"Reasoning draws a conclusion and makes us grant the conclusion,
but does not make the conclusion certain,
nor does it remove doubt".

***Roger Bacon** (1220?–1292), English monk, philospher, and scientist.*
Opus Majus.

CHAPTER 9

CONCLUDING REMARKS AND RECOMMENDATIONS

"Advice is seldom welcome;
and those who want it the most
always like it the least".

***Lord Chesterfield** (1694–1773),*
British statesman and writer, January 29, 1748.
Letters to his Son.

9.1 INTRODUCTION.

This chapter summarizes the conclusions drawn through the course of the present work. For this purpose, the chapter is divided into sections entitled according to the topics studied. In the same way, recommendations for further work, when applicable, are also presented. A final section is presented at the end of the chapter, which concisely states the important conclusions and emphasises the main significance of the present work.

9.2 RAW MATERIALS CHARACTERISATION.

The basis about the use of dodecylbenzenesulfonic acid (DBSA) and zinc dodecylbenzene sulphonate ($Zn(DBS)_2$) as the doping and Zn compounds, respectively, in the manufacture of the pellets of PANIPOL^{TM} was elucidated by means of a combination of analysis techniques, namely X-ray diffraction, gravimetry and infrared spectroscopy. The gravimetric analysis confirmed that the content of the polyaniline salt and $Zn(DBS)_2$ in the PANIPOL^{TM} complexes was about 25 and 75 weight percent, respectively.

The thermal limitations of the PANIPOL^{TM} complexes were established through TGA and DSC analyses. These analyses confirmed that the samples could be safely processed up to a maximum temperature of about 250°C without exposing them to severe degradation and loss of their electrically conductive characteristics. However, the DSC analysis suggested an inhomogeneous distribution of the components (especially the additives) in the samples during the manufacturing process. Also, it was found that the pellets might not maintain their intrinsic properties even when exposed to the so-called safe processing range of temperatures, thus implying that there are limitations regarding their reprocessability.

The rheological analysis evinced the inhomogeneity of the samples of PANIPOL^{TM} and a high degree of brittleness and poor surface finish in their extrudates. It was observed, however, that the degree of brittleness was most evident at lower extrusion speeds and at higher temperature levels. The analysis also suggested that, compared with the LDPE and PP, the SBS seemed to be the most suitable material to be blended with the PANIPOL^{TM} samples as this would best favour the in-situ formation of

polyaniline fibres in the blends. This is because it possesses the required level of viscosity, together with a suitable processing temperature for processing the conductive complex without risking its electro-conductive performance. In the same way, the analysis suggested that using PANIPOL^{TM} 2 would produce better results as this sample proved to be the most viscous of the three samples studied, thus suggesting that in a blend, with say SBS, it would possess better stability, which would aid in maintaining the desired morphology. PANIPOL^{TM} 2 was therefore selected to be the conductive filler in the polymer systems further investigated.

The overall average value of conductivity of about 3 x 10^{-3} S/cm, measured in the PANIPOL^{TM} complex, compares well with that of 10^{-4} S/cm reported by the supplier.

The morphological analysis showed the presence of spherical features surrounded by a continuous phase in the pellets of PANIPOL^{TM}. These features, which were about 7 μm in diameter or smaller, are believed to be the particles of the polyaniline salt. It is believed that the morphology observed originated as a result of the clustering of aggregates (formed of primary doped polyaniline nanoparticles) into globular shaped agglomerates.

9.3 COMPOUNDING AND FORMING: PRELIMINARIES.

Regarding the experimentation with different compounding techniques in order to find the most appropriate one, it was noted that melt mixing in a batch mixer was the most favourable one because the instrument offered the possibility of varying the mixing speed, which assisted in the optimisation of the process. The special geometry of the mixer rotors also provided better dispersion and mixing action, which favoured the production of blends with a higher degree of homogeneity. In addition, the final composition of the blends was better controlled because the possibilities of losing material during the feed and mixing stages were minimised due to the fact that the compounding took place in an enclosed space, which also promoted a cleaner process.

It should be kept in mind, however, that the films PANIPOL^{TM}2/LDPE obtained by using a single screw extruder and a flat die (refer to the samples provided in section 5.2.3) displayed a texture that may indicate that this compounding technique has

potential for the in-situ deformation of the polyaniline phase into fibres. It is therefore recommended that this process be explored further, paying especial attention to the methodical analysis of the extrudates' microstructure in order to verify whether the observed morphology truly corresponds to fibres of the PANI complex fully aligned within the LDPE matrix.

