Structure formation in polyaniline-based polymer blends

RICARDO H. CRUZ-ESTRADA, CARLOS V. CUPUL-MANZANO
Unidad de Materiales, Centro de Investigación Científica de Yucatán, Calle 43, No. 130, Colonia Chuburná de Hidalgo, C.P. 97200, Mérida, Yucatán,, México

This paper provides evidences on the feasibility of using an *in-situ* deformation process to produce elongated structures of a polyaniline complex (PANI CX), embedded in the bulk of filament-like polymer composites, and longitudinally oriented along the composites' main axial direction. The polyaniline complex was thermally blended with polystyrene-polybutadiene-polystyrene (SBS) at different weight compositions, and the resultant blends were capillary extruded into filaments. The extrudates' microstructure was analysed by scanning electron microscopy (SEM). The results of the analysis revealed a phase-separated morphology in the extrudates, which consisted of elongated domains of PANI CX embedded in the bulk of the SBS. The elongated structures displayed a considerable degree of uniformity and continuity, and were preferentially oriented in the extrusion direction. The formation of these structures was ascribed to a combination of factors, the main ones including elongational and shearing flows occurring in the molten/softened blends during the processing, and the stresses transferred from the highly viscous matrix to the particles of the PANI complex filler. © *2005 Springer Science + Business-Media, Inc.*

1. Introduction

Blending traditional insulating polymers with intrinsically electro-conducting polymers (ICPs) is a research area that has generated polymer composites with potential applications in many fields of interest including the storage of energy [1], the protection from electromagnetic interference [2], the design of electro-optical devices [3, 4], the welding of plastics [5], and the preparation of antistatic materials [2, 6], just to mention a few of them. Moreover, filaments of electro-conducting polymer composites could be used for electrostatic discharge protection (i.e., as antistatic materials) in the carpets and textiles industries [2, 7–15].

In general, antistatic carpets are manufactured by interweaving antistatic filaments consisting of one or many elongated electro-conductive structures embedded in the bulk of an insulating material, and oriented parallel to the main axial direction of the filament. At present, the majority of the processes used for the manufacture of antistatic filaments involve the co-extrusion and/or co-spinning of two materials to obtain the so-called sheath-core filaments [8–13]. The material acting as a sheath is an insulating polymer, whereas the core is a conducting material that functions as a conducting elongated nucleus oriented all along the main axial direction of the filament. In general, the conducting core consists of a blend of the same insulating material and a conducting filler (generally carbon black), which is usually incorporated to the insulating matrix by melt mixing in a two-piece batch mixer or in an extruder. For the co-extrusion and co-spinning processes is necessary the use of two extruders and several accessories, which could make the processes extremely complex and, especially, expensive. One promising and simpler approach for the manufacture of antistatic filaments would be to generate the electro-conductive structures *in-situ*, that is, during the actual forming process of the filaments. This strategy would involve the formation of continuous electro-conducting structures embedded in the bulk of an insulating polymer matrix by means of one single process and instrument. Moreover, such conducting structures could consist of intrinsically electro-conductive polymer fibres embedded in the insulating polymer matrix.

For the *in-situ* production of electro-conducting fibres is necessary to consider the study of the rheological properties and microstructure of extruded binary blends. The phases should be immiscible, with one phase being well dispersed (i.e., the conducting phase) in the matrix phase. This is a research field that has been extensively investigated, and it has shown that under certain materials' characteristics and processing conditions (i.e., processing equipment, type of flow field, shear rate levels, the viscosity ratio between the dispersed phase and the matrix, and interfacial tensions, among others) the action of the matrix over the dispersed phase may be to such extent to change it into elongated structures (layers, ellipsoids or even fibres) [16–18]. Among the aforementioned parameters however, the relationship between the viscosities of

the dispersed phase and the matrix (viscosity ratio, p) can be initially used to suggest the size and, what is more relevant in this case, the shape of the dispersed phase.

Regarding to the electro-conductive phase (i.e., the disperse phase in this particular case), it is well-known that doped polyaniline (PANI) is presently one of the most promising intrinsically electro-conductive polymers. Special interest has been focused on PANI due to a number of important reasons including its excellent chemical stability combined with relatively high levels of electrical conductivity, which can be controlled. Additionally, this polymer is soluble in particular common solvents and also can be used to easily prepare melt processable blends with low percolation limits [2, 4, 5, 19–31].

In previous reports [32, 33] we gave an account on preliminary experimental results concerning the subject we are dealing with in the present paper. Consequently, we now report on later results that strongly evince the viability of using an *in-situ* deformation process for producing fibres of an ICP-based complex (i.e., a PANI complex) in the bulk of a filament-shaped composite, with the PANI complex fibres longitudinally oriented along the main axial direction of the composite.

2. Materials

The electro-conductive filler material used in this work was a PANI complex provided by NESTE Oy Chemicals (nowadays Panipol Ltd.). It is identified as PANIPOL™ CX (grade CX100X03) and will be referred to throughout the text as PANIPOL. The dark-green-coloured cylindrical compressed pellets were used as received and had an approximate composition of 25 weight percent (wt%) of electro-conducting PANI and 75 wt% of an organic compound of zinc, identified as zinc dodecyl-benzene sulphonate [34, 35]. The typical density, volume conductivity and maximum recommended processing temperature for this complex are, respectively, 1100 kg/m^3, 1×10^{-4} S/cm and 230°C. The insulating matrix used was a block copolymer of polystyrene-polybutadiene-polystyrene (SBS), which was provided by Shell Chemicals, and is identified as KRATON™ D-1102CU (formerly Cariflex TR-1102).

