at extrusion speeds below 2.5 mm/min (section 5.4.4). Consequently, the processing of the blends was performed, using the same instrument, at a fixed extrusion speed lower than that previously pointed out. This, together with other relevant information, is indicated here in the pertinent section. Based on the results from the preliminary morphological analysis (section 5.5.3), the morphology of the extrudates was analysed in more detail following a combination of different microscopy techniques. These, as well as the results from the analysis, are also detailed here. This chapter also includes a section dedicated to the evaluation of the level of conductivity in the extruded blends. Information on the technique employed, followed by the results, is available in section 7.4. Finally, general conclusions are presented at the end of the chapter.

7.2 FORMING PROCESS.

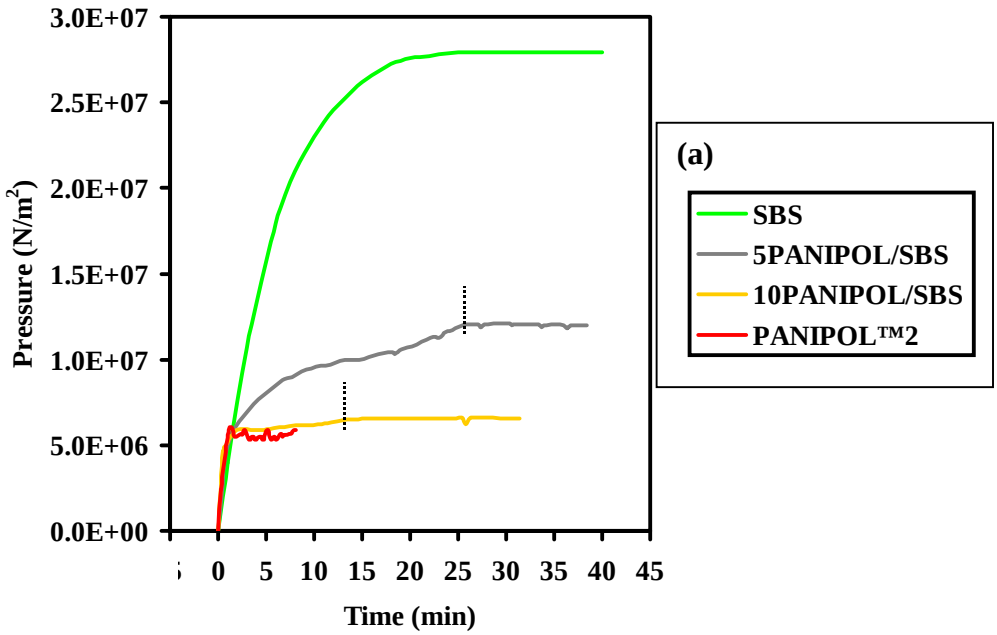
The processing of each blend was executed by ram extrusion with the same Davenport extrusion rheometer and capillary die (L = 35 mm, r = 0.8 mm) used for the rheological analysis (section 4.6) and preliminary experimentation (section 5.4). The blends were formed into filaments at an extrusion speed of 1.25 mm/min. A temperature of 120°C was selected for the processing as previous experiments indicated that extrudates of improved quality were produced at this temperature (refer to section 5.4.4). The processing was performed in accordance with the procedure described in section 5.4. Before the processing, the blends were granulated using the granulating machine (USI-Cumberland, Model 5X7) described in section 5.3. During the extrusion, a transducer situated near to the entrance of the capillary (see fig. 4.19 in section 4.6) sensed the pressure of the melt so that the behaviour of pressure with respect to time for

each blend was registered. Extrudates approximately 1.6 mm in diameter were produced, which were properly stored to await further characterisation.

The behaviour of pressure with respect to time for each blend is presented in figure 7.1 (note the difference in the pressure-axes scale). The variation of pressure with time for the SBS and conductive complex, processed at the same extrusion conditions to those used for the processing of the blends, is also depicted in fig. 7.1 for comparison purposes.

As can be noticed, during the extrusion of the blends the pressure did not display the characteristic behaviour observed during the extrusion of a homogeneous material (e.g., SBS), that is, a gradual increase with time up to a level at which it remains constant. On the contrary, the pressure gradually increased up to a certain value and then started to display erratic behaviour. This behaviour suggests that the blends were not completely homogeneous. Additionally, fig. 7.1 also indicates that, in general, the erratic behaviour of pressure appeared to increase with an increase of PANIPOL™ content in the blends, which may suggests that the homogeneity degree of the blends decreased in the same manner. The latter trend may be due to the fact that batches of the same size were used during the compounding regardless of the blends' composition. As explained before, the optimum batch size should increase with an increase of the content of conductive complex in the blends (refer to Table 6.3 in section 6.2). Since the difference between the batch size actually used and the optimum batch size increased with the increase of PANIPOL™ content, the level of shearing occurring in the melt required to disperse the conductive complex within the SBS phase also decreased in the same fashion, which in turn resulted in a reduction of homogeneity in the blends.

On the other hand, it should be noted that the higher the content of PANIPOL™ the more similar the blend is to the conductive complex. In consequence, it is possible that the increment in the erratic behaviour of pressure was also due to the increase of the content of conductive complex in the blends. As can be seen in fig. 7.1, the behaviour of pressure during the extrusion of PANIPOL™ was considerably erratic. Consequently, it is very likely that the blends "inherited" this behaviour, which was more evident at higher PANIPOL™ contents.



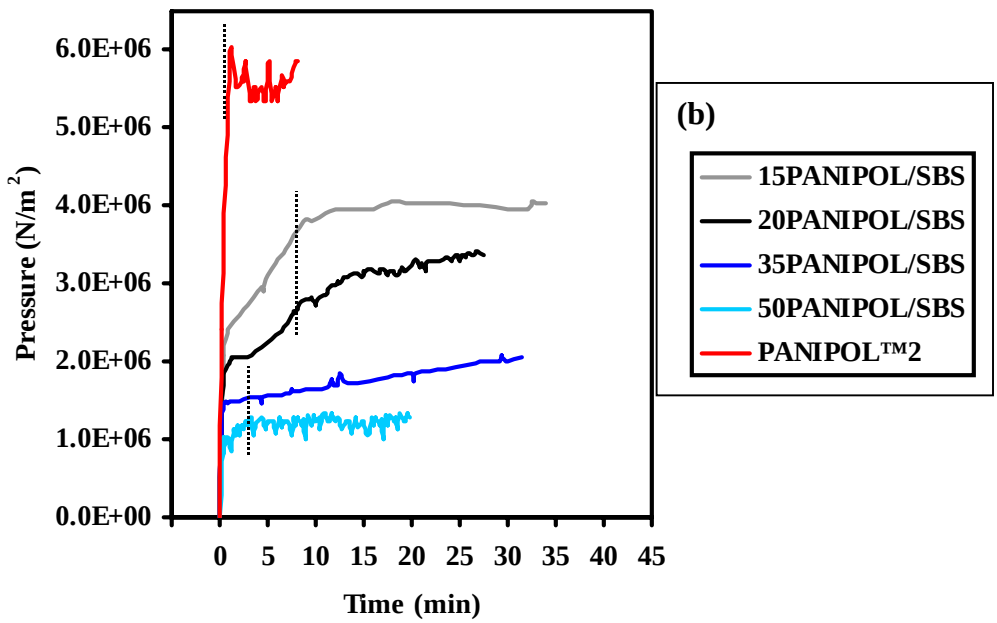


Figure 7.1. Variation of pressure with time during the extrusion of the blends PANIPOL/SBS, SBS and PANIPOL™2 at 1.25 mm/min and 120°C. The values to the right of the broken lines were used in the calculations of the apparent viscosity.

The erratic behaviour of pressure observed during the extrusion of the blends could be explained as follows: As the blends are not homogeneous and since the PANIPOL™ is considerably less viscous than the SBS, on emerging from the capillary, portions of the fluid melt rich in PANIPOL™, would generate a sudden drop in the

level of pressure sensed by the transducer. On the other hand, portions of the blend rich in SBS would generate a sudden increase in the pressure. As the melt was constantly flowing through the capillary, it generated the intermittent effect observed in the pressure-time curves.

With respect to the extrudates' exterior appearance, it was observed that the quality of the surface finish improved considerably in comparison with that observed in the extrudates produced during the preliminary experimentation (refer to section 5.4.4). Their surface was smoother and showed a glossy texture. This is because the compounding method was modified in such a way that it enhanced the level of homogeneity in the blends (refer to section 6.2). The latter, as has already been explained in section 5.4, appears to have a clear influence on the quality of the extrudates.

It was observed, however, that although the quality of the surface finish was enhanced, the extrudates of blends 35PANIPOL/SBS and 50PANIPOL/SBS presented sections that were brittle. This was observed especially in the extrudates of the latter blend, in which the brittle sections were more abundant. What is more, it was not even possible to obtain a continuous piece of filament of regular length. The extrudate appeared to be divided into short sections of about 3-5 mm long, which were connected by very weak ring-like features, which in turn caused the sections to break very easily during handling. It is believed that the ring-like "connectors" correspond to portions of the flowing melt that were rich in PANIPOL^{TM}, which generated the sudden drops in the level of pressure observed in fig. 7.1b. On the other hand, the opposite should apply to the "connected sections", which should correspond to regions rich in SBS.

This phenomenon was also observed, although to a larger extent, during previous experiments carried out using comparable processing conditions and blend's composition (refer to section 5.4.4). As has already been discussed, the phenomenon observed is characteristic of melt fracture occurring in the flow of the melt during processing. Since at a fixed extrusion speed and temperature, melt fracture was most evident at higher concentrations of conductive complex and, assuming that the degree of homogeneity of the blends decreased in the same fashion; this implies that its occurrence should be a function, not only of the extrusion speed, but also of the blends'

homogeneity. In other words, the less homogeneous the blends are, the more possibilities for melt fracture to occur.

A corollary to the above observations is that in order to obtain extrudates of improved quality, the blends' homogeneity degree must be as high as possible, and for this, the correct batch size must be used in their preparation.

It is interesting to notice, however, that contrary to what was expected, the level of pressure generated during the extrusion of the PANIPOL^{TM} pellets was higher than that generated by the blends with 15, 20, 35 and 50 wt.% of conductive complex processed under the same conditions (fig. 7.1b), which implies that the pellets are more viscous than some of their blends. This effect is better illustrated in fig. 7.2, which shows the variation of the apparent viscosity with respect to the PANIPOL^{TM} content. The data presented in the figure was calculated using the Poiseuille Law for capillary flow (that is, *Eq. 4.4* in section 4.6), the dimension of the capillary die and piston ram (19.05 mm in diameter), the piston drive speed (V = 1.25 mm/min) and the maximum level of pressure generated during the extrusion of each material. An average value was used when the pressure displayed erratic behaviour. For each case, this was calculated considering all the values to the right of the broken lines shown in fig. 7.1. The apparent viscosity of the pellets of PANIPOL^{TM}, together with that of the SBS are depicted in fig. 7.2 as 100 and 0 wt.% of conductive complex, respectively.