With respect to the preliminary experiments carried out in the forming instrument (i.e., an extrusion rheometer) with the purpose of determining the optimum processing conditions, it was observed that 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 melt 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 morphological analysis carried out on the extrudates revealed that the PANIPOL^{TM} phase was deformed into elongated domains by the carrying action of the polymer matrices. The elongated domains were preferentially oriented in the extrusion direction and also displayed a reasonable degree of uniformity. Furthermore, signs of continuity were also observed in some cases. The presence of uniform and continuous elongated domains of polyaniline was most evident in extrudates containing 15 wt.% of PANIPOL^{TM} and in those in which the polymer matrix was SBS. Therefore, this polymer was selected to serve as the matrix in the blends subjected to additional experimentation. The extrusion temperature did not appear to affect the morphology of the examined extrudates.

Although elongated structures of the conductive complex were most evident in the extrudates containing SBS, it is also possible that a great number of these structures were also present in the extrudates containing LDPE and PP. With respect to this, it is possible that the limitations of the technique used for obtaining proper sections for morphological analysis impeded the observation of elongated structures of PANIPOL^{TM}

in the two aforementioned matrices. A more sophisticated technique is thus called for. For example, the use of ultramicrotomy to produce thinner sections, which could be further analysed using a transmission electron microscope. The specimens for analysis could be obtained by embedding the extrudates in an epoxy resin such that flat surfaces are exposed for microtomy.

9.4 PRODUCTION OF PANIPOL™-SBS BLENDS.

The compounding was performed in the BRABENDER® batch mixer at 130°C. The modifications performed to the compounding conditions, namely the increase of the mixing speed and time to 15 rpm and 5 min, respectively, considerably improved the dispersion of PANIPOL™ in the blends due to the increase of the shear stresses occurring in the melt. Additionally, the conductive complex was given more time to mix properly with the polymer matrix. Although the degree of homogeneity was increased, some of the blends, especially those with the higher contents of conductive complex, were still lacking the required level of homogeneity. As has been seen in section 6.2, this was due to the fact that batches of the same size were used in the preparation of the blends regardless of their composition. As explained in the aforementioned section, this is not strictly correct, as the batch size should increase with the increase of conductive complex in the blends (the reader is invited to revisit Table 6.3, which shows the correct average batch size for each blend composition). It is therefore recommended that the correct batch sizes should be observed in the preparation of the blends to attain the desired levels of homogeneity.

On the other hand, one must be more critical when selecting the correct compounding conditions. For this, a proper experimental design is recommended in which the most important processing conditions are varied between certain limits and the desired properties of the blends evaluated for each combination of processing conditions. For example, if it is assumed that the more homogeneous the blends are the higher their level of conductivity, this could help in choosing the correct processing conditions. More specifically, assessing the effect of different levels of mixing speeds and times on the level of electrical conductivity in the blends at a fixed blend composition could aid in indicating which levels of these parameters (i.e., time and

mixing speed) are the most suitable ones. An analysis like this could be carried out following the Taguchi's technique for the design of experiments [196].

The blends were compression moulded into flat plaques and the relationship between the volume conductivity and content of conductive complex was evaluated. It was found that this was characteristic of a percolating system. The percolation threshold seemed to occur at a PANIPOL^{TM} content of about 5 wt.%. The results from the conductivity measurements suggested that blending SBS with no more than 20 wt.% of conductive complex could produce an electrically conductive composite with a reasonably good level of conductivity.

The morphological analysis suggested that the morphology responsible for the conductivity in the compression moulded blends consisted of a continuous network of polyaniline within the SBS matrix. There were strong evidences that this network was mainly composed of layered structures of polyaniline together with other morphological arrangements of PANI, including interconnecting paths and discrete aggregates. The analysis also proved that the connectivity degree among the aforementioned morphologies is a function of the content of conductive complex, which explains the increase of the level of conductivity in the blends with the increase of the PANIPOL^{TM} content.