3. Experimental work
3.1. Capillary rheometry
The rheological behaviour of both the PANIPOL and SBS was investigated using a Davenport ram-extrusion capillary rheometer with a piston with a diameter of 19.05 mm. The Poiseuille Law for capillary flow [36, 37] was used to calculate the apparent shear viscosity at different apparent wall shear rates for each material. No end pressure drop correction was performed for the calculations. For the experiments, the materials were extruded using a capillary die with a length (L) = 35 mm and a radius (r) = 0.8 mm. The analysis was performed at selected piston drive speeds ranging from 0.25 to 50.00 mm/min. The experiments were carried out at 120°C.

3.2. Compounding
PANIPOL was melt blended with the SBS using a two-piece batch mixer mounted on a torque rheometer instrument (BRABENDER® PLASTI-CORDER® PLE 330). The compounding was performed at 130°C and 15 rpm for 5 min. Blends with 5, 10, 15, 20, 35 and 50 weight percent of the conductive complex were prepared. Before subjecting the blends to the forming process, they were granulated using a USI-Cumberland granulating machine (Model 5X7) with a metal screen plate with holes of about 3 mm in diameter. To obtain samples for conductivity measurements, the blends were compression moulded into flat plaques about 1 mm thick. The compression moulding was performed using a GRASEBY SPECAC filmmaker. About 0.3 g of each blend were placed between the preheated plates of the press. The moulding was then performed at 120°C and at a pressure of 25.5×10^3 N/m^2 for 5 min.

3.3. Forming process
Each blend was capillary extruded using the Davenport ram-extrusion rheometer and the capillary die previously described. The blends were formed into filaments at an extrusion speed (i.e., piston drive speed) of 1.25 mm/min. A temperature of 120°C was selected for the processing. During the extrusion, the piston forced the melt through the capillary die, and then it was cooled and solidified by contact with the surrounding air. The extrudates flowed downwards aided by the gravity and were collected on a metal tray where they coiled themselves and finally cooled down to room temperature. Extrudates approximately 1.6 mm in diameter were produced.

3.4. Morphological characterisation
3.4.1. PANIPOL-SBS compression moulded blends
Microstructural analysis was conducted on the compression moulded blends using two techniques, namely transmission electron microscopy (TEM) on sections obtained by cryoultramicrotomy, and scanning electron microscopy (SEM) on gold coated cryogenically fractured specimens. The instruments employed for the specimens' preparation and analysis were a 701701 Reichert ultramicrotome, a JEOL 2000 FX TEM microscope, a E5000 SEM coating unit (Polaron Equipment Limited), and a JEOL JXA-840-A electron probe microanalyzer. The analysis was performed on sections cut parallel to the compression direction.

3.4.2. PANIPOL-SBS extrudates
The effect of the forming process on the morphology of the PANIPOL phase in the extrudates was investigated by scanning electron microscopy using the same SEM instrument previously described. Initial examination was performed on the extrudates' fracture surfaces parallel to the extrusion direction. The specimens for the analysis were obtained fracturing the extruded blends at cryogenic temperatures. To obtain the

specimens, short sections (about 10 mm long) were immersed in liquid nitrogen for about 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. The "frozen" extrudates were placed on a solid metal surface and they were promptly impacted such that the applied impact forces opened a crack that propagated longitudinally across the whole body of the specimen. SBS extruded under the same extrusion conditions to those used for the blends was also analysed for comparison purposes.

Morphological analysis was also performed on the extrudates' longitudinal sections etched with a mixture of chromic and phosphoric acids, which mostly removed the PANIPOL phase from the surface of the specimens and left the SBS phase exposed. Details of the etching procedure are reported elsewhere [34]. The analysis was also carried out by scanning electron microscopy using the SEM instrument previously described. Longitudinal sections of the SBS extrudates, obtained under the same processing conditions to those used for extruding the blends were also analysed. All the sections used for the analysis were obtained by longitudinally cutting the extrudates into halves in such 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. For all the SEM analyses, all the specimens were gold coated for 4 min in the coating unit previously described.

3.5. Conductivity evaluation

The volume conductivity (σ) was evaluated for the pellets of PANIPOL, the compression moulded blends, and the extrudates. The conductivity was calculated using the electrical resistance readings from a Keithley 614 electrometer, the specimens' dimensions, and assuming that the resistance readings were performed at an ohmic regime. Five to ten specimens of each type were tested using mercury as electrical probes according to the method described by Cruz-Estrada

et al. [32, 34, 35]. The evaluation of the conductivity for PANIPOL was carried out on the as-received cylindrical shaped pellets assuming that they were perfect cylinders. For the compression moulded blends, the conductivity was evaluated on specimens 2.5 mm long, 2.0 mm wide and 1.0 mm thick, that were cut from their respective compression moulded plaques. The conductivity was evaluated perpendicular to the direction of compression. The conductivity for the extruded blends was evaluated on samples 2.0 mm long and 1.6 mm in diameter cut from their respective extrudates. The specimens were cut at random from different sections of the extrudates and the conductivity was evaluated in the extrusion direction. The extrudates' sections produced at the beginning of the extrusion process (stabilization stage) were excluded from the analysis.