As commented above, one would expect that the PANIPOL^{TM} pellets were less viscous than their corresponding blends. The level of viscosity that one would expect would be around the value indicated in figure 7.2, that is, the red circle at 100 wt.% of PANIPOL^{TM} content. This value was calculated using a power law equation (*Eq. 7.1*), which described the behaviour of the experimental data with a considerably high degree of accuracy (hence the high value of the squared correlation coefficient, r^2, of 0.9982).

$$\textit{Apparent viscosity} = (48165)(\textit{PANIPOL}^{TM}\ \textit{content})^{-1.0011} \ldots\ldots\ldots \textit{Eq. 7.1.}$$

The situation depicted in fig. 7.2 is due to the fact that the blends were subjected to two processing cycles (compounding and forming), whereas the pellets of PANIPOL^{TM} were subjected to only one (forming). Such an explanation is supported by the fact that the shearing history (among other factors) of the polymer melt affects its

viscous flow during processing. As the flow occurs when the macromolecular chains of the polymer slide past each other, the ease of flow will depend on the mobility of the molecular chains and the forces or entanglements holding them together. Since both the SBS and PANIPOL™ composing the blends were pre-sheared during the compounding, it is very likely that the reason for some of the blends being less viscous than the pellets of PANIPOL™ themselves was due to a macromolecular chain disentanglement effect occurring in both the SBS and PANIPOL™. Additionally, it should be considered that the blends were also subjected to a size reduction process in a granulating machine in which they were exposed to very high levels of impact and shear, which should have contributed to the occurrences illustrated in fig. 7.2.

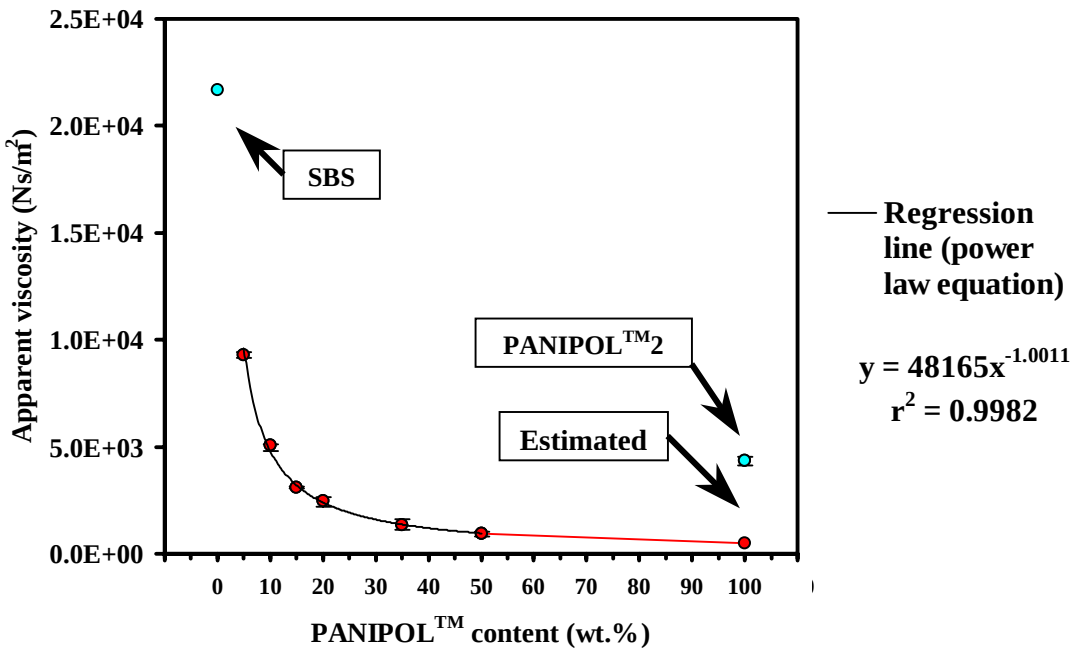


Figure 7.2. Variation of the apparent viscosity of the blends with respect to the PANIPOL™ content.

As has been seen in section 4.8.2, the morphology of the pellets of PANIPOL™ consisted of globular shaped agglomerates formed of primary doped PANI nanoparticles, which may be composed of highly entangled macromolecular chains of doped PANI. Therefore, it is possible that chain disentanglement occurred upon shearing during the processing stages. In consequence, it may also be possible that the chains of the DBSA-PANI complex were oriented in the direction of the extrusion during the forming process.

7.3 MORPHOLOGICAL ANALYSIS.

The effect of the forming process on the morphology of the polyaniline phase in the extrudates was investigated by means of a combination of analysis techniques. Morphological analysis was carried out on cryogenically fractured and etched specimens, respectively, using scanning electron microscopy. The details are presented in the subsequent sections.

7.3.1 SCANNING ELECTRON MICROSCOPY: FRACTURED EXTRUDATES.

The analysis was performed using the instrument and techniques described in section 6.4.1. The specimens examined were the extrudates' fracture surfaces parallel and transverse to the extrusion direction, respectively. Short sections (ca. 10 mm long) were immersed in liquid nitrogen for 3 min. The fracture surfaces parallel to the extrusion direction (i.e., longitudinal sections) were obtained by impacting the specimens immediately after they were removed from the liquid nitrogen (fig. 7.3). The "frozen" extrudates were placed on a solid metal surface and they were promptly impacted with a hammer such that the applied impact forces, perpendicular to the extrusion direction, opened a crack that propagated longitudinally across the whole body of the specimen. The latter fact initially suggested anisotropy in the morphology of the extrudates.

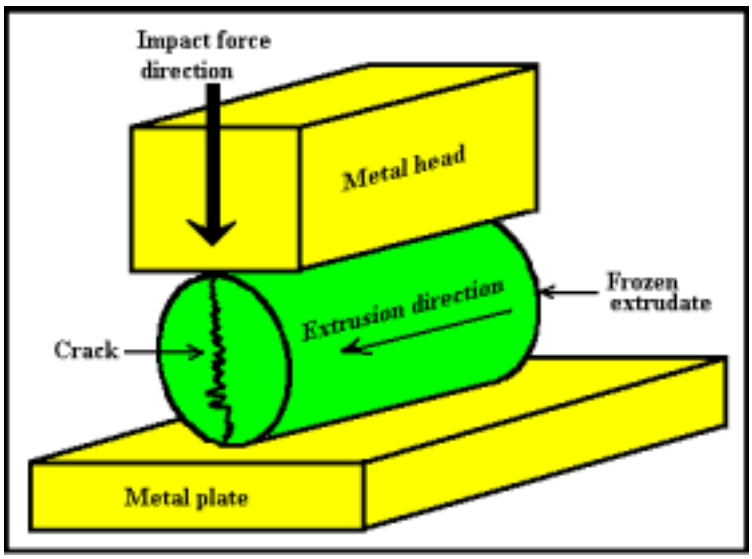


Figure 7.3. Schematic representation of the extrudates' fracture. Production of fracture surfaces parallel to the extrusion direction.

Extrudates produced from the blends with 10, 20 and 50 wt.% of conductive complex were selected for the analysis. SBS extruded at comparable extrusion conditions to those used in the extrusion of the blends was also analysed for comparison purposes. As in the compression moulded blends (chapter 6), the morphological analysis revealed that the mode of failure in the extrudates was predominantly brittle. The reason for this is that the glass transition points of the extrudates' components are above the fracture temperature. Both phases, the PANI and SBS, failed in a very similar manner. This, to some extent, impeded their identification on the extrudates' fracture surface during the analysis. However, by comparing the morphology of the specimens free of the conductive complex (extruded SBS) with those in which this was present, it was possible to establish the effect of the PANIPOL^{TM} phase on the morphology of the extrudates, differentiate the conductive phase from the SBS, and assess the effect of the forming process on the morphology of the conductive phase. The morphology observed together with a corresponding discussion is presented in the subsequent figures. The extrudates will be referred to throughout the text using the nomenclature of the blends from which they were produced (refer to Table 6.1 in section 6.2).

The fracture surfaces of the extrudate 10PANIPOL/SBS are presented in figure 7.4. Figure 7.4a corresponds to the longitudinal section, whereas fig. 7.4b corresponds to the transverse section. As in all the figures that will be presented in this chapter, the black arrows in fig. 7.4 indicate the extrusion direction on the longitudinal section unless otherwise stated.

As can be seen, fig. 7.4a shows a number of interesting features well worthy of comment. First, continuous elongated features, highly oriented in the extrusion direction, are clearly observed. Evidently, some of these features (e.g., those encircled in red) correspond to cracks longitudinally opened on the body of the specimen as a result of the impact force applied. Other features however, look more like continuous surfaced tracks instead of actual fissures (e.g., those encircled in yellow). In addition, some elongated structures (e.g., those indicated by yellow arrows), displaying a certain degree of continuity, are also observed. The second types of feature, relevant to the present discussion and observed in fig. 7.4a, are structures displaying a globular-like morphology. These, like those encircled in black, seem to be present on the whole fracture surface.

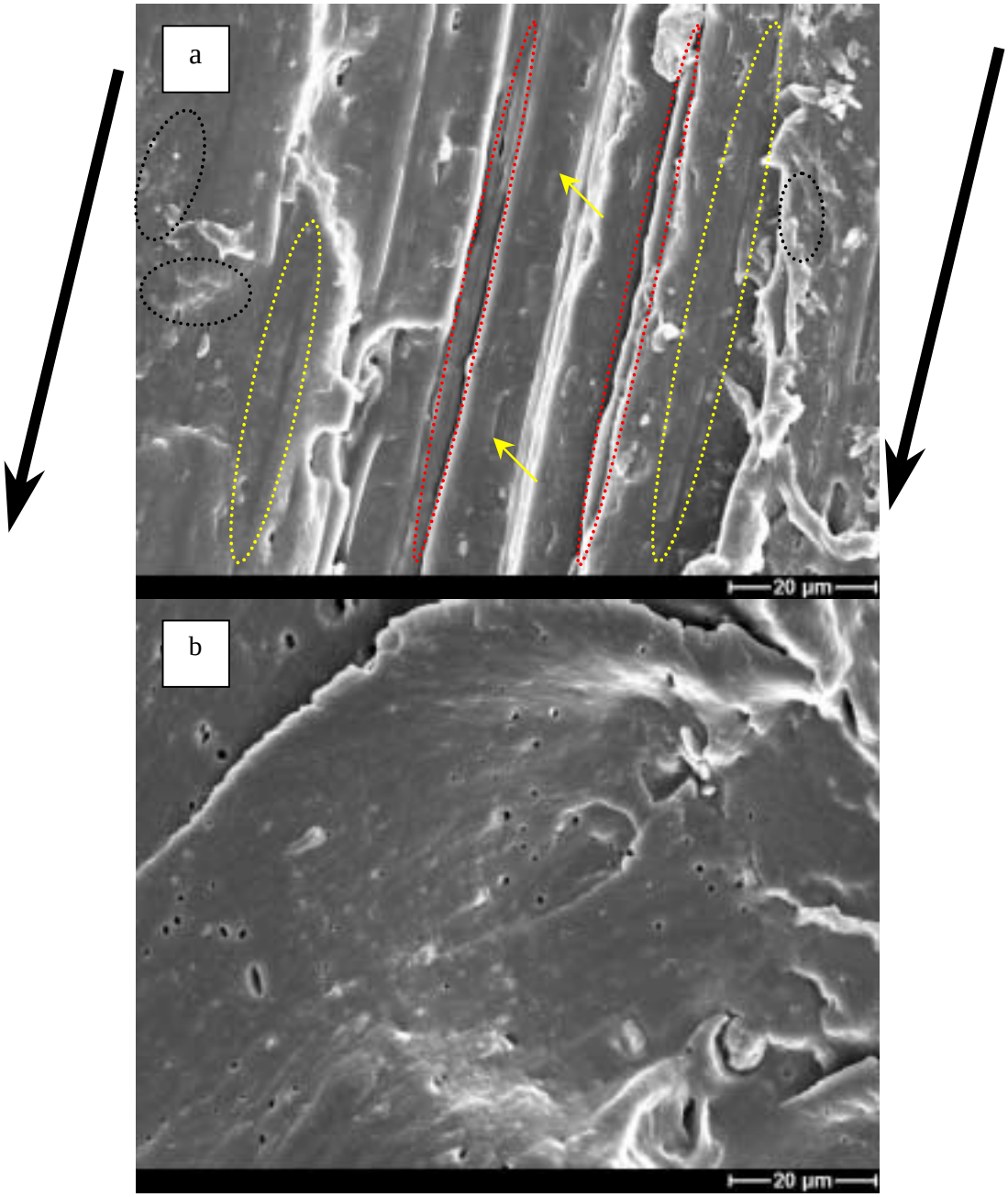


Figure 7.4. SEM micrographs of the longitudinal (a) and transverse (b) sections of the extrudate 10PANIPOL/SBS cryogenically fractured.