9.5 RAM EXTRUSION OF PANIPOL^{TM}-SBS BLENDS.

The forming process was carried out at a piston drive speed and temperature of 1.25 mm/min and 120°C, respectively. 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 modifications performed to the compounding method. The pressure generated during the forming process behaved erratically with respect to time, which implied that the blends were still lacking the desired level of homogeneity. 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 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 the aforementioned materials 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. Regarding this, it is advisable to conduct a set of controlled experiments following a similar experimental design like the one recommended in the previous section in order to fully optimise the forming process.

Experimenting with different extrusion speeds is recommended. For example, the use of piston drive speeds below that at which the blends were processed, and other ones above that level but below 2.5 mm/min, which was observed to be the average critical extrusion speed above which melt fracture occurred (refer to section 5.4.4). In the same way, experimentation with different capillary die dimensions could also help to increase the possibilities of forming continuous fibres of the conductive filler within the matrix. For example, it has been reported that fibres of the dispersed phase, initially formed in the converging region of the capillary, retained their shape when extruded in very short capillary dies [144,145]. However, when longer dies were used no elongated

structures were observed. The loss of the fibrillar form during flow through a long capillary is attributed to high shear near the walls of the capillary, which caused breakup of the fibrils. In addition, the orientation relaxation time of the elongated phase could have been lower than the average time for the polymer to flow through the capillary.

Another approach would be to "freeze" the fibrous morphology so that there is almost no time for the fibres to recoil. This could be achieved by promptly cooling down the extrudate emerging from the die in a water bath so that the fibres' recoiling energy is minimised. Additionally, a drawing force could be applied, at the same time that the extrudate is cooling down in the bath, to maintain the elongated morphology.

9.6 MODELLING OF THE CONDUCTIVITY.

Percolation theory and a generalisation of effective media theories were used to model the conductivity behaviour in the compression moulded PANIPOL^{TM}-SBS blends. Both approaches yielded similar values for the critical parameters, these being t = 1.355 and ϕ_c = 0.04376 from the percolation theory, and t = 1.35 and ϕ_c = 0.047 from the GEM approach. The values calculated for ϕ_c are in good agreement with that of 0.0430 corresponding to the compression moulded blend with 5 wt.% of PANIPOL^{TM}, which was initially suggested as the percolation threshold. The critical parameters calculated from the percolation theory are consistent with those calculated by other researchers for other PANI-based systems following a similar method to that employed in this work. The morphology observed in those composites at the percolation threshold consisted of segregated conducting PANI domains within the matrix phase, which is also consistent with the morphology observed in the PANIPOL^{TM}-SBS blend with 5 wt.% of conductive filler (refer to fig 6.15 in section 6.4.3).

The low value of the depolarisation coefficient calculated through the GEM approach for the PANIPOL^{TM} phase suggests that, at the percolation threshold, the polyaniline particles would exhibit a morphology of extremely flattened spheroids, which is in good agreement with the layered structures of the conductive filler observed in the compression moulded blend with 5 wt.% of PANIPOL^{TM} complex. This enables us to visualize the morphology of the composite at the percolation threshold as aggregates of flattened polyaniline particles within the SBS matrix. The conductivity at

the percolation threshold may be attributed to the incipient formation of very long layers of polyaniline in the direction of the current flow.

As has been seen in this section and explained in chapter 8, the modelling of the conductivity was not performed on the extruded blends because, for most of them, their electrical resistance was higher than the maximum reading achievable by the measuring instrument. This impeded the calculation of their conductivities and resulted in a lack of experimental data to perform the mathematical modelling. However, in the event of having enough experimental data for the analysis, a simple approach for modelling the behaviour of the conductivity would be the rule of mixtures, assuming that the composites displayed an anisotropic morphology (refer to section 2.4.4).

9.7 CONCLUSIONS.

The morphological analysis performed on the extrudates of PANIPOL^{TM}-SBS blends suggested that the conducting phase was deformed into elongated domains, aligned parallel to the extrusion direction, which in some cases displayed a considerable degree of continuity and uniformity.

The feasibility of producing electrically conductive polyaniline fibres within a suitable polymer matrix by means of an in-situ deformation process, so as to allow the fabrication of an anisotropically conducting composite, was therefore established.

Morphological analysis also evinced the formation of layered structures of the conducting filler within the matrix material in compression moulded specimens of PANIPOL^{TM}-SBS blends. The observed morphology was in good agreement with that inferred by means of a mathematical model.