4. Results and discussion
4.1. Capillary rheometry

Apparent shear viscosity-apparent wall shear rate relationships for the PANIPOL and SBS at 120°C are presented in Fig. 1, which clearly shows that the viscosity level of the SBS is the highest. The particles of PANIPOL could be deformed into elongated structures or even fibres following an *in-situ* deformation process. In principle, this type of deformation would be favoured due to the stresses transferred from the highly viscous SBS matrix to the less viscous electro-conductive dispersed phase, which means that the polymer matrix could act as a carrier for the dispersed PANIPOL phase.

4.2. Morphological characterisation
4.2.1. PANIPOL-SBS compression moulded blends

The morphology of the sections analyzed by TEM is presented in Fig. 2, which corresponds to specimens containing 5 (Fig. 2a) and 50 (Fig. 2b) wt% of PANIPOL. Numerous elongated domains of the conductive filler (i.e., the dark regions) are observed within the SBS matrix (i.e., the pale areas) perpendicular to
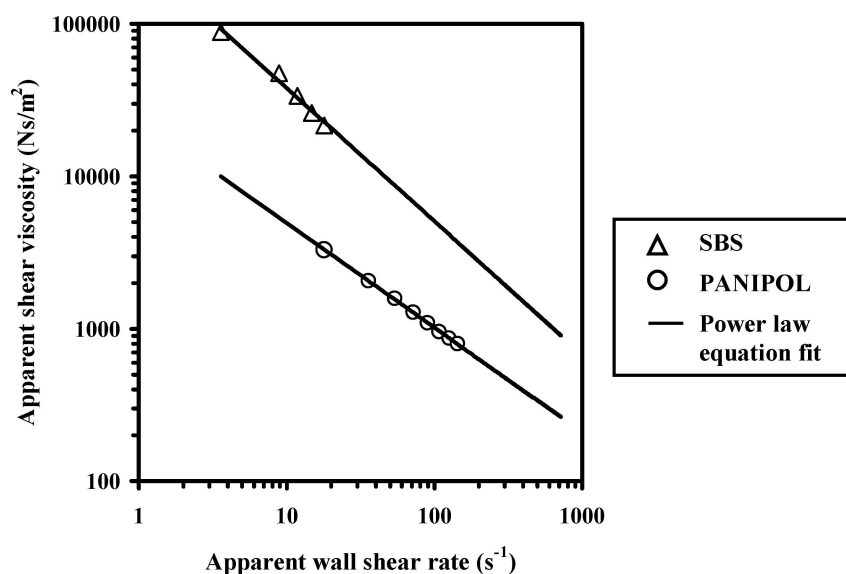

Figure 1 Apparent shear viscosity-apparent wall shear rate relationships for PANIPOL and SBS at 120°C.
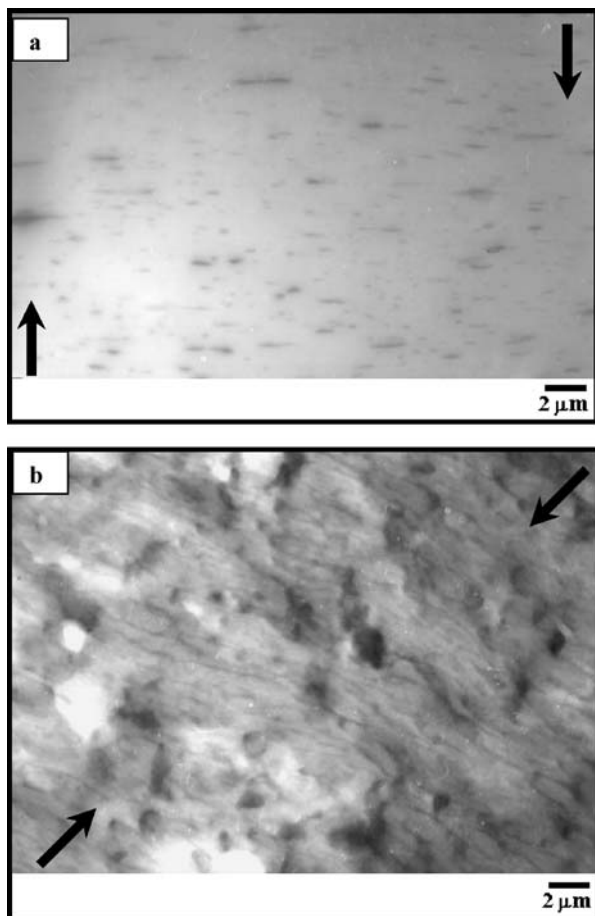
Figure 2 TEM micrographs of the transverse sections of the compression moulded blends with 5 (Fig. 2a) and 50 wt% of PANIPOL (Fig. 2b). The arrows indicate the compression direction.
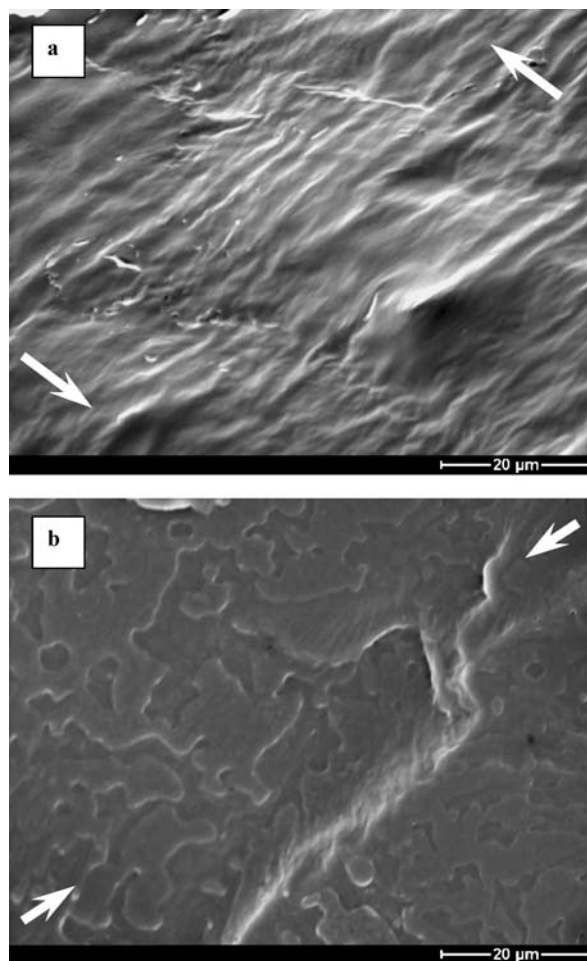
Figure 3 SEM micrographs of the fracture surfaces of the cryogenically fractured compression moulded blend with 50 wt% of PANIPOL (Fig. 3a) and a compression moulded specimen of SBS (Fig. 3b). The arrows indicate the compression direction.