With respect to the extrudate's transverse section (fig. 7.4b), it is interesting to note that this presents a remarkably different type of morphology to that observed on the longitudinal section. As can be seen, elongated features with a well-defined degree of orientation and continuity are not present. Instead, features displaying a globular-like morphology are most evident. These are better illustrated in fig. 7.5, which corresponds to the same fracture surface, but analysed using a higher magnification. As can be observed in the micrograph, numerous globular-like features are present (e.g., those

indicated by yellow arrows). Some of these features, like those ones indicated by the white arrows, are cavities on the surface of the specimen.

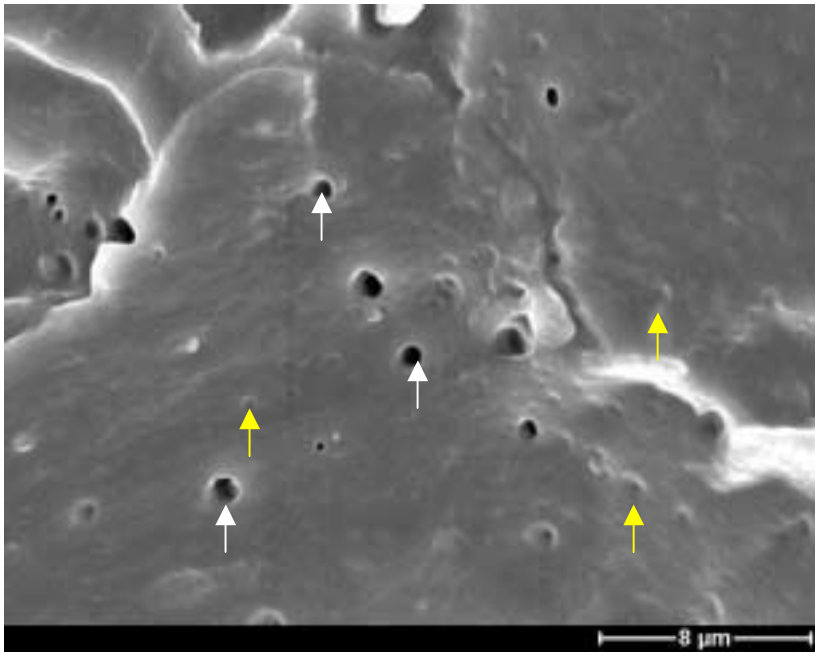


Figure 7.5. As fig. 7.4b but analysed under a higher magnification.

The analysis and comparison of the previous micrographs enable us to establish the following hypotheses:

- The elongated structures found on the longitudinal section may correspond to polyaniline domains, whereas the continuous pathway-like features may correspond to regions in which these elongated domains were originally present, and that were detached from the SBS matrix during the extrudate's fracture.
- Some of the globular-like features observed on the longitudinal section may correspond to polyaniline domains that were not deformed during the extrusion.
- A certain number of the globular features found on the transverse section may correspond to the ends of elongated polyaniline domains emerging from the SBS matrix. It is also possible that some of the features are undeformed clusters of polyaniline particles.
- The cavities found on the transverse section may have resulted from the pull out of elongated domains of polyaniline during the extrudate's fracture.

The veracity of the above stated hypotheses is reasonable considering the fact that the morphological features were not observed on the fracture surfaces of the extruded SBS analysed under the same level of magnification (fig. 7.6) to that used for the analysis of the extrudate 10PANIPOL/SBS. As can be noticed, fig. 7.6 shows different type of morphological feature to that observed in fig. 7.4. Specifically, elongated features oriented in the extrusion direction (i.e., on the longitudinal section), and globular-like features on the transverse section, were not observed.

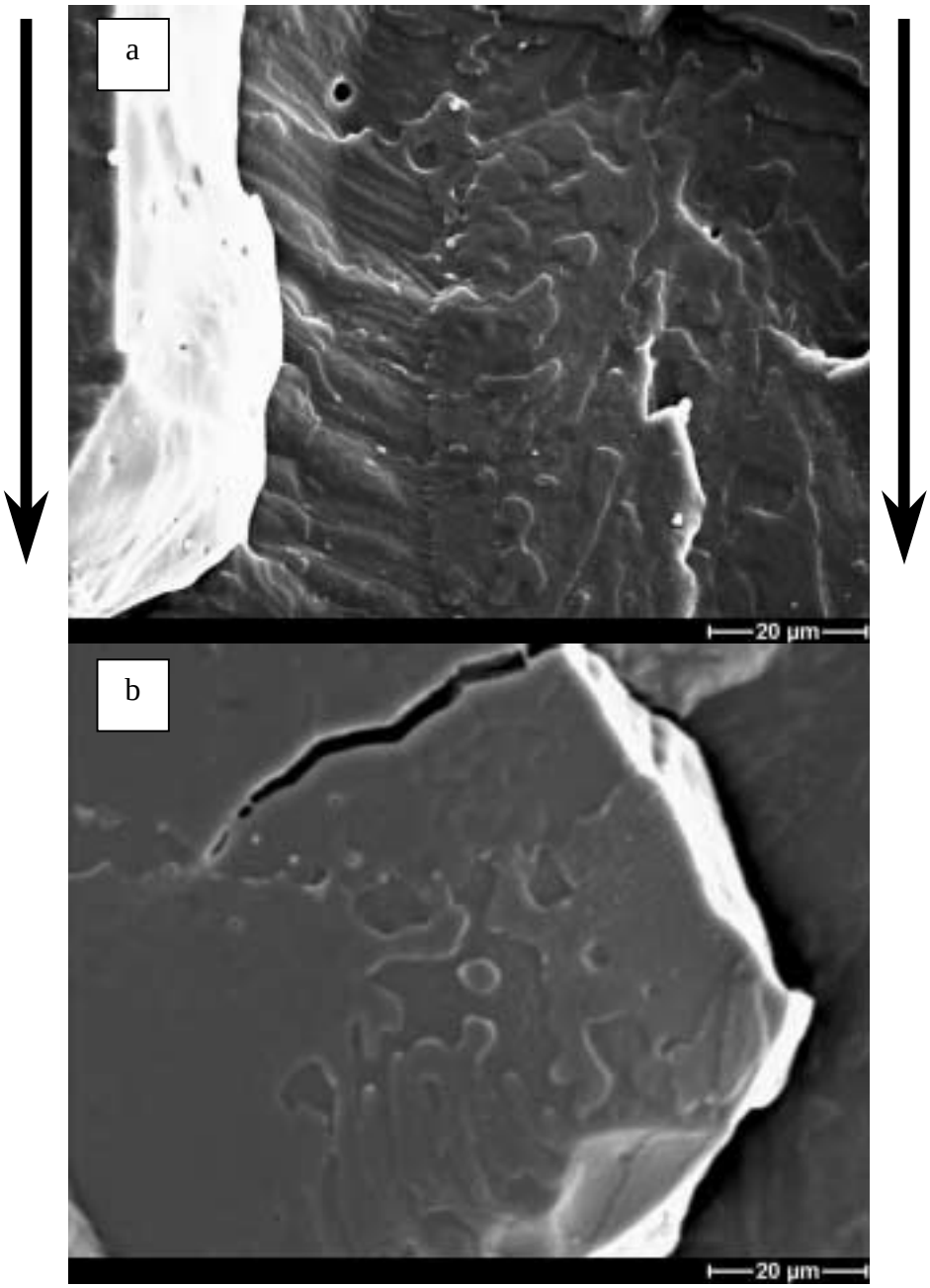


Figure 7.6. SEM micrographs of the longitudinal (a) and transverse (b) sections of the cryogenically fractured extrudate of SBS.

Regarding the extrudate 20PANIPOL/SBS, the morphology observed on its fracture surfaces is presented in figure 7.7. As can be noticed, a great number of elongated features, oriented in the extrusion direction, are abundant on the longitudinal section (fig. 7.7a). These features are not present on the transverse section (fig. 7.7b). Instead, pointed features, like those encircled in red (or indicated by red arrows), are most predominant.

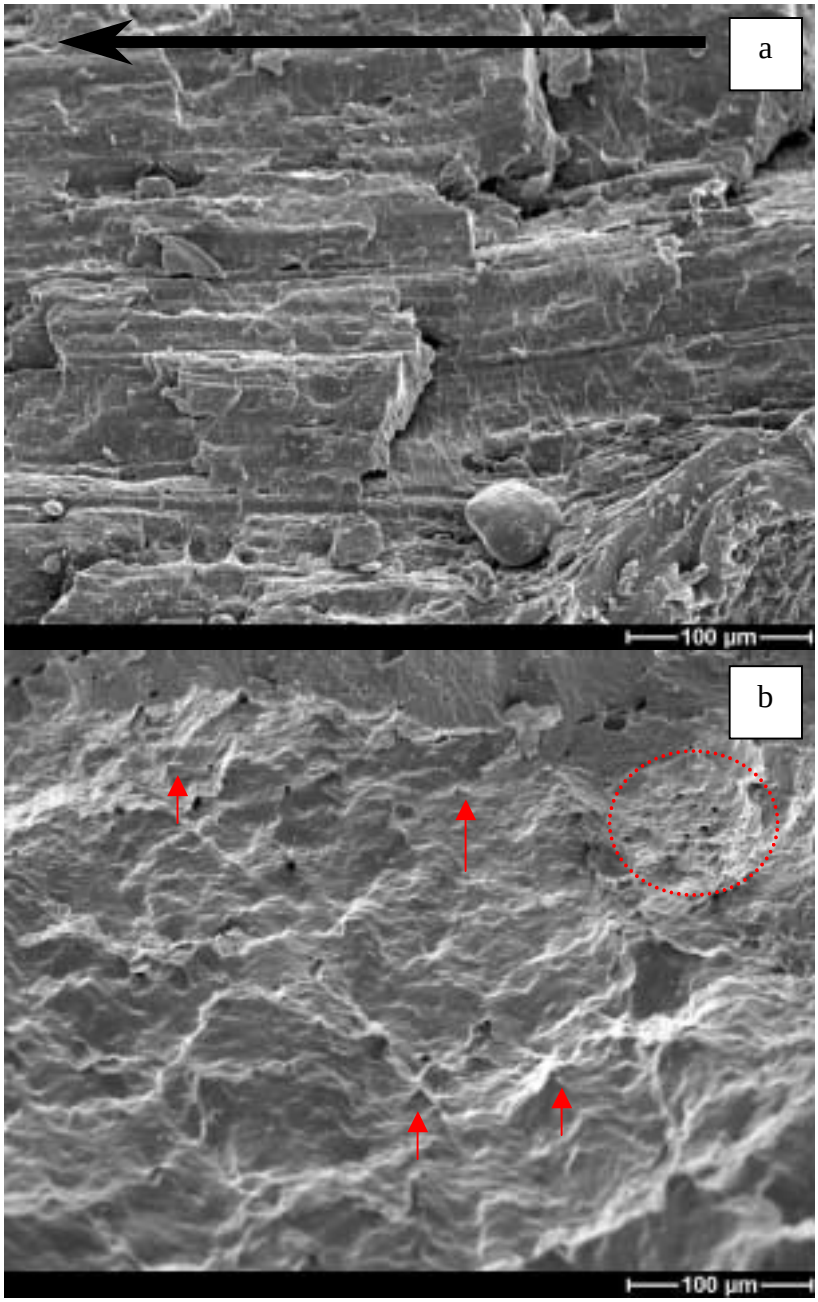


Figure 7.7. SEM micrographs of the longitudinal (a) and transverse (b) sections of the extrudate 20PANIPOL/SBS cryogenically fractured.