the compression direction, which is indicated by arrows in the micrographs. These features are believed to correspond to the edges of layered structures that were formed during the compression, resulting from the biaxial flow experienced by the aggregates of PANIPOL. These aggregates may have contracted parallel to the compression forces and expanded in all directions on planes perpendicular to the compression direction. A large number of elongated structures of PANIPOL are observed in the specimen with the highest content of conductive filler. These are also larger in size than those observed in the specimen with the lowest content of PANIPOL.

Fig. 3a corresponds to a SEM micrograph of a section of the cryogenically fractured plaque with the highest content of PANIPOL. As noticed, numerous elongated features, perpendicular to the compression direction, are present in the specimens. This type of feature was not observed in a cryogenically fractured plaque containing only SBS (Fig. 3b), which was also obtained by compression moulding under the same conditions to those used for producing the conductive PANIPOL-SBS plaques. In consequence, the elongated features observed in Fig. 3a may have originated as a result of the formation of layered structures of the conductive filler within the SBS matrix.

4.2.2. PANIPOL-SBS extrudates
The effect over the morphology of the conductive phase during the forming process was assessed comparing the

specimens free of the conductive complex (extruded SBS) with the composites. It was possible to establish the effect of the PANIPOL phase on the morphology of the extrudates, and differentiate the conductive phase from the SBS. For simplicity, only the morphology observed in the extrudates with 10 and 20 wt% of PANIPOL will be presented for discussion. The SEM micrograph of the fracture surface of the extrudate with 10 wt% of PANIPOL is presented in Fig. 4a. As in all the subsequent micrographs that will be presented in this paper, the continuous arrow in Fig. 4 indicates the extrusion direction unless otherwise stated.