None of the features observed in fig. 7.7 were observed on the fracture surfaces of the SBS capillary extruded material under comparable conditions to those used for the production of the extrudate 20PANIPOL/SBS. As an example, compare fig. 7.7 with fig. 7.8, which corresponds to the fracture surfaces of the SBS extrudate analysed under the same magnification to that used in the analysis of the extrudate 20PANIPOL/SBS.

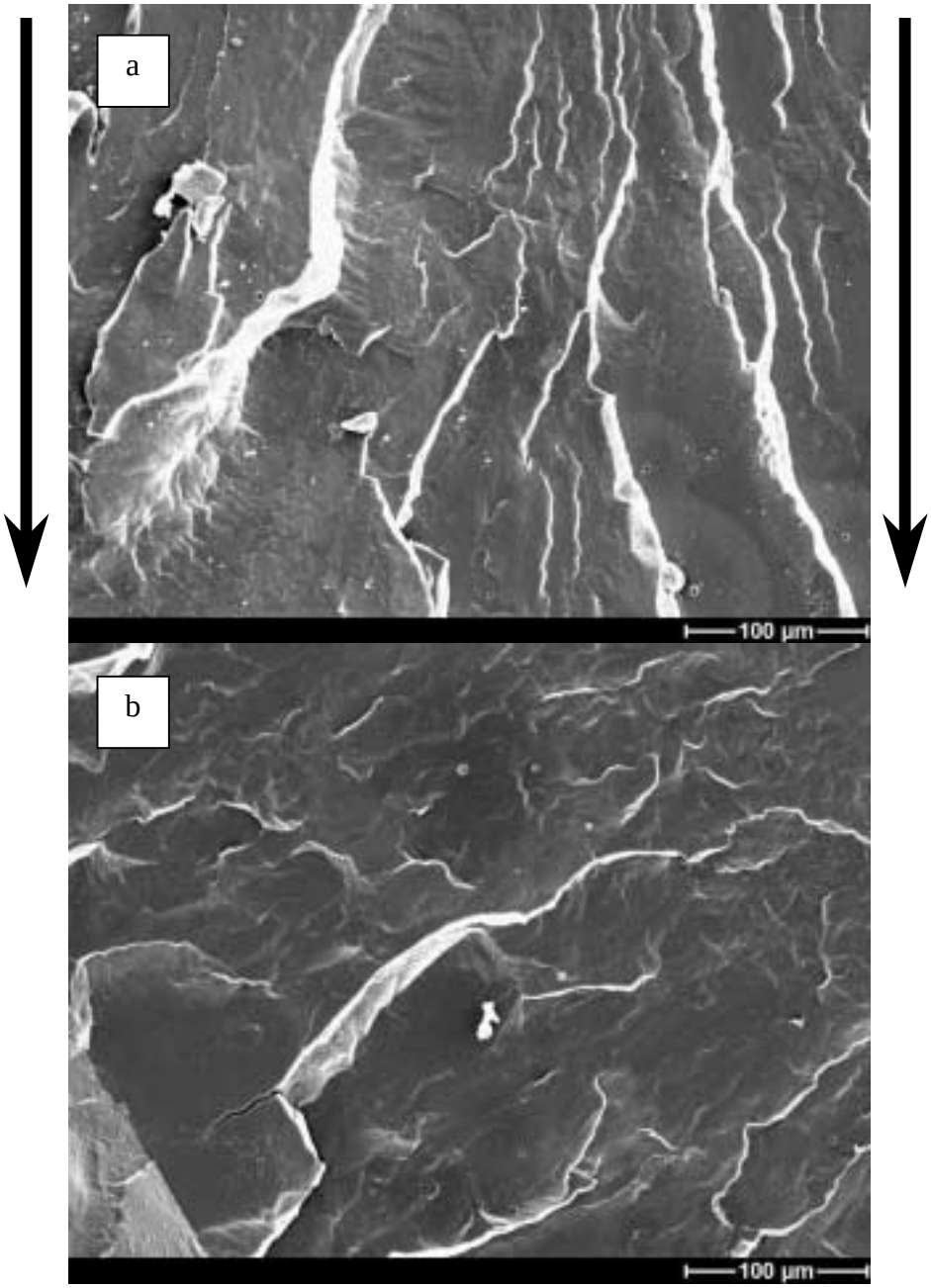


Figure 7.8. SEM micrographs of the longitudinal (a) and transverse (b) sections of the cryogenically fractured extrudate of SBS. As in fig. 7.6, but analysed under a lower magnification.

The fact that the morphology of the SBS extrudate's fracture surfaces was considerably different to that of the fracture surfaces of the extrudate 20PANIPOL/SBS reinforces even more some of the hypotheses previously proposed. More precisely, the hypotheses that suggest that the elongated structures found on the extrudates' longitudinal section correspond to elongated domains of polyaniline, and that the globular-like features found on the transverse section (or the tip of the pointed features, as in the case of those seen in fig. 7.7b), correspond to the ends of the elongated domains of PANI emerging from the SBS matrix.

A closer examination of the extrudate 20PANIPOL/SBS's fracture surfaces (figs. 7.9 and 7.10) reveals that the elongated domains of PANI are more abundant in this extrudate than in that of blend 10PANIPOL/SBS (compare fig. 7.9 with fig. 7.4). This is expected as the former extrudate has a higher content of conductive complex. Typical elongated structures of PANI, oriented in the extrusion direction, are indicated in figs. 7.9a and 7.10 by the red arrows. The estimated diameter for these structures is about 2 μm, although, as indicated in the micrographs, thinner structures should also occur. With respect to the transverse section, figure 7.9b shows more clearly what seems to be the ends of the elongated structures of PANI. For example, note the features indicated in the micrograph by the yellow arrows, or those encircled in yellow.

With regard to the extrudate 50PANIPOL/SBS, the transverse section showed an undefined morphology, which did not provide any relevant information. In contrast, the longitudinal section displayed interesting morphological features, which are presented in figure 7.11a. As can be seen in the micrograph, numerous elongated features oriented in the extrusion direction were found in the extrudate with the highest content of conductive complex. Again, these features should correspond to elongated domains of PANI. This is very likely, considering that these were not observed on the fracture surface of the extrudate containing only SBS (compare fig. 7.11a with fig. 7.6a). As can be noted from the figure, some of these structures display a high level of continuity. However, in contrast to the extrudates 10PANIPOL/SBS and 20PANIPOL/SBS, very different morphologies were found in different regions of the fracture surface. This is exemplified in the encircled area of fig. 7.11b, which corresponds to the same specimen shown in fig. 7.11a, but analysed under a lower level of magnification.

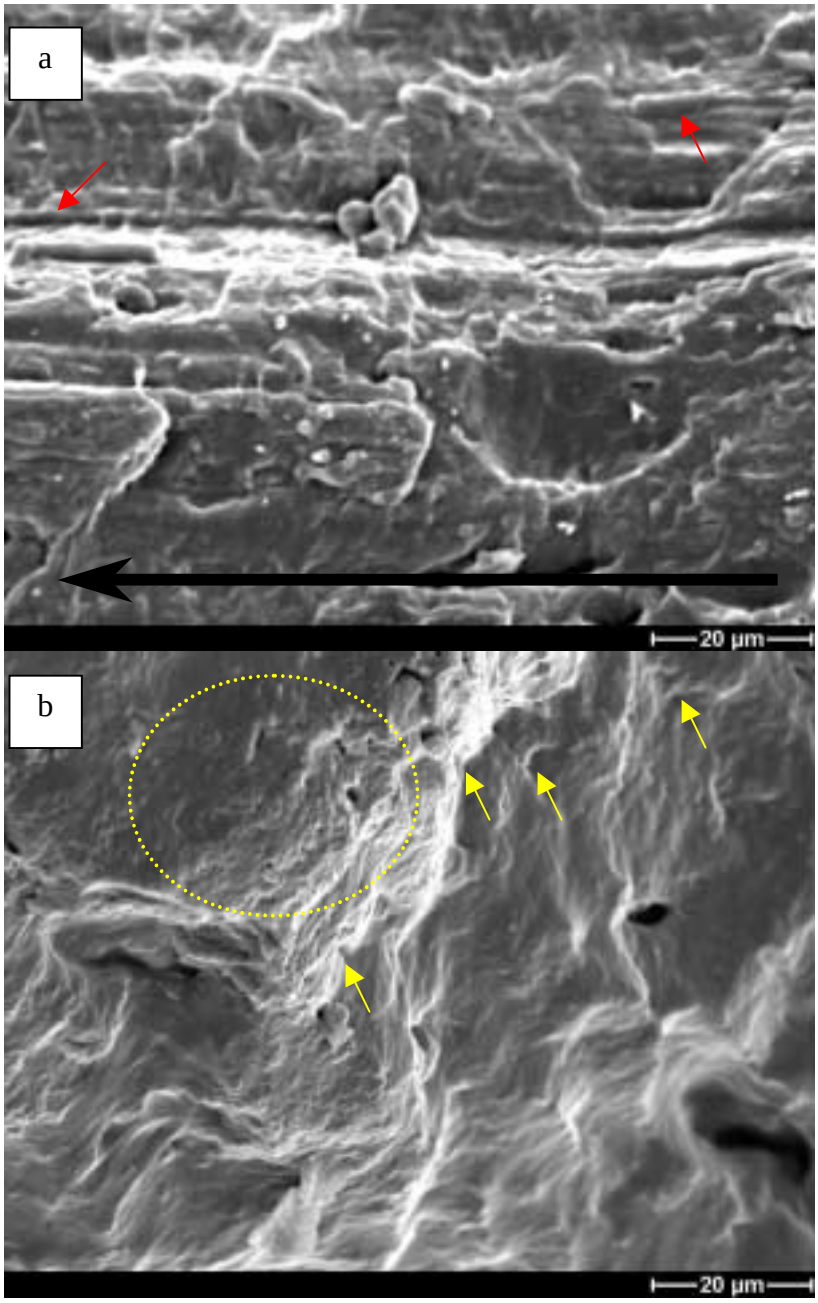


Figure 7.9. SEM micrographs of the longitudinal (a) and transverse (b) sections of the extrudate 20PANIPOL/SBS cryogenically fractured. As fig. 7.7, but analysed under a higher magnification.