Fig. 4a shows a number of interesting features well worthy to comment. First, continuous elongated features, highly oriented in the extrusion direction, are clearly observed. Some of these features are believed to correspond to cracks longitudinally opened on the specimen body as a result of the impact force applied during the specimens' preparation (see Section 3.4.2). Other features however, look more like continuous surfaced tracks instead of actual fissures (e.g., those circled in white). In addition, some elongated structures (e.g., those indicated by dotted arrows), displaying a certain degree of uniformity, are also observed. These may correspond to the PANIPOL domains. On the other hand, the continuous pathway-like features may correspond to regions in which these elongated domains were
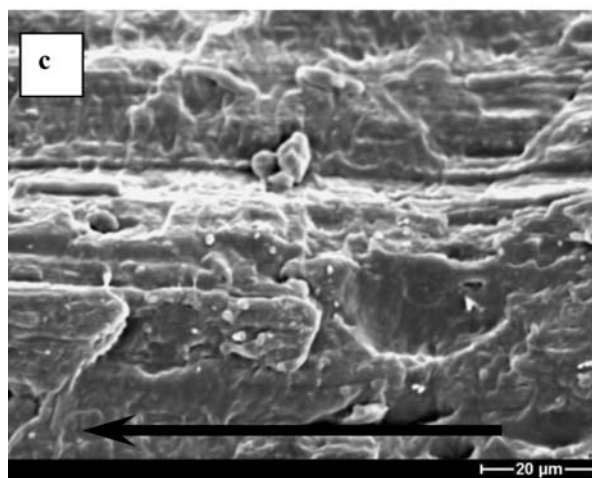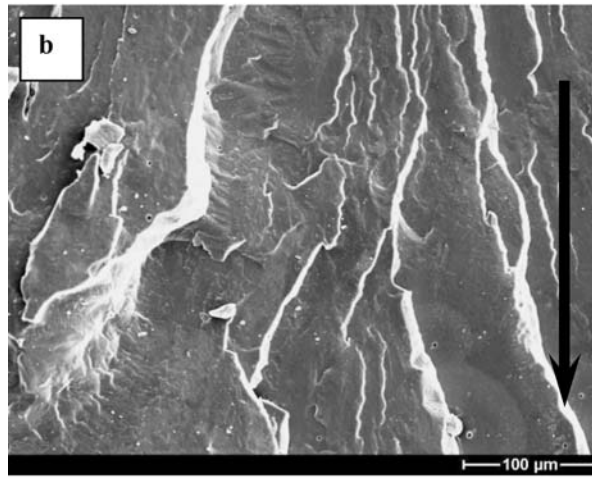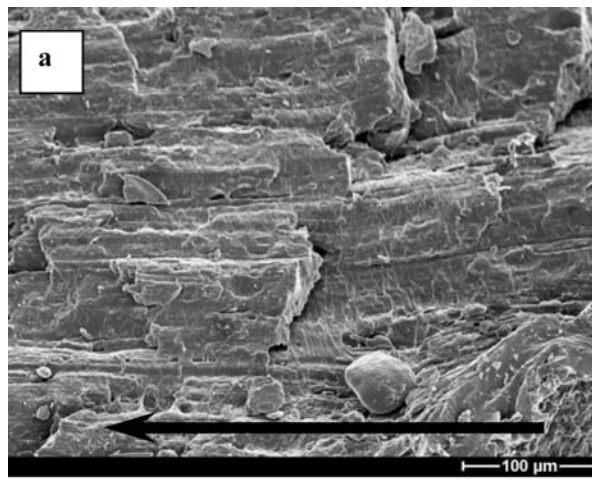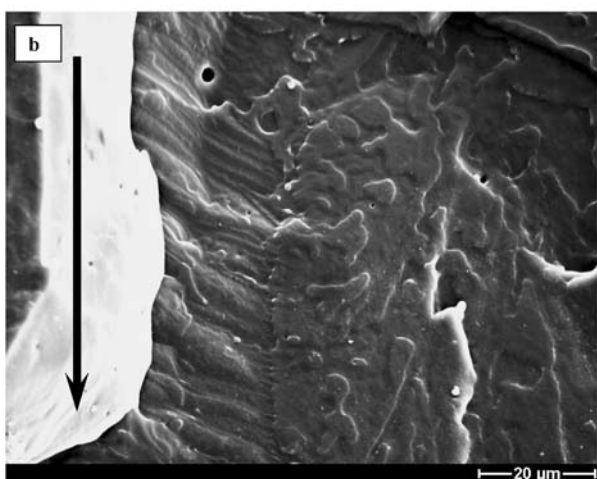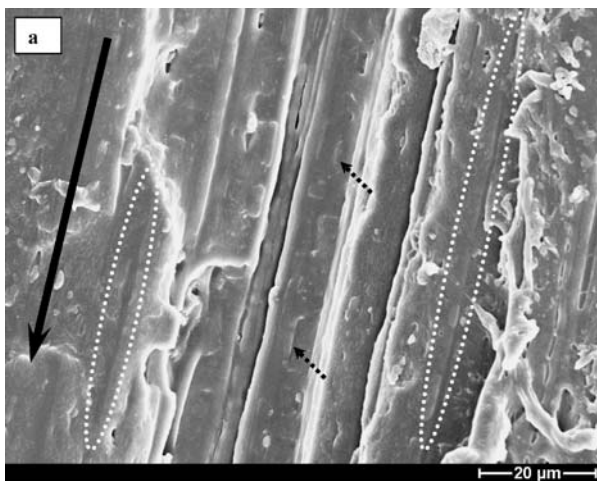
Figure 4 SEM micrographs of the longitudinal sections of a cryogenically fractured PANIPOL-SBS extrudate with 10 wt% of PANIPOL (Fig. 4a) and an extrudate of pure SBS (Fig. 4b). Continuous arrows indicate the extrusion direction. Track-like features are circled in white. Dotted arrows indicate elongated structures.

Figure 5 SEM micrographs of the longitudinal sections of a cryogenically fractured PANIPOL-SBS extrudate with 20 wt% of PANIPOL analysed with different levels of magnifications (Figs 5a and c), and an extrudate of pure SBS (Fig. 5b). Continuous arrows indicate the extrusion direction.

originally present, and that were detached from the SBS matrix during the extrudate's fracture. The veracity of the above stated hypotheses is reasonable considering the fact that the aforementioned morphological features were not observed on the fracture surfaces of the extruded SBS, analysed under the same level of magnification (Fig. 4b). As can be noticed, Fig. 4a shows different types of morphological features to those observed in Fig. 4b. Specifically, elongated features oriented along the extrusion direction were not observed.

The morphology observed on the fracture surface of the extrudate with 20 wt% of PANIPOL is presented in Fig. 5a, which shows numerous elongated features on the longitudinal section along the extrusion direction. These features are not observed on the fracture surface of the SBS capillary extruded under the same conditions (Fig. 5b).

The fact that the morphology of the SBS fracture surface was considerably different to the one of the extrudate with 20 wt% of PANIPOL, reinforces the hypothesis suggesting that some of the elongated structures found on the longitudinal section correspond to elongated domains of the polyaniline complex. A closer examination to the fracture surface of the extrudate with 20 wt% of PANIPOL (Fig. 5c) reveals that the elongated features are more abundant in this extrudate than in the one with 10 wt% of the conductive complex (compare Fig. 5c with Fig. 4a), which suggests a higher number of the elongated domains of PANIPOL due to a higher content of the conductive complex.