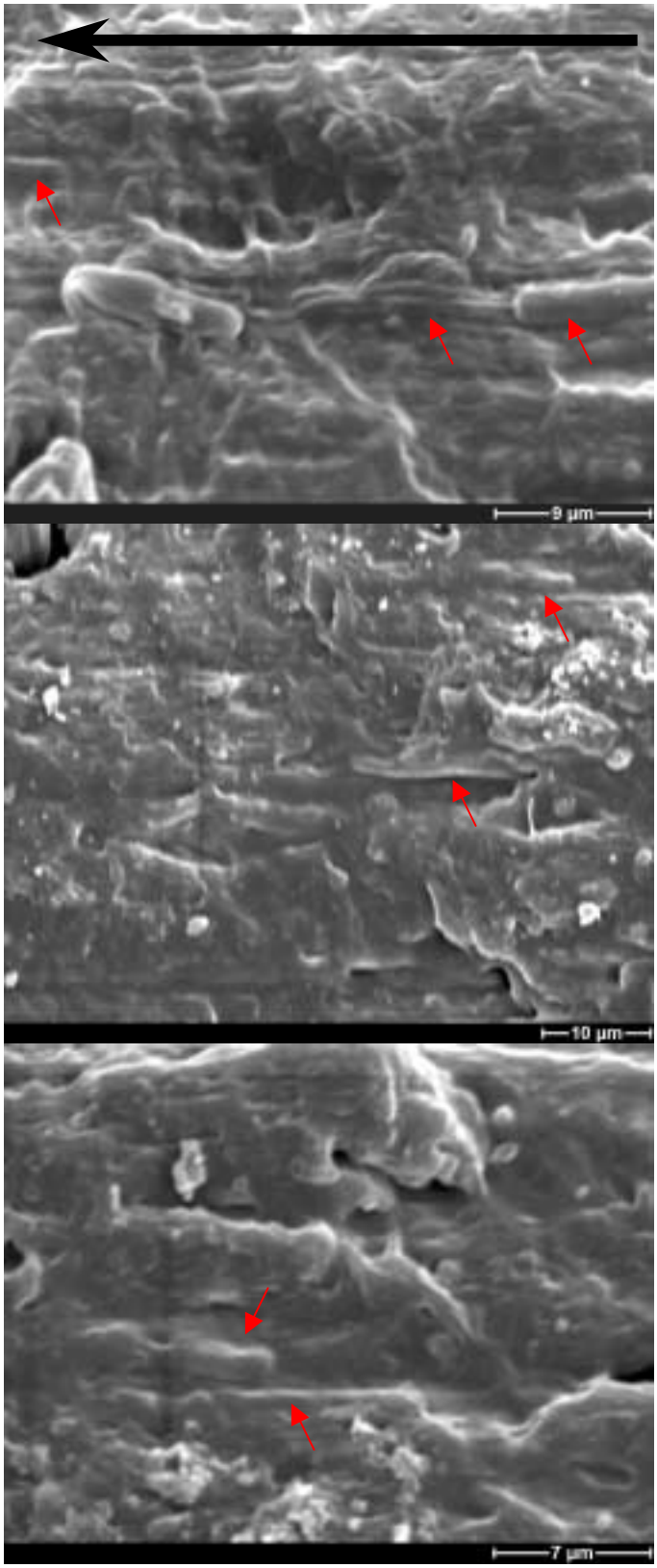


Fig. 7.10. SEM micrographs of the longitudinal section of the extrudate 20PANIPOL/SBS cryogenically fractured. As fig. 7.9a, but higher magnifications and different areas of the fracture surface.

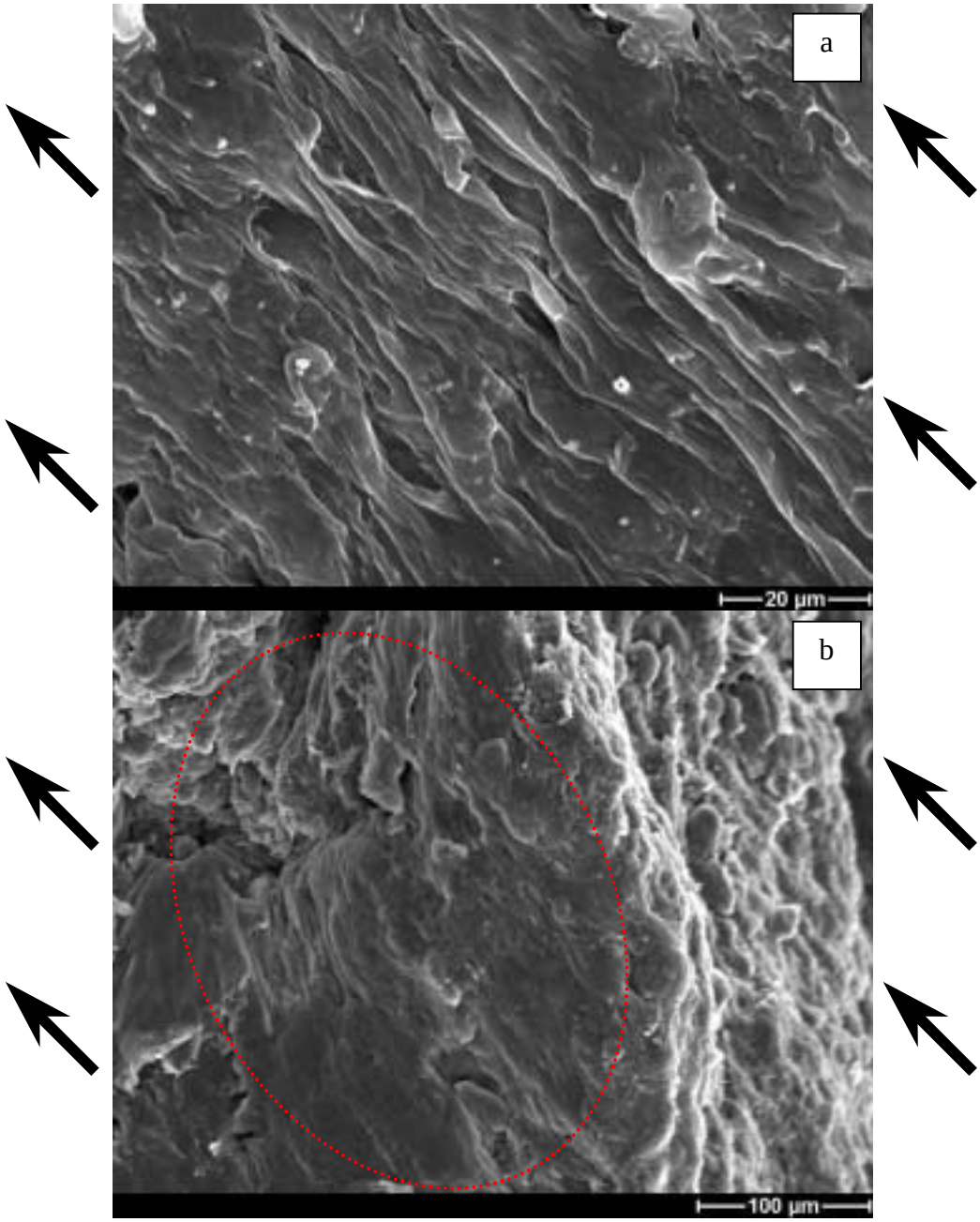


Fig. 7.11. SEM micrograph of the longitudinal section of the extrudate 50PANIPOL/SBS cryogenically fractured.

Perhaps the micrographs shown in this section do not provide enough evidence about the formation of continuous and uniform elongated structures of polyaniline (i.e., fibres) in the examined extrudates. However, they do prove the occurrence of anisotropically formed structures. As has been deduced from the analysis of the micrographs, it is a fact that these structures correspond to the polyaniline phase that was deformed during the ram extrusion process. As has been seen, the typical mode of

failure in a fibre-reinforced composite was not observed, especially in the transverse section in which the typical fibre-pull-out effect was not clearly displayed. A possible explanation is that the structures of polyaniline were extremely brittle and did not sustain the failure stresses imposed during fracturing.

7.3.2 SCANNING ELECTRON MICROSCOPY: ETCHED EXTRUDATES.

The analysis was performed using the instrument and technique described in section 6.4.2. The specimens examined were, respectively, the extrudates' longitudinal and transverse sections etched with a mixture of chromic and phosphoric acids.

The specimens for etching were produced by cutting the extrudates with a scalpel, following the method described in section 5.5 (refer to fig. 5.7 in chapter 5). The extrudates were longitudinally cut into halves in such a way that flat surfaces parallel to the extrusion direction, as close as possible to the extrudates' central axis, were obtained for etching and further examination (fig. 7.12). With respect to the transverse sections, specimens about 1.5 mm thick were obtained.

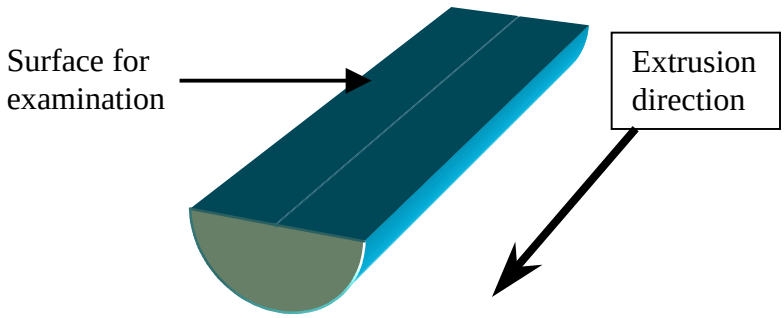


Figure 7.12. Representation of a sectioned extrudate.

The specimens were etched by immersing them, for 72 hrs, in 1 ml of the acidic solution described in section 6.4.2. After immersion, the specimens were washed with distilled water, dried overnight in a vacuum oven at 40°C, and kept in a desiccator to await further analysis. Extrudates 10PANIPOL/SBS, 20PANIPOL/SBS and 50PANIPOL/SBS were selected for the analysis. SBS extruded at comparable extrusion conditions was also analysed for comparison purposes.

The etching was performed with the primary purpose of removing selectively the SBS phase from the specimens' surface, leaving the polyaniline phase exposed for examination. However, as has been seen in section 6.4.2, the conductive phase is more susceptible to attack, by the etching agent, than the SBS matrix. In principle, as was explained in the aforementioned section, PANIPOL^{TM} is at least about 20 times more susceptible to attack than the SBS phase. Therefore, what was shown on the surface of the specimens examined, were mostly elongated cavities (in the case of the longitudinal sections) formed by the removal of the conductive complex, which was washed away (dissolved) by the acidic solution during the etching. On the other hand, the transverse sections presented a porous morphology, which is mainly attributed to cavities created on the surface of the specimens as a result of the polyaniline domains being removed by the etching agent. The results from the analysis are presented next.