Figs 4a, 5a and 5c therefore prove the occurrence of anisotropically formed structures along the extrudates and it is likely that these structures correspond to the PANIPOL phase that was deformed during the extrusion process.

The SEM analysis performed on etched longitudinal sections of the extruded blends revealed the presence of elongated features parallel to the extrusion direction. As it has been mentioned before, the etching agent mostly attacked the PANIPOL phase, revealing elongated cavities (or elongated "footprints") formed by the removal of the conductive complex, which was washed away (or dissolved) from the SBS phase. For simplicity, only micrographs corresponding to the extrudates with 10 and 20 wt% of the conductive complex are presented. Fig. 6a corresponds to the etched surface of the extruded blend with 10 wt% of PANIPOL. This micrograph shows the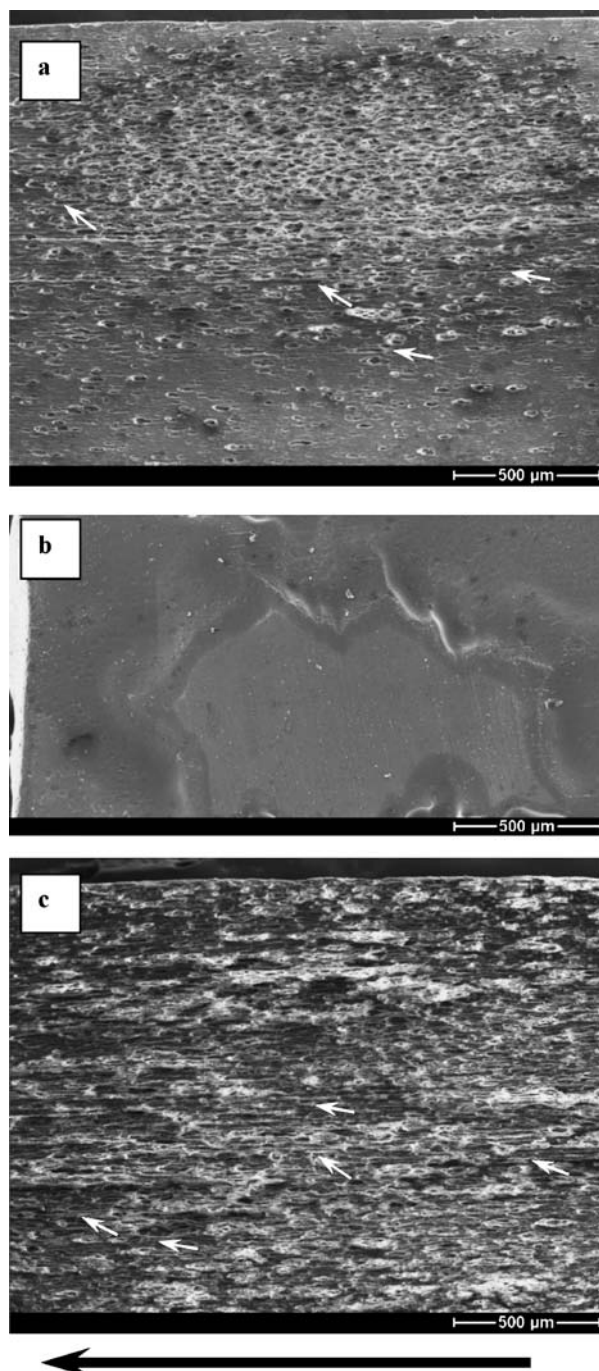 presence of numerous elongated cavities aligned parallel to the extrusion direction (a few of them are indicated in the micrograph by white arrows). In some cases, it was found a high degree of continuity and uniformity along the extrusion direction. By comparing Fig. 6a with Fig. 6b, which corresponds 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.

The presence of the elongated "footprints" of PANIPOL, parallel to the extrusion direction is exemplified markedly in Fig. 6c, which corresponds to the etched surface of the extrudate with 20 wt% of the conductive complex (see for example the features indicated by the white arrows). A higher content of elongated cavities is observed, which seem to be concentrated at the central region of the specimen. The degree of continuity and uniformity of the elongated cavities also appears to be higher than that observed in the extrudate with 10 wt% of PANIPOL. This is more evident in Fig. 7, which corresponds to different regions near to the edges of the specimen (represented in Fig. 7d) presented in Fig. 6c (i.e., extrudate with 20 wt% of PANIPOL), analysed with different levels of magnification. The concentration of elongated cavities along the longitudinal direction of the extrudates is consistent with their content of conductive complex. A few of the elongated cavities are indicated in the figure by white arrows.

The micrographs presented in Figs 6 and 7 reinforce the concept of the *in-situ* formation of PANIPOL structures highly oriented in the extrusion direction. Their footprints left on the surface of the examined specimens displayed a considerably high level of continuity, especially in the extrudate with 20 wt% of PANIPOL. This suggests that the elongated structures of PANIPOL should be highly continuous. However, the continuity of the elongated structures extending all along the extrusion direction inside the body of the extruded blends is difficult to establish through the present SEM analysis. Advanced analysis techniques are thus needed to be employed. However, the results so far presented in this paper clearly evince the feasibility to produce fibres of a polyaniline complex within a suitable polymer matrix by means of an *in-situ* deformation process that allows the fabrication of an anisotropically conducting composite.

There may be many factors that, may contribute to the formation of the elongated structures of the polyaniline complex oriented in the extrusion direction. Among them, we believe that the main ones include:

(a) The type of flow field occurring during processing. In this respect, the convergent flow at the entry of the capillary die should have generated a strong elongational flow that drew the PANIPOL domains into elongated structures. It is also possible that the shear flow 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 of the melt temperature leaving the die, should have aided to retain the elongated morphology of the dispersed electro-conductive filler.
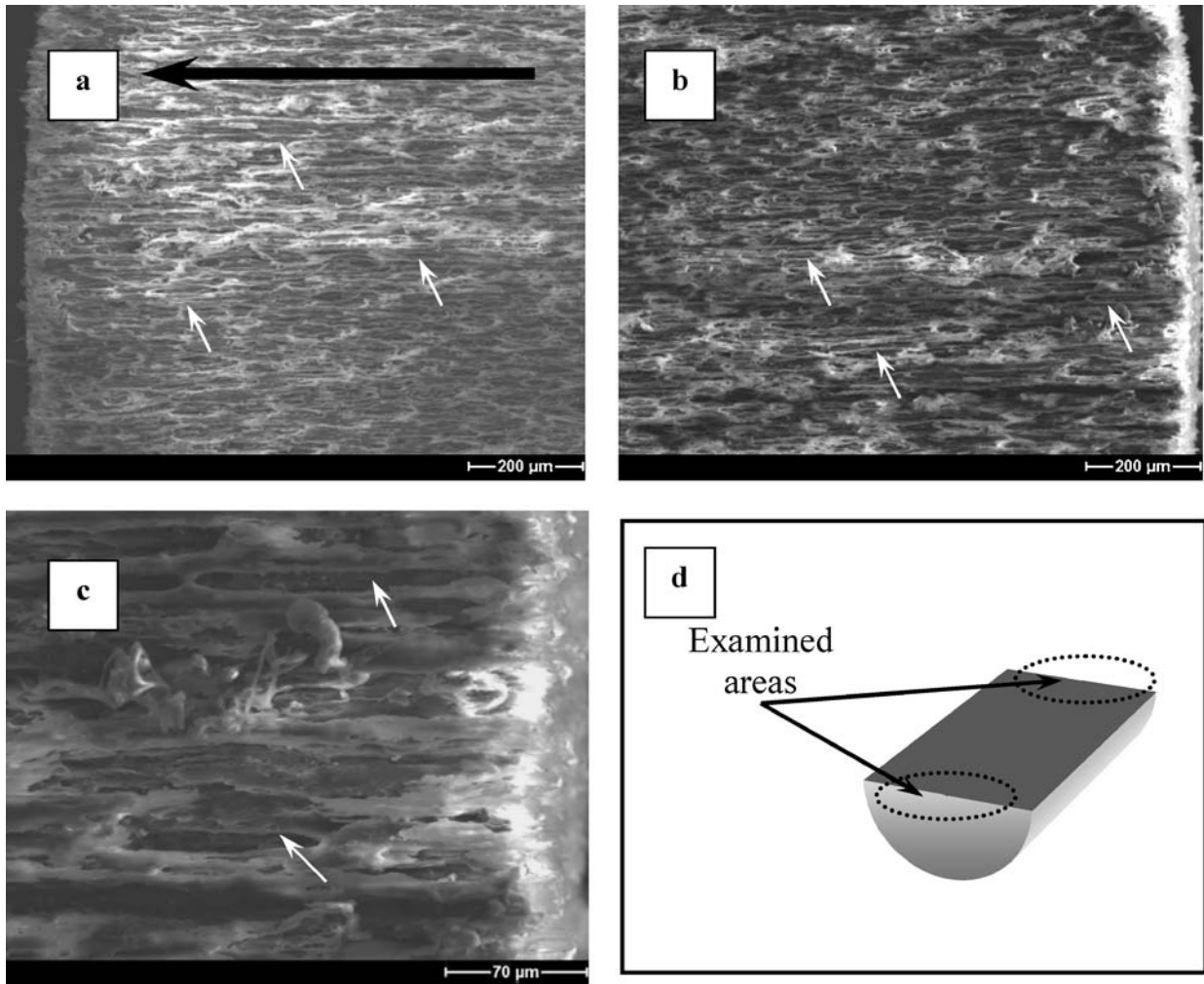

Figure 6 SEM micrographs of the etched surfaces of the longitudinal sections of an extrudate with 10 wt% of PANIPOL (Fig. 6a), an SBS extrudate (Fig. 6b), and an extrudate with 20 wt% of PANIPOL (Fig. 6c). Continuous arrow indicates the extrusion direction and white arrows indicate elongated cavities parallel to the extrusion direction.

Figure 7 SEM micrographs of the etched surfaces of the longitudinal sections of an extrudate with 20 wt% of PANIPOL. As Fig. 6c, but different magnifications. Areas near to the edges of the specimen (Fig. 7d). Black arrow indicates the extrusion direction in all the specimens, whereas the white ones indicate a few elongated cavities.

(b) The considerably higher viscosity of the polymer matrix could make possible that significant stresses were transferred from the matrix to the dispersed electro-conductive phase, thereby aiding the PANIPOL's drawing process.