Figure 7.13 corresponds to etched surfaces of the extrudate 10PANIPOL/SBS. As can be noticed, fig. 7.13a, which corresponds to the extrudate's longitudinal section, shows the presence of numerous elongated cavities aligned parallel to the extrusion direction. These features present, in some cases, a high degree of continuity and uniformity along almost all of the extrusion direction. It is also clear that most of the elongated cavities are concentrated in central regions of the extrudate. By comparing fig. 7.13a with fig. 7.14a, which corresponds to the etched surface of the extrudate containing only SBS, it is clear that the observed morphology resulted from the presence of the conductive complex in the composite. As commented before, the majority of the elongated cavities should correspond to regions on the surface of the specimen that were originally filled with polyaniline structures.

A very different morphology is observed in fig. 7.13b, which corresponds to the transverse section of the extrudate. This porous morphology is consistent with the morphology observed in fig. 7.13a in such a way that some of the observed pores should correspond to cavities on the surface of the specimen formed by the removal of the ends of elongated polyaniline structures, which were dissolved by the etching solution. However, it is also possible that some of the pores correspond to voids opened by the etching agent on less dense regions of the SBS matrix. For example, compare fig.7.13b with fig. 7.14b, which correspond to the transverse section of the extrudate of SBS. As can be seen, the transverse section of the SBS extrudate shows two types of

morphologies, a porous one, and another one displaying a smoother appearance (encircled in yellow in fig. 7.14b). The latter, is the type of morphology expected to see (under the level of magnification at which the analysis was performed) on an etched SBS surface. In consequence, it is very likely that an irregular etching process occurred on the SBS specimen as well as on the specimens of the extruded blends.

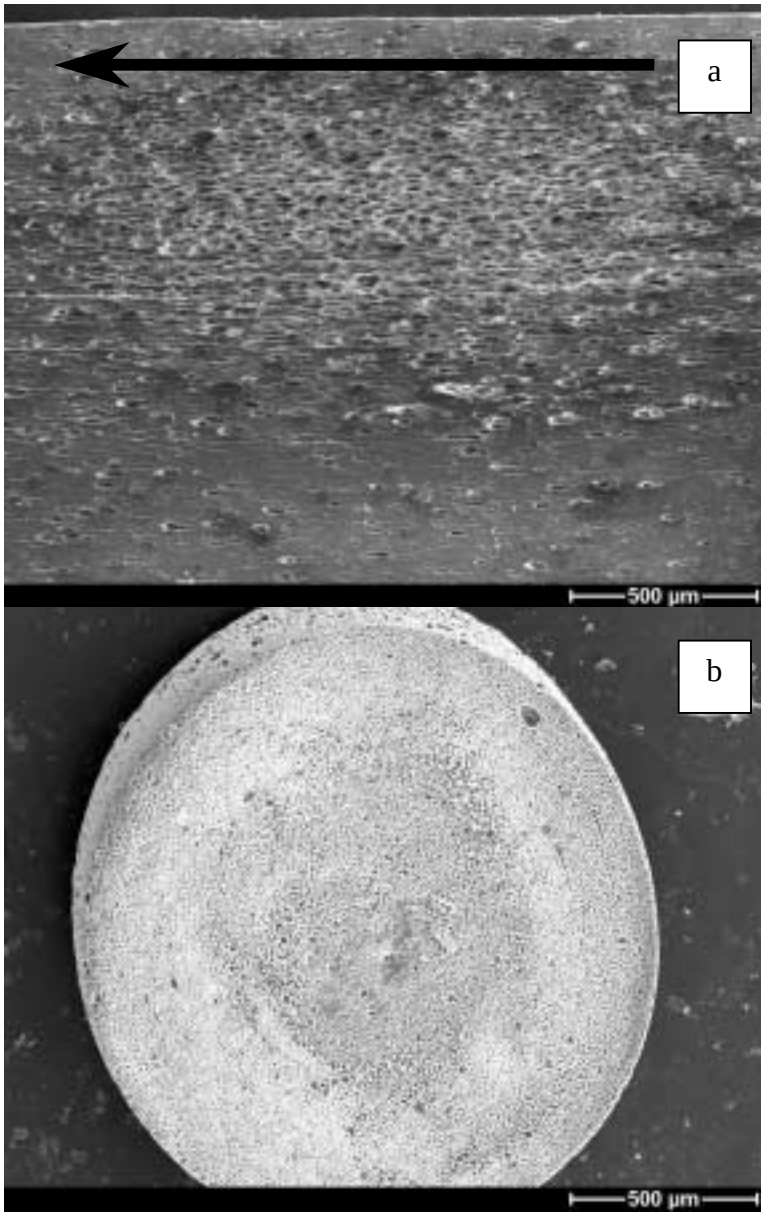


Figure 7.13. SEM micrographs of the etched surfaces of the extrudate 10PANIPOL/SBS. Longitudinal (a) and transverse (b) sections.

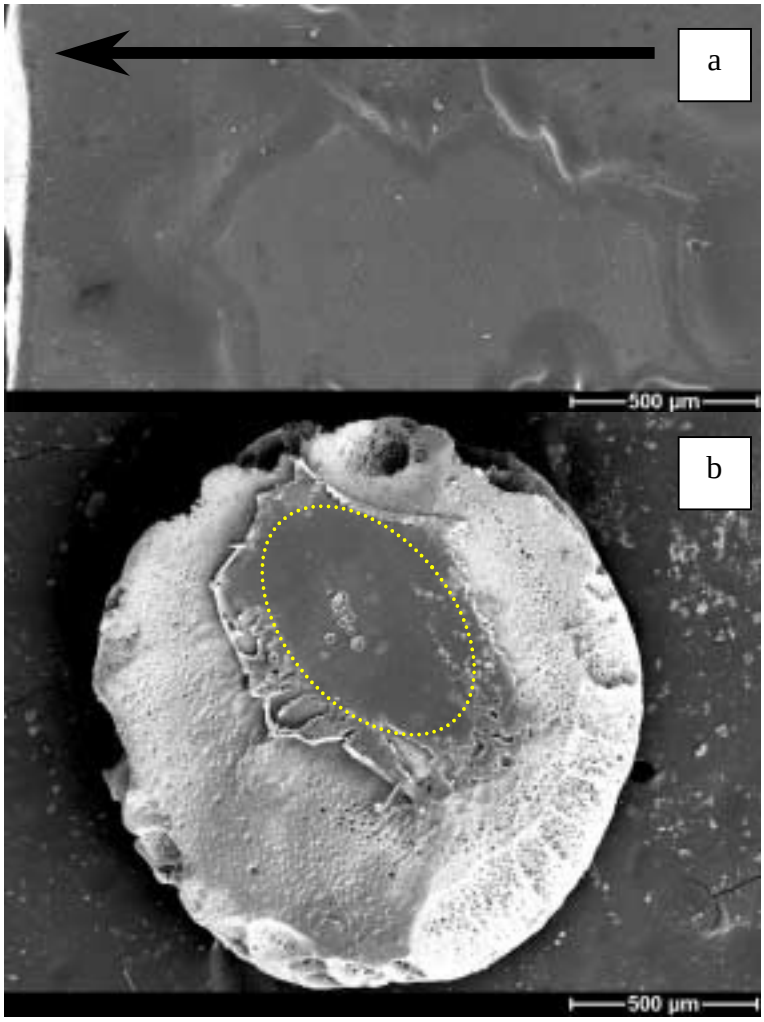


Figure 7.14. SEM micrographs of the etched surfaces of extruded SBS. Longitudinal (a) and transverse (b) sections.

In fig. 7.13b two types of morphologies can be seen, one in which the diameter of the pores seems to be bigger (centre of the specimen) and another one in which the pore diameter is smaller. It is believed that the regions showing pores of bigger diameter correspond to areas in the extrudate in which the ends of the elongated structures of polyaniline were highly concentrated. On the other hand, the regions showing pores of smaller diameter should correspond to the SBS matrix that was attacked irregularly by the etching solution. The above observation is based on the fact that the morphologies observed in fig. 7.13 are in good agreement with those observed by optical microscopy during the preliminary morphological analysis, that is, fig. 5.15 in section 5.5.3. As has been seen, the latter figure showed that elongated domains of polyaniline, oriented in the extrusion direction, were highly concentrated in the extrudate's central regions.

The presence of elongated cavities formed by the removal of the polyaniline phase is shown more clearly in fig. 7.15, which corresponds to different regions of the specimen shown in fig. 7.13a, but viewed under different levels of magnification. Moreover, fig. 7.15c gives an indication about the possible diameter of a typical elongated cavity. Assuming that the elongated cavities are in the form of long longitudinally sectioned microtubes (as exemplified in the model presented in fig. 7.16), and that they were created by the polyaniline phase that was originally in the form of elongated continuous structures, an average diameter for these in-situ formed PANI structures of about 4 μm can be estimated. This dimension compares very well with that of 2 μm estimated through the SEM analysis performed on the cryogenically fractured specimens (refer to figs. 7.9a and 7.10 in section 7.3.1).

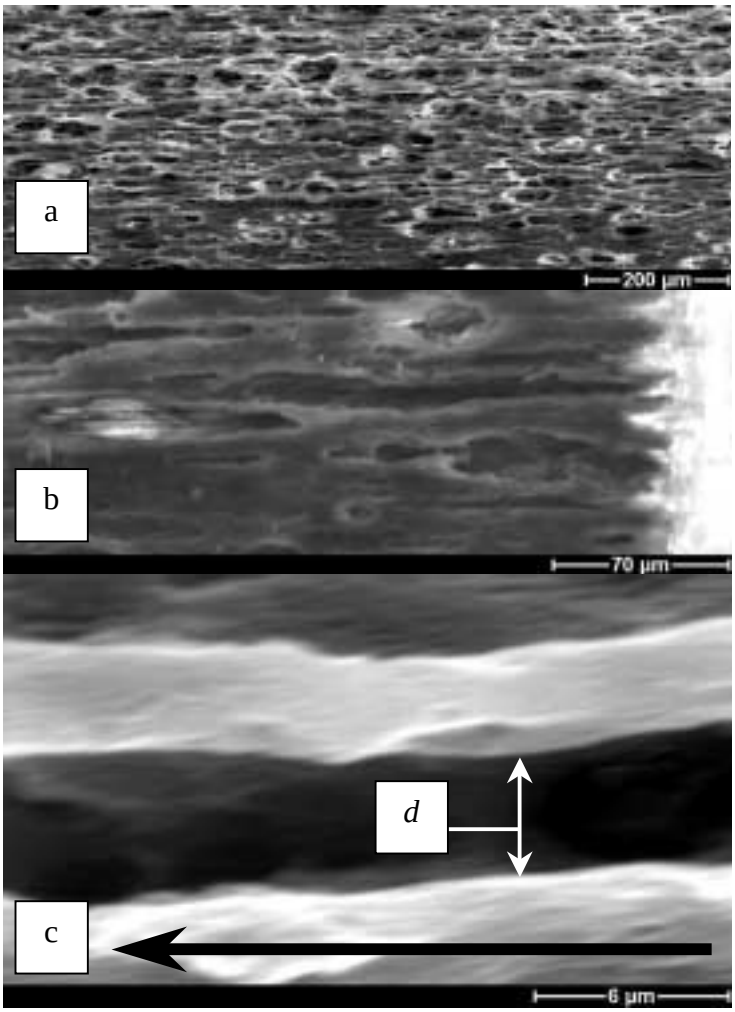


Figure 7.15. As fig. 7.13a, but different areas and magnifications. Micrographs (a) and (b) correspond to views at the centre and near to the edge of the specimen, respectively. In micrograph (c), *d* indicates the diameter of a typical elongated cavity.

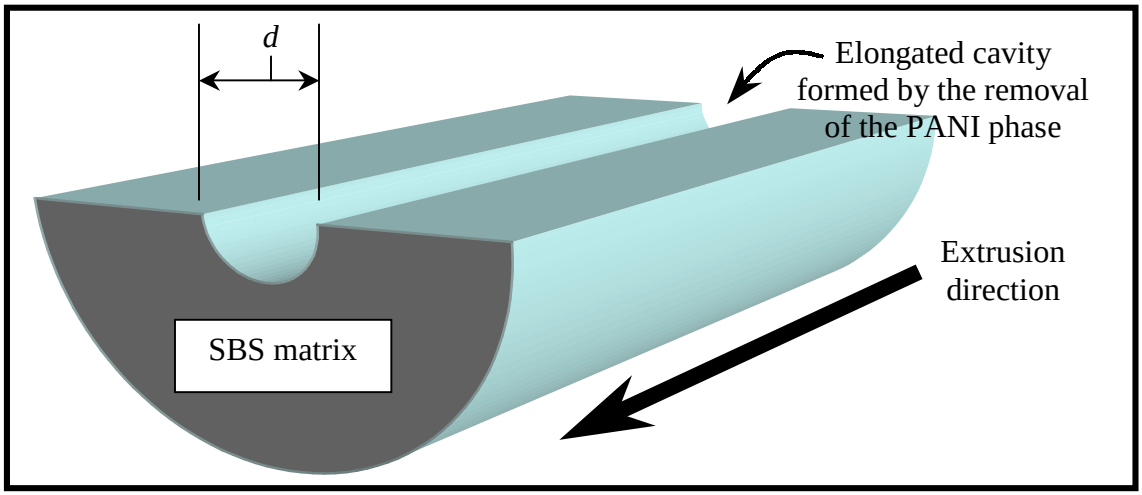


Figure 7.16. Model exemplifying a typical elongated cavity of diameter *d*, formed on the SBS matrix by the removal of the PANI phase.

The presence of the elongated "footprints" of PANI, aligned parallel to the extrusion direction is exemplified more markedly in fig. 7.17, which corresponds to the etched surfaces of the extrudate 20PANIPOL/SBS. From the figure, a much higher content of elongated cavities is observed (fig. 7.17a). These features, as well as the cavities of relatively bigger diameter on the transverse section (fig. 7.17b), seem to be concentrated in central regions of the specimens. The degree of continuity and uniformity of the elongated cavities, also appears to be higher than that observed in the specimens of the extrudate 10PANIPOL/SBS. This is most evident in fig. 7.18, which corresponds to different regions near to the edges of the specimen (refer to fig. 7.19) shown in fig. 7.17a that were analysed using higher levels of magnification. The observations about the concentration of elongated cavities on the longitudinal section, and cavities of bigger size on the transverse section, are consistent with the content of conductive complex in the extruded blends.

Very different morphologies to those previously described were observed on the etched surfaces of the extrudate 50PANIPOL/SBS (fig. 7.20). Fig. 7.20a, corresponding to the longitudinal section, shows some oriented structures (see the encircled area in the micrograph). However, the typical elongated "trails" of PANI oriented in the extrusion direction were not identified. Moreover, even when a porous morphology is observed in the transverse section (fig. 7.20b), the characteristic pores formed by the removal of the ends of the elongated structures of PANI were not identified either. Also, both longitudinal and transverse sections show a very irregular surface (e.g., cracks and

different types of morphological features) that may have resulted from irregular flow of the melt, taking place in the capillary die entry region or, perhaps, even inside the capillary die itself. The morphologies observed in fig. 7.20 thus corroborate the phenomenon of melt fracture that occurred in the flow of the melt during the extrusion of blend 50PANIPOL/SBS (refer to section 7.2). Moreover, the morphologies observed, also suggest that the PANI phase could co-exist in this particular extrudate as both randomly dispersed aggregates and oriented structures, respectively.

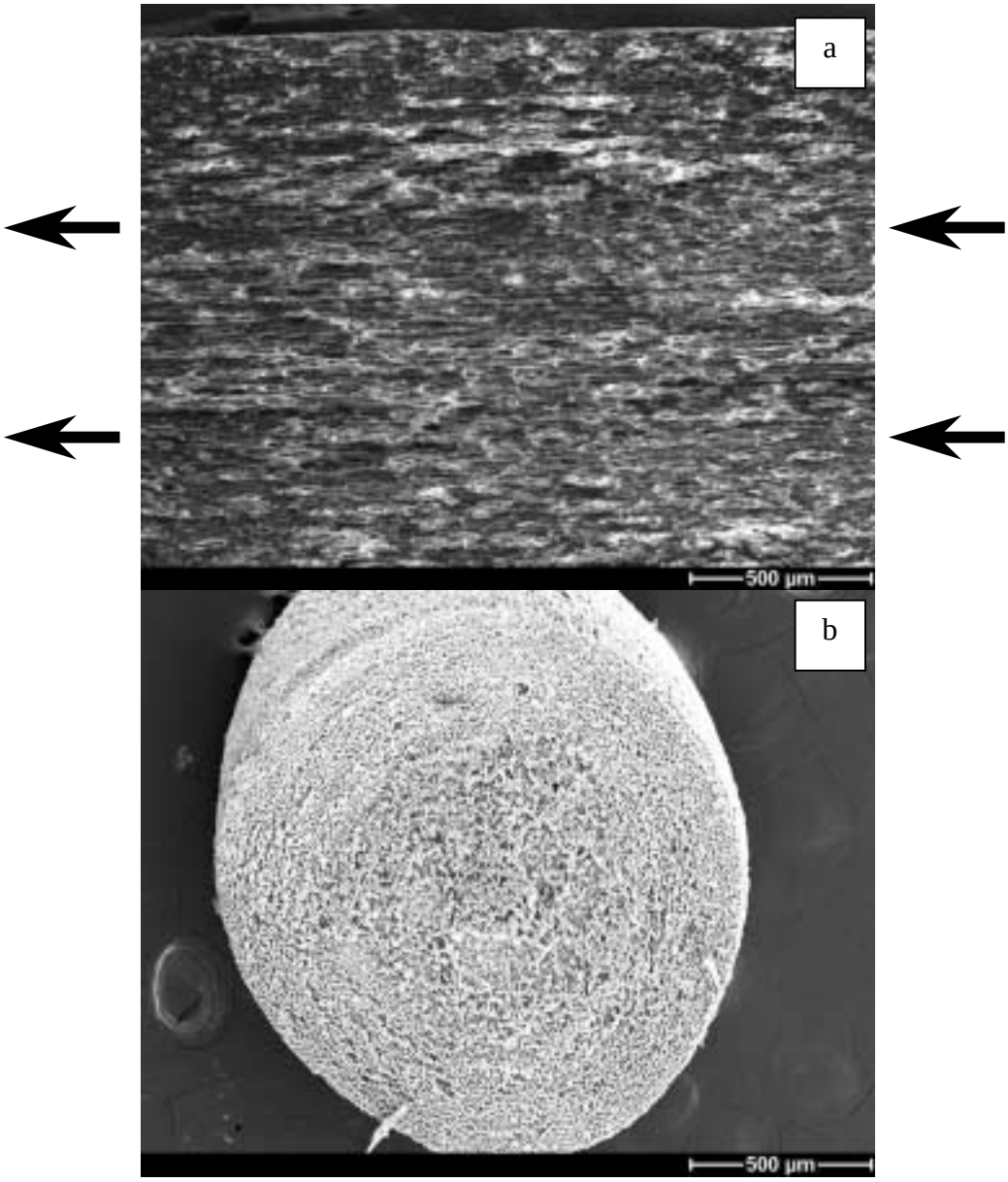


Figure 7.17. SEM micrographs of the etched surfaces of the extrudate 20PANIPOL/SBS. Longitudinal (a) and transverse (b) sections.

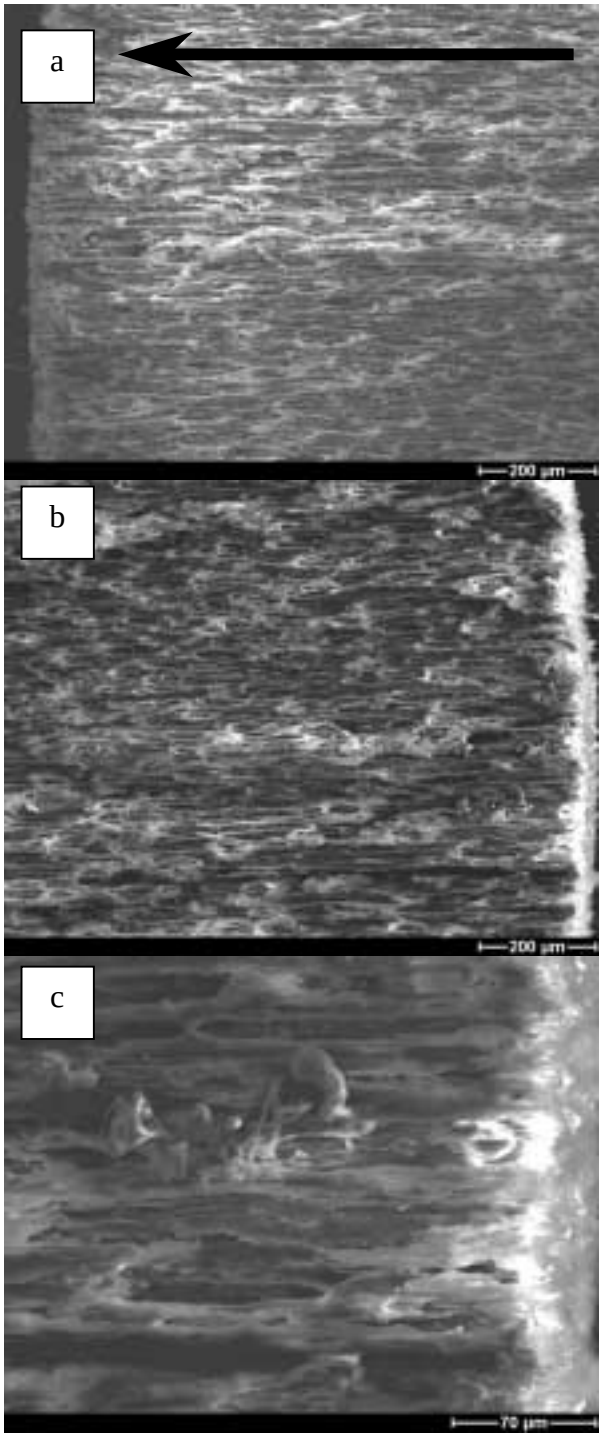


Figure 7.18. As fig. 7.17a, but higher magnifications. Areas near to the edges of the specimen.

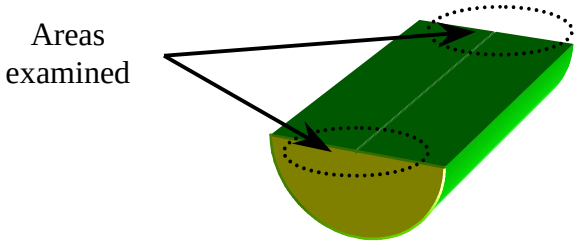


Figure 7.19. Schematic representation of the regions observed in fig. 7.18

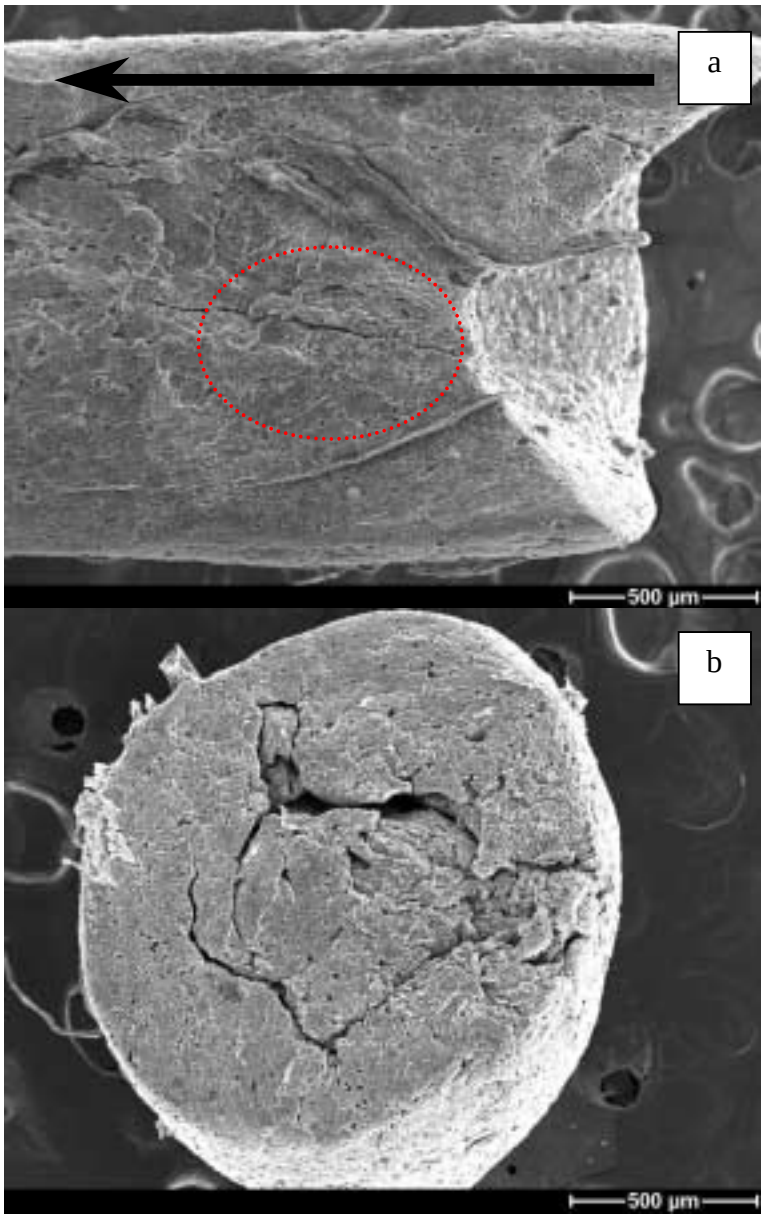


Figure 7.20. SEM micrographs of the etched surfaces of the extrudate 50PANIPOL/SBS. Longitudinal (a) and transverse (b) sections.

The micrographs presented in this section reinforce the concepts about the in-situ formation of polyaniline structures highly oriented in the extrusion direction. Although the structures themselves were not seen, signs of their existence in the extruded blends were evident. As has been seen, their footprints left on the surface of the examined specimens displayed a considerably high level of continuity, especially in the extrudate 20PANIPOL/SBS. This suggests, as was also observed by optical microscopy, that the elongated structures of PANI should be highly continuous. However, whether the elongated structures are in the form of continuous and intact fibres, extending all along the extrusion direction inside the body of the extruded blends is difficult to establish through the present SEM analysis.

The formation of elongated structures of polyaniline oriented in the extrusion direction is thus ascribed to a combination of factors, the main ones including:

- The type of flow field occurring during processing. The convergent flow at the entry of the capillary die should have generated a strong elongational flow that drew the polyaniline domains into elongated structures. It is also possible that the shear flow taking place inside the capillary contributed to generate elongated structures, especially in the neighbourhoods of the melt near to the capillary walls. In addition, the sudden drop in the temperature of the melt leaving the die, and cooling down in the surrounding air, should have aided in retaining the morphology.
- The degree of viscosity of the SBS. The apparent shear viscosity of the SBS matrix was considerably higher than that of the PANIPOL^{TM} complex (refer to fig. 4.26 in section 4.6). Therefore, it is possible that significant stresses were transferred from the matrix to the dispersed polyaniline phase, thereby aiding the drawing process.
- The surfactant character of the SBS. It is very likely that the SBS phase lowered the surface energy of the dispersed polyaniline domains thus promoting their deformation into continuous elongated structures.
- The content of PANIPOL^{TM} in the blends. Except for the blend 50PANIPOL/SBS, it was observed that the formation of elongated structures of PANI was most evident in the extruded blends with higher content of conductive complex. As discussed before, irregular morphological features were found on the specimens of the extrudate 50PANIPOL/SBS, the main reason being the occurrence of a melt fracture

phenomenon in the melt during processing associated with a lower degree of homogeneity.

In one way or another, the concepts above stated have also been studied and applied by other researchers in the production of polymer-based composites, which involved in-situ deformation of the dispersed phase into elongated structures. For example, consult the works of Wong et al. [116], Lee et al. [122], Ehtaiatkar et al. [102], Folkes et al. [103], many other workers [117-120,123,124], and the references cited therein.

7.4 CONDUCTIVITY MEASUREMENTS.

The volume conductivity was evaluated by measuring the extrudates' electrical resistance using the same instrument (Keithley 614 electrometer), auxiliary equipment and method described in section 4.7. For each extrudate, five to ten specimens, whose length ranged from about 0.5 to 2 mm, were tested. The specimens' diameter was about 1.6 mm. The specimens were cut at random from different sections of the extrudates. The extrudates' sections produced at the beginning of the extrusion process (stabilization stage) were excluded from the analysis. Assuming that the resistance readings were performed in an ohmic regime and that the specimens were perfect cylinders, the volume conductivity was calculated in accordance with the diagram presented in fig. 4.32, using *Eq. 4.5* (refer to section 4.7).

Except for the specimens corresponding to the extrudate 50PANIPOL/SBS, all the specimens showed resistance levels above the maximum reading achievable by the electrometer (i.e., 200 GΩ). The results from the measurements corresponding to the extrudate 50PANIPOL/SBS are presented in Table 7.1.

As can be realized, the level of conductivity of the extrudates was considerably lower than that of their corresponding non-extruded blends. As can be seen from the results presented in Table 7.1, the average conductivity of the extrudate 50PANIPOL/SBS (i.e., 2.15 x 10^{-6} S/cm) was even lower than that of 4.26 x 10^{-5} S/cm measured on the compression moulded specimens of blend 15PANIPOL/SBS (refer to Table 6.5 in chapter 6).

Table 7.1. Results form the volume conductivity measurements on the extrudate 50PANIPOL/SBS.

Specimen	***d* (mm)**	***l* (mm)**	***R* (MΩ)**	**σ (S/cm)**
1	1.53	1.85	1.77	5.69×10^{-6}
2	1.54	1.49	39.7	2.02×10^{-7}
3	1.59	1.48	3.21	2.32×10^{-6}
4	1.62	0.91	2.71	1.63×10^{-6}
5	1.50	0.75	14.34	2.96×10^{-7}
6	1.59	0.80	1.21	3.33×10^{-6}
7	1.56	0.54	1.76	1.61×10^{-6}
			Average	**2.15×10^{-6}**
			Standard deviation	**1.90×10^{-6}**

Note: *d* = specimen diameter, *l* = specimen length, *R* = volume resistance, σ = volume conductivity.

Initially, it was believed that the decay in the conductivity was due to a negative effect of the heating-cooling-heating cycle (i.e., compounding-cooling-forming cycle) on the conductivity of the PANIPOL^{TM} complex. This could be possible, especially if the number of cycles is very high. However, this was not the case in the present work. What is more, the average conductivity of some of the compression moulded blends (i.e., subjected to a thermal mixing-cooling-thermal moulding cycle) was only one order of magnitude lower than that of the unprocessed PANIPOL^{TM} pellets (refer to fig. 6.2 in section 6.3). Furthermore, it is clear that the conductivity of the PANIPOL^{TM} complex, extruded under the same conditions to those used for the processing of the blends, was not affected (refer to Table 4.5 in section 4.7).

Therefore, it is very likely that the decrease in the conductivity of the extrudates, relative to that of the compression moulded blends, is due to a lack of continuity in the polyaniline structures produced in-situ inside the SBS matrix.

7.5 CONCLUSIONS.

The quality of the extrudates improved considerably in comparison with that observed in the extrudates produced during the preliminary experimentation. This is attributed to a higher level of homogeneity in the blends, which resulted from the optimisation of the compounding method.

The pressure generated during the forming process behaved erratically with respect to time, which implied that the blends were not completely homogeneous. This behaviour increased with the increase of PANIPOL^{TM} content, which suggested that the degree of homogeneity in the blends decreased in the same fashion. The diminishment in the homogeneity is attributed to the fact that the batches used in the preparation of the blends were not of the optimum size. This indicated that the shearing levels occurring in the melt required to disperse fully the conductive complex within the SBS matrix were not adequate.

The extrudate 50PANIPOL/SBS was very brittle due to the occurrence of melt fracture in the flow of the molten blend during processing, which is associated with a lower degree of homogeneity in the blend.

The level of pressure generated during the forming process decreased with the increase of PANIPOL^{TM} content. This was attributed to the fact that the conductive complex is much less viscous than the SBS and also acts as a processing aid.

The apparent shear viscosity of the blends with 15, 20, 35 and 50 wt.% of conductive complex was lower than that of the PANIPOL^{TM} pellets. It is likely that this was due to disentanglement of the macromolecular chains of SBS and doped PANI as a result of them being pre-sheared and impacted during the compounding and size reduction processes, respectively. It may also be possible that the chains of the DBSA-PANI complex were oriented in the direction of the extrusion during the forming process.

The morphological analysis evinced the in-situ formation of elongated polyaniline structures highly oriented in the extrusion direction. The maximum diameter estimated for these structures was about 2 μm. The formation of these structures was ascribed to a combination of factors including elongational and shearing flows occurring in the molten blends during the processing, the stresses transferred from the SBS to the PANI phase, and the lowering of the PANI domains' surface energy by the SBS.

Except for the extrudate 50PANIPOL/SBS, which showed irregular morphological features, it was observed that the formation of elongated structures of PANI was most evident in the extruded blends with higher content of conductive complex. The irregular morphology observed in the extrudate 50PANIPOL/SBS was

associated with the occurrence of melt fracture and a lower degree of homogeneity in the blend.

The conductivity of the extrudates was considerably lower than that of their corresponding non-extruded blends. This was mainly attributed to a lack of continuity in the polyaniline structures produced in-situ inside the SBS matrix.