In one way or another, these concepts have also been studied and applied by other researchers in the production of polymer-based composites with *in-situ* deformation of the dispersed phase into elongated structures. See for example the works of Ehtaiatkar *et al.* [16], Folkes *et al.* [17], Lee *et al.* [38], Wong *et al.* [39], and many others [40–45] and the references cited therein.

4.3. Conductivity evaluation

The evaluated average volume conductivity of the PANIPOL pellets was of 2.6×10^{-3} S/cm. On the other hand, the average volume conductivity *versus* PANIPOL content in the compression moulded blends is presented in Fig. 8. For comparison purposes, the reported volume conductivity of the SBS (i.e., 1×10^{-14} S/cm [46]) and the evaluated conductivity for the PANIPOL pellets are also presented as 0 and 100 wt% of PANIPOL, respectively. The conductivity levels of all the PANIPOL-SBS compression moulded blends were generally within the typical range reported by
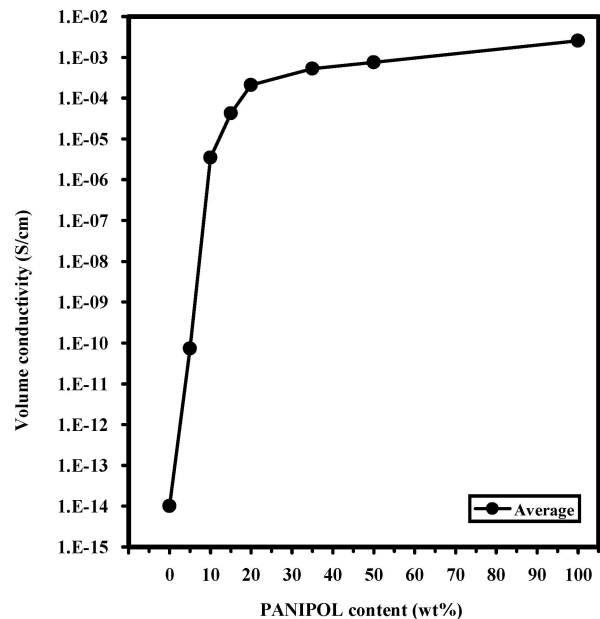

Figure 8 Volume conductivity of the PANIPOL-SBS compression moulded blends with respect to PANIPOL weight percent.

the supplying company for PANIPOL-based blends: 10^{-10}–10^{-1} S/cm.

Fig. 8 shows that the average conductivity of the blend with 10 wt% of conductive complex ($\sim$4 $\times$

10^{-6} S/cm) represents an abrupt increase of about eight orders of magnitude with respect to the conductivity reported for the SBS. Beyond this point, the conductivity level gradually increases with the increase of PANIPOL content, reaching an average conductivity of about 2×10^{-4} S/cm for the blend with 20 wt% of PANI complex. This conductivity level has the same order of magnitude for the blend with 50 wt% of conductive complex ($\sim 8 \times 10^{-4}$ S/cm), and both levels are close to the conductivity of the PANIPOL pellets ($\sim 3 \times 10^{-3}$ S/cm). The difference is less than one order of magnitude.

The extruded blends (except the specimens with the highest PANIPOL content) showed resistance levels above the maximum reading achievable by the electrometer (i.e., 200 GΩ), suggesting a level of conductivity of the extrudates considerably lower than that of their corresponding non-extruded blends. The average conductivity of the 50 wt% PANIPOL extrudate (i.e., 2.15×10^{-6} S/cm) was even lower than the conductivity of the compression moulded specimens with 15 wt% of PANIPOL (4.26×10^{-5} S/cm). 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 high. However, this was not the case in the present work. Even 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 pellets. 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 PANIPOL structures produced *in-situ* in the SBS matrix. This suggests that the process to obtain the extrudates needs to be optimised. On the other hand, the conductive paths in the form of layered structures of PANIPOL in the compression moulded blends may have had a higher level of continuity than the structures of the conductive complex in the extrudates. This may have caused a higher conductivity in the compression moulded specimens than in the extruded ones.

5. Conclusions

A combination of microscopy techniques served to elucidate the microstructure of polyaniline-based polymer blends. In the case of PANIPOL-SBS compression moulded blends, the analysis revealed that the conducting filler was in the form of layered structures within the matrix material. The layered structures may have formed during compression due to biaxial flow of the PANIPOL aggregates, which were contracted on planes parallel to the compression forces and expanded in all directions on planes perpendicular to the compression direction.

The analysis performed on longitudinal sections of PANIPOL-SBS extrudates revealed the formation of elongated domains of the electro-conductive complex of polyaniline in the bulk of the insulating matrix. The formation of these structures, which were preferentially oriented along the extrusion direction and showed a certain degree of uniformity and continuity, was mainly attributed to elongational and shearing flows occurring in the molten blends during the processing, and to the stresses transferred from the highly viscous matrix to the PANIPOL phase. These results therefore evince the feasibility of producing electrically conductive fibres of a PANI complex within a suitable polymer matrix by means of an *in-situ* deformation process, so as to allow the fabrication of an anisotropically conducting composite.

The PANIPOL-SBS extrudates showed a volume conductivity considerably lower than that of their corresponding compression moulded blends. This was mainly attributed to a lack of continuity in the PANIPOL structures produced *in-situ* in the SBS matrix, suggesting that the process for obtaining the extrudates needs to be optimised.